3rd AUSTRIAN • ITALIAN • YUGOSLAV CHEMICAL ENGINEERING CONFERENCE

276th Event of the European Federation of Chemical Engineering


PROCEEDINGS
Volume I

— Phase Equilibria and Fluid Phase Properties
— Separation Process
— Reaction Engineering
Proceedings of
The third
Austrian — Italian — Yugoslav
Chemical Engineering Conference

Volume I

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Preface by Federal Minister Dr. Hertha FIRNBERG for the Proceedings of the 3rd Austrian-Italian-Yugoslav Chemical Engineering Conference

Chemical engineering and chemical process technology are more and more becoming one of the most comprehensive branches of the technical sciences. As in few other disciplines, scientific research is closely followed by industrial and technological development, thus ensuring the economic prosperity of an industry which occupies a key position in the overall economic structure of Europe.

This close interaction between practical orientation on the one hand and theoretical research on the other makes this science not only an important economic factor but in particular a model example of modern, technologically oriented natural science. But in addition to these aspects the fact deserves to be mentioned that chemical engineering has a special role to play in the process of cross-fertilisation between technology and society not only in view of its economic importance but also by virtue of its pre-eminent position in the fields of environmental protection and energy and raw material conservation.

Everywhere in the world enormous scientific efforts are being made in this field and great successes are being achieved. Hence it is essential in this rapidly expanding sector of science to seek international cooperation. For the countries of Europe, in particular, such focused cooperation is imperative if their research resources are to be put to good use.

It is therefore the fundamental aim of the Austrian-Italian-Yugoslav Chemical Engineering Conference to encourage this cooperation between the three countries on the basis of good, neighbourly relations and common ties dating far back in history. The relationship between the founder countries is moreover imbued by a special spirit of friendship.
and closeness so that the Conferences have already fostered many personal contacts, going beyond the strictly scientific sphere, between the participants. The third session of the Conference, hosted by Austria, has attracted especially great interest among scientists from all our neighbouring countries.

It is my hope that the special spirit of togetherness typical of this Conference will not only be preserved but will widen to include scientists from all parts of Central Europe, and that this 3rd CEC will be a success and a stimulus for cooperation in our region.
Preface by Dr. Josef KRAINER, Gouverner of the Styrian Federal State

For Europe and the whole world, the regions, countries and republics of the Eastern Alpes are a living example how, inspite of political and linguistc differences, common aimes can be pursued and a fertile cooperation can be realized. The diversities of these regions, countries and republics of the Eastern Alpes are not an expression of difference but of special manifestation within a original entity. This entity was and still is molded by common values and an long common tradition and culture.

The CEC, like Trigon and the ARGE Alpen-Adria, is an essential part of these multilateral activities. These contacts on various levels not only enhance the cooperation but initiate a dynamic activity as a result of mutual understanding. The individual good relationships between the people of different countries translates itself to a friendly relationship of good neighbours between the countries.

After Triest and Bled, Graz has the honour to host the third meeting of the CEC. The importance of the CEC can be measured by the fact, that the European Federation of Chemical Engineering has decided to include this conference as the 276th event in their programm.

I want to present my compliments to the participants of the 3rd CEC and hope, that everybody has a pleasant stay in Styria. At the same time I hope that, besides the exchange of scientific ideas and the review of the state of the art - which is of course the main interest of the conference - the members can gain a lasting impression of our beautiful country and its people.
CONTENT

F. Moser, Graz
"The Technological and Social Relevance of Research in Chemical Engineering" 1

SESSION A: PHASE EQUILIBRIA AND FLUID PHASE PROPERTIES

Plenary lecture

P. Rasmussen, Lyngby
Phase Equilibria and Fluid Phase Properties 43

A 1 R. Paunovic, Novi Sad
Representing both the Vapor and Liquid Phases by a Generalized Redlich-Kwong Equation of State with Separate Sets of Parameters for Each Phase 72

A 2 St. Jovanovic, R. Paunovic, A. Mihajlov, Novi Sad
An Efficient Method to Avoid Trivial Solutions in Bubble Point Pressure Calculations from a Cubic Equation of State 80

A 3 M.C. Annesini, F. Gironi, L. Marelli, Roma
Prediction of Second Virial Coefficients of Polar Fluids by an Improved Corresponding States Method 88

A 4 M. Fermeglia, I. Kikic, R. Lapasin, Trieste
Comparison Between Different Models for the Excess Free Energy 98

A 5 S. Kemeny, Gy. Balog, Gy. Radnai, Budapest
Phase Equilibrium Calculation Using Quasilattice Models 106

A 6 M. Orlandini Visalberghi, P. Alessi, Trieste
Group Contribution Methods and Molecules with Two Functional Groups 114

A 7 J. Matous, P. Stastka, J.P. Novak, J. Sobr, Prague
Vapour Pressure of Bourbonal and its Derivates Measured by the Saturation Method 122

A 8 I. Cibulka, Prague
Excess Volumes and Excess Enthalpies of Tetrachloromethane and of Chloroform with Cycloalkanes: Comparison with Theory 130

A 9 M. Orlandini Visalberghi, M. Fermeglia, Trieste
Liquid-Liquid Equilibrium for Ternary Systems Water-Alcohol-Chlorocompounds 138

A 10 K. Wortl, H. Huemer, F. Moser, Graz
A New Apparatus for Measurement of Liquid-Liquid Equilibrium Data 145

A 11 W. Arlt, K. Kleinhenz, Leverkusen
Possibilities of the Description of Liquid-Liquid Equilibria 153
A 12 P. Vonka, J.P. Novak, J. Pick, Prague
Calculation of Equilibrium Composition of Coexisting Phases for Liquid-Liquid Equilibrium

A 13 G. Carvoli, L. Cori, P. Delogu, Milano
Liquid-Liquid Data Correlation with Maximum Likelihood

A 14 J.P. Novak, A. Malijevsky, V. Ruzicka, J. Matous, Prague
The Double Application of the Newton Method (DAN Method) for Calculating Composition of Coexisting Phases Using an Equation of State

A 15 K. Kollar-Hunek, S. Kemeny, E. Thury, J. Manczinger, Budapest
Thermodynamic Consistency Test for Binary Vapor-Liquid Equilibrium Data

A 16 V. Ruzicka, Jr., Prague
Prediction of Bubble- and Dew-Points of Petroleum Fractions

A 17 P. Allessi, E. Cressi, I. Kikic, Trieste
Unifac Model and the Gas-Solubility

A 18 A. Alessandrini, P. Allessi, F. Fermeglia, I. Kikic, Trieste
Activity Coefficients at Infinite Dilution: Programs

A 19 J. Savkovic-Stevanovic, A. Tasic, B. Djordjevic, Beograd
Vapour-Liquid Equilibrium of Ternary Associated Systems with Association of One Component in Both Phases

A 20 F. Zitz, H. Huemer, Graz
The Calculation of Complex Absorption Equilibria of Ionogen Substances in Aqueous Solvents with Reaction Models

A 21 A. Chuchvalec, L. Hudcova, Prague
The Comparison of Methods for the Prediction of the Thermal Conductivity of Liquids

SESSION B: SEPARATION PROCESSES

Plenary lecture

M. Molzahn, Kassel, D. Wolf, Ludwigshafen
"Distillation, Absorption, Extraction - Is there any Scope for Research left?"

B 1 J. Golob, V. Grilc, Ljubljana, V. Gulic, V. Dolecek, Maribor
Design Aspects of a Continuous Stripping Process

B 2 C. Scali, S. Zanelli, Pisa
Pressure and Gas-Liquid Mixture Oscillations on Sieve Trays

B 3 P. Hentrlich, A. Vogelpohl, Clausthal-Zellerfeld
Fluid Dynamics and Mass Transfer in a Periodically Cycled Column Equipped with Sieve Plates and Short Packings in Series
B 4 J. Savkovic-Stevanovic, Beograd
Mathematical Model of Unsteady State Distillation Column with Association Reaction

B 5 H. L. Mahendru, A. Hackl, Viena
How to Improve the Performance of Dual Flow Trays

B 6 P. Canepa, S. Munari, M. Nicchia, Genova
R. F. Plasma Preparation of Gas Separation Membranes: Preliminary Results

B 7 L. Boyadzhiev, Sofia
Liquid Pertraction or Liquid Membranes

B 8 D. Melzner, A. Mohrmann, W. Poppe, W. Halwachs, K. Schügerl, Hannover
Continuous Extraction of Metals with Liquid Membrane Emulsions in a Kühni Extractor

B 9 M. Mitrovic, Beograd, Wu Qiulin, Peking
Carrier Meditated Extraction in a Mixer-Dual Filter System

B 10 F. Carassiti, G. Liuzzo, A. Morelli, Rome
A Computer Code for Calculation of Solvent-Extraction Separation in a Multicomponent System with Reference to Nuclear Fuel Reprocessing

B 11 F. A. Popovska, C.A. Tonic, A.N. Grizo, Skopje
Extraction of Copper with Kelex 100

B 12 T. Koloini, I. Suligoj, M. Zumer, Ljubljana
Continuous Ion Exchange in Ternary System Ca-H-Na

B 13 L. Steiner, S. Hartland, Zürich
Modelling of Liquid/Liquid Extraction Columns

B 14 W. Gregor, Karlsruhe
The Influence of a Disperse Phase on the Turbulence in a Fluid

B 15 K.-H. Reissinger, Leverkusen
Backmixing and Concentration Profile in a Pulsed Sieve Plate Extractor (PSE)

B 16 E.v. Fischer, L. Steiner, S. Hartland, Zürich
Agitated Liquid-Liquid Extraction Column with EC-Plates

B 17 W. Gaubinger, G. Husung, R. Marr, Graz
Operating Behavior of the Selfstabilizing High Performance Extractor "SHE"

B 18 V. Grilc, J. Golob, R. Modic, Ljubljana
Secondary Dispersion Separation on Fibrous Beds
SESSION C: REACTION ENGINEERING

Plenary lecture

S.C.R. Turner, Exeter
Reaction Engineering 455

C 1 R. Conti, S. Sicardi, G. Baldi, Turin
Hydrodynamic Regimes in Gas-Liquid Stirred Vessels 476

C 2 G. Marton, J. Havas-Dencs, L. Szokonya, Vesprem
Kinetical Studies in a Stripping-Out-Furfural Reactor 484

C 3 G. Oliver del Castillo, L. Rivolta, Milan
A Semitheoretical Model to Evaluate the Behavior of a Gas-Liquid Reactor for the Oxidation of Acetaldehyde to Acetic Acid 492

C 4 A. Trotta, S. Giudice, Padova
A Finite Element Solution of Boundary Layer Problems with Surface Reaction 500

C 5 S. Zrncevics, Z. Gomzi, Zagreb
Catalyst Poisoning on the Benzene Hydrogenation 509

C 6 Z. Kurtanjek, Zagreb
Some Effects of Phase Change of Catalyst Surface on Heterogeneous Reactions 519

C 7 A. Pavko, J. Levec, Ljubljana
Particle Wetting in a Laboratory Rotating Basket Reactor for Gas-Liquid-Solid Kinetic Measurement 527

C 8 L. Petrus, R.W. de Roo, E.J. Stamhuis, G.E.H. Joosten, Groningen
Direct Hydration of Linear Butenes to 2-Butanol Catalyzed by Strong Acid Ion Exchangers 535

C 9 R. Kiprijanova-Radanovic, L. Markovska, Skopje
Mathematical Model of Flow Process Vessels for Continuous Copolymerization of Acrylonitrile-Vinylacetate 542

C 10 L. Rizzuti, P.C. Yue, Bath
The Measurement of Light Transmission through a Fluidized Photocatalytic Reactor 550
The purpose of this paper is to point out possible shortcomings in research methodology and aims as well as research coordination between universities and industry in the field of chemical engineering and to make some proposals with regard to this subject.

The Situation

During the last three or four decades some far reaching changes in the design philosophy for the development of new plants, as regards the application of design concepts and in the way the scientific research efforts developed in the chemical engineering profession must have been noticed. All of these aspects are closely interrelated and of great importance not only to industry but to our societies in general as they determine to some extent the effectiveness of chemical engineering efforts and thereby the effectiveness of the process industries. It therefore seems appropriate to consider in general the technological and social relevance of the research efforts in chemical engineering.

Chemical engineering work in these last decades was influenced and characterized by the application of large scale computers, the new concept of transport phenomena and the use of mathematical modelling.

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1) Dr. F. Moser, Professor of Chemical Engineering, Technological University of Graz, Austria, Kopernikusgasse 24, A-8010 Graz
By these measures the ultimate goal of scientific engineering effort seemed to be in sight in the early sixties: the possibility to design plants from first principles. As G.H. REMAN put it in 1964 (Ref.1): "We may expect that the trend as indicated is going to continue. As time progresses more methods, techniques, data etc. will become available which will make lighter the task of the chemical engineer involved in process development work and plant design. In this respect we might even wonder whether in future the design of a commercial plant will become possible starting from a perfect knowledge of the chemical reaction, which may in principle be obtained in laboratory-scale equipment, and using further only first-principle engineering information. Such a state of affairs is the ideal of more than just a few chemical engineers. They are convinced that eventually it will come.....".

Today we seem to have abandoned this ideal. Too many failures involving heavy monetary losses have taught us that chemical engineering is and probably will continue to be a combination of an art (i.e. know-how) and science. The know-how involved in designing chemical and process plants is at present beyond the possibilities of scientific description.

In the light of this experience, how does chemical engineering present itself today?

As regards design philosophy we seem to have left the idea of a design based exclusively on first principles and returned to the concept of process development by pilot plant equipment. This seems to be necessary in order to reduce the monetary risks involved in large scale plants.
The design concepts of unit operations and transport phenomena exist side by side and although they defy unification they seem to suffice for design purposes. However, a tremendous gap still exists between chemical engineering science and chemical engineering practice. In spite of the overwhelming amount of scientific publications, large fields of the practical work remain uncovered. Since decades chemical engineering science and chemical engineering practice seem to live side by side a life of their own and the communication between them is not satisfactory. Scientific research seems to follow mostly established lines of work branching off into more and more detail. In this respect the word of the German sociologist TENBRUCK is applicable: "Science comes to an end, when the results of scientific effort are correct but not of much value" (Ref.2).

The basic question for all of us - the academic as well as the practicing chemical engineer - is: What kind of research is important for the task we have to fulfill? What do we know and what do we not know? What field is of value to us and which fields are of little value? Where are the fields of knowledge so far neglected?

Very often if we work absorbed by the problems of a special field of science or technology we are likely to forget the technological or social relevance of what we do. A general survey, yardsticks of how we should go about in our own work and in the coordination of our work might therefore be of value.

Recently several members of the scientific community of chemical engineers have offered similar critical remarks as to the subjects and methods of scientific chemical engineering work. JAMES WEI, of MIT, reviewing the present situation in chemical engineering (Ref.3) feels that the
old concept of unit operations is showing signs of "maturity and decline", while publications on analytical transport phenomena would "eventually elicit a yawn of familiarity from the readers". He proposes to attend to new areas of work that need awakening. Similar opinions came from Germany. H. BRAUER, of Berlin, and H. ZLOKARNIK, of Bayer ask for "revolutions instead of evolution" in chemical engineering research (Ref. 4). They feel that too much goldplating of formulas to more and more decimal points is in the forefront of established fields of research, while there would be not enough courage to take the risk and start into new fields. The comments by M. MOLZAHN and D. WOLF (Ref. 5) two researchers from industry are even more critical. In a paper "Distillation, Absorption, Extraction - are there any research tasks left?" they state:

"Looking back on more than half a century of intensive research and taking account of a good deal of more recent work which has been carried out more under the incentive of scientific activity and publication than with the object of tilling gaps....."

and

"....... anyone concerned with chemical engineering problems in this area will, again and again, encounter obstacles and almost untrodden path."

JAQUES VILLERMAUX, in a paper surveying the general situation in France as regard the chemical engineering research, expressed his view that "rather the propagation of existing knowledge as compared to the establishment of new knowledge" would be required (Ref. 6). This in a sense also asks for
consolidation of existing knowledge rather than further elaboration.

The importance of such opinions can hardly be overstressed and although these expressions do not explicitly state it, they indicate, that in general the scientific community is ill coordinated, if at all, and we are wasting time, money and human effort because of this lack of coordination and of neglecting to define the goals for our work. In the light of the increasing stress on monetary expenditures for academic education and scientific research efforts, it seems justified to reconsider the means and ways a scientific community operates.

What seems to be needed in chemical engineering at the moment can be summarized as follows:

1) Consolidation of existing knowledge rather than elaboration into more detail in existing fields.

2) A general survey of all areas of chemical engineering to establish - in close cooperation between industry and universities - areas so far neglected and areas which require further work.

3) Reappraisal of research methodology and yardsticks for determining research effectiveness.

4) Reappraisal of academic standards and research conditions at universities.

The elaboration into existing fields i.e. the gold-plating of formulas and theories etc. is to some extend due to the academic standards, which call for original and unpublished
work. Therefore many young scientists in order to comply with the slogan "publish or perish" start with insufficient financial support into elaborating existing fields of research. Thereby the concentrated effort of such manpower in the research of a larger team, that could start a new field of research, is wasted. Furthermore it should also be considered an academic achievement to analyse, compare, scrutinize and summarize existing research results. In this respect a plea should be made here to all editors of scientific journals to call for more review papers and summaries instead of "original work" which largely goes through literature undigested.

As regards the survey of existing knowledge and the indication of areas which require further work a noteworthy effort was started by the Science Research Council of the UK, who invited Prof. H.R.C. PRATT to study the chemical engineering situation of the UK. The result was a report "Research and Development Priorities in Separation Processes" (Ref.7). The report is to be used as the basis for research coordination in the UK and also was used by the European Federation of Chemical Engineers working group on Separation Processes for their coordination work (Ref.8). The importance of such work is illustrated in FIG.1 and FIG.2 which give indications for research areas in distillation and absorption as examples from the PRATT-Report. National and international coordination of research efforts in this way seems possible and necessary 1).

1) The PRATT-Report gives recommendations for future work for practically every field of chemical engineering. It is felt, however, that these recommendations need reconsideration by the appropriate specialists in the respective fields.
The final part of this paper shall deal with questions of research methodology and yardsticks for determining research effectiveness. Both are part of the "Theory of Research" or the "Philosophy of research" a field which has developed only in this century as a separate field of science while before that it was part of general philosophy or Natural philosophy.

RESEARCH THEORY

It is surprising for oneself to find out how little one knows about the means and ways research is carried out - our rather: should be carried out - after one has been in the business of research even for quite some time. The only consolation is - and in fact it is none - that one is in good company. Not many people doing research seem to concern themselves with questions about how to do research.

One is - implicitly - in general agreement that BACON's method of induction is the method of research. BACON's method it is true was generally accepted and relatively unchallenged until KARL POPPER, a young Viennese philosopher at the age of 32, published his book "Die Logik der Forschung" in 1934. Since then the views about research methodology began to change.

1) In this respect compare the very frank remarks of SIR JOHN ECCLES in (Ref. 10)

2) To a certain extend this statement neglects the scientific disputes between L. BOLTZMANN and E. MACH in the last decades of the 19th century and also the views of H. POINCARE, DUHEM and M. PLANCK put forward early in the 20th century. However, the author wishes to emphasize the main trends which prevailed within the scientific communities.
Definition of Research

What does a scientist actually do? POPPER's definition is: "A scientist whether theorist or experimenter, puts forward statements, or system of statements, and tests them, step by step. In the field of the empirical sciences, more particularly, he constructs hypotheses, or systems of theories, and tests them against experience by observation and experiment" /Ref.9/.

Now, the difference between BACON's inductive view of the way we conduct science and POPPER's deductive view is significant. It may not seem so in the beginning - one could say: there is not much difference anyhow - but this is not so: the consequences are most significant.

Research Methodology (POPPER's Theory of Science)

What exactly now is the difference between BACON's and POPPER's view of the methods of scientific research. It is the so called "Problem of Induction".

According to a widely accepted view the empirical sciences can be characterized to use "inductive methods". According to this view the logic of scientific discovery would be identical with inductive logic, i.e. with the logical analysis of the inductive methods /Ref.9/.

By "inductive" one means that one passes from singular statements - such as an account of the results of observation or experiments - to universal statements, such as hypotheses or theories.

POPPER's logical argument against this is: We are not justified to infer from singular statements to general statements - from a logical point of view. For any con-
clusion drawn in this way may always turn out to be false, no matter how often it was confirmed. No matter how many white swans we may have observed, this does not justify the conclusion all swans are white. It does not justify it on a logical basis and as POPPER could show also not on a "most probable" basis. To base the inductive principle thus on the basis of an "inductive probability" also is not fruitful, because this would need a new "inductive probability principle", which cannot be justified and so on, i.e., it leads to an infinite regress.

Now, the work of POPPER was rather shattering, as the views on how to conduct research untill then were rather firm. REICHENBACH, a strong supporter of the inductive method, said: 1)

"The principle of induction determines the truth of scientific theories. To eliminate it from science would mean nothing less than to deprive science of the power to decide the truth or falsity of this theories. Without it, clearly science would no longer have the right to distinguish its theories from the fanciful creations of a poets mind".

But what are now the factual differences and gains of POPPER's view?

1) quoted in /Ref.9/
We could say that BACON's method of induction consists of the following steps: (comp. Fig. 2)

1\textsuperscript{st} step - careful and methodical experiments

2\textsuperscript{nd} step - hypothesis

3\textsuperscript{rd} step - comparison hypothesis/experiment

1) There are also other philosophers and scientists in support of inductive methods among them: JOHN STEWART MILL, E. MACH, R. CARNAP, W. V. QINE, H. REICHERNBACK, C. G. HEMPEL

2) In a more differentiated way one separates at the moment the phenomenon "induction" into two aspects:

- a) inductive logic
- b) inductive methods

CARNAP has unsuccessfully tried to show that a justification of theories is possible by inductive logic. However, inductive methods, as there are: analogies, generalisations, similarities, extrapolation, interpolation, reproduction etc. are standard methods in all scientific ways of working, therefore also within the methods of deductive testing of a hypothesis. These methods are however, unsatisfactory for the formation or justification of theories.
In contrast to this POPPER's method of deduction would consist of the following steps: (comp. Fig. 1)

1) step - the stating of a problem

2) step - the conceiving of a new idea i.e. the stating of an hypothesis

3) step - testing of the hypothesis i.e. comparison with experiments and/or other theories

4) step - verification/falsification of the hypothesis

POPPER's theory of the deductive method is therefore the view that an hypothesis can only be empirically tested - and only after it has been advanced. The 2) step - the conceiving of a new idea is - according to POPPER - an irrational, intuitive process, which has nothing to do with logic. In this respect he is supported by EINSTEIN, who said about his theories of relativity (Ref. 2):

"There is no logical path leading to these laws. They can only be reached by intuition, based on "Einfühlung" (= something like intellectual love) of the objects of experience".

From a new idea, put up tentatively and not yet justified in any way - i.e. the hypothesis - conclusions are drawn by logical deduction.
These conclusions are compared with experiments and other theories. Four ways of testing an hypothesis are possible:

1) logical comparison of the conclusions among themselves

2) investigation of the logical form of the theory

3) comparison with other theories

4) testing of theory by comparison with experiments

Important to note is that every theory is verified only, for the time being i.e. it is "corroborated by past experience". If the hypothesis is falsified, then this falsification also falsifies the theory from which it was logically deduced. A positive verification, thus, can only temporarily support a theory.

Now at this point I would like to indicate the way in which we generally work - or rather we should work in research (comp. Fig. 3). Starting with the problem, an hypothesis should be formulated and only thereafter the planning of the experiments envisaged. Evaluation of the experiments will result in the functional relationships which should be compared with other theories and the hypothesis. In case the new hypothesis can be verified it should be taken-up by the paradigm, which is the general concept underlying the thinking in a field in question at a certain time. The dotted line indicates the way in which - according to POPPER - we should not work. We all know from our own work, however, how easily we are led to neglect the very important steps of stating a hypothesis and comparing our results with existing theories and the paradigm. The scientific
literature is overwhelmed with publications of such sort. In some way this can be understood as we are barely able to follow the vast mass of publications even in a small field.

Fig.4 gives a more specific application of the working method proposed for the case of kinetic studies in the field of biokinetics in order to give a very specific example. /Ref.11/.

Induction and deduction are the two extremes of the possible methods used in research. POPPER's achievement, which can hardly be underestimated, was it to point out the shortcomings of the inductive method in research with the incurring detrimental effects on science itself. However, at present although one can acknowledge POPPER's findings, it is also apparent that the practical way of working, at least in the technical sciences, consists of a combination of inductive and deductive steps. MILLENDORFER /Ref.15/ has proposed a cybernetic model involving inductive and deductive steps which seems to come near the actual practical situation (comp. Fig.6). However, this should not mean that we are back to the inductive way of working. Rather we should, for didactic reasons always start in the way which POPPER has pointed out: stating the hypothesis and verifying or falsifying it.

Furthermore the last considerations will not influence the general considerations as regards our outlook on science which shall be discussed below.
Conclusions from POPPER's theory

The conclusions from POPPER's theory of deduction, which includes the epistemological position of fallibilism, are far reaching. They can be summarized in the experiences of Sir JOHN ECCLES /Ref.10/ and Sir PETER MEDAWAR /Ref.12/ as follows:

If theories are fallible it is no longer necessary to believe that the excellence of a scientist is judged by the reliability of his developed theories and by how much they stand firm as a secure foundation for further advance.

It thus is not a sign of failure and regrettable if a scientist epauses an hypothesis which is falsified by new data and therefore has to be scrapped.

Many scientists have some naive belief, that science is concerned with the making of scientific observations with the best techniques available and that out of these observations there emerges some coherent story or hypothesis.

This misunderstanding of the nature of science has serious consequences both for science itself and for individual scientists. Scientific publication become too much occupied with the reporting of experimental observations, that achieve status because they have been carried out by the latest and most expensive techniques, and not because they have been designed to test some particularly interesting scientific idea or postulate. As a consequence scientific literature is overwhelmed by mere reportage of observations that are published just as observations, without organic relationship to precisely formulated hypo-
theses. Such formulated hypotheses. Such observations are scientifically meaningless. They are boring and soon to be forgotten. There is thus a great wastage in every aspect of scientific endeavour - in the efforts of the scientists themselves, in the usage of scientific equipment and technical personnel, and in the facilities for scientific publications.\(^1\)

Besides this wastage there is a real danger, that the misunderstanding of the scientific endevour may have serious consequences on the scientist himself. The erroneous belief that science eventually leads to the certainty of a definite explanation carries with it the implication, that it is a grave scientific mistake to have published some hypotheses that eventually is falsified. As a consequence scientists have often been slow to admit the falsification of such an hypotheses, and their lives may be wasted in defending the no longer defensible.

The inductive way of working and the erroneous belief that science eventually leads to certainty and not to a theory corroborated by past experience, which can be falsified any time when somebody comes up with a better theory, has led to situation where scientists themselves, politicians and the general public at large have taken science almost as a substitute for religion with all the detrimental effects connected with such an unjustified expectation i.e. have overestimated what science can do, themselves.

\(^1\)In previous discussions on this subject /Ref.14/ the usefulness of the mere reporting of data e.g. phase-equilibrium-data was pointed out. This is correct. However, from a strictly scientific point of view the mere reporting of data, without construction of an hypotheses or theory is not scientific work. It is pre-scientific work. Thus such data are usefull only if somebody will use them, which although this seems obvious is not always a necessary condition in producing such data.
It is important to stress in research the intuitive way of working. A very vague "horizon - of - expectations" way of working, open to new ideas, however, based on a well developed hypothesis or theory extending far into the unknown, is the best way to follow for productive research.

There is no such thing as "the objective experiment" the "experimentum crucis". Unprejudiced observation is a myth. In all sensation we pick and choose, interpret, seek, and impose order and devise and test hypothesis about what we witness. The way we set up an experiment is determined by what we expect to find out from the experiment.

Therefore, in conclusion, we can say: The conventional ways to conduct research have produced results, however, at a high cost. In order to economize we should work more methodical, scrutinize better, be systematic, but above all, always work to verify or falsify a hypothesis or a theory. This must be the nucleus around which all work should be arranged.

RESEARCH EFFECTIVENESS/THE GROWTH OF KNOWLEDGE

A study of the effectiveness of research must on the one hand include the methods used in research (research methodology) - which was dealt with in the preceding chapter - and on the other hand with the way science develops. In order to say something about the effectiveness of a process we must somehow characterize the process itself.

Since about 10 to 15 years interesting new views as regards the way science develops have been brought forward. Until then the general view was held that scientific knowledge
accumulates linearely i.e. all scientific discoveries add to the scientific knowledge: we will know more about everything untill in due time we will be able to explain everything, cure everything etc.etc. This was - in a simple way - the view widely held, and some times still is held - by positivists.

In 1962, Thomas S. KUHN, at that time professor of history at Princeton University, USA, put forward another theory /Ref.13/ which contradicts this assumption of a linear accumulation of scientific knowledge. His theory can be presented in the form of Fig.5 and shows the typical features of a biological growth curve.

Basic to KUHN's theory of scientific growth is the concept of the paradigma - a constellation of accepted theories and knowledge, effective methodologies and tools, past achievements and successful applications, standards and values, university curricula and textbooks /Ref.3/ (comp.Fig.6).

If we accept the basic assumptions of KUHN's theory then we have in scientific growth, as in biological growth, three distinct phases:

- the lag phase
- the logarithmic growth phase
- the phase of deterioration

Applying this view to a typical unit operation - as e.g. distillation - we obtain the growth curve for the specific knowledge in distillation as given in Fig.8, for the three different stages.
With this basic material we can now proceed to tackle the question of research effectiveness. If we define the ratio of research output to research input as the research-effectiveness-factor (REF) we have

\[ \text{REF} = \frac{\text{research OUTPUT}}{\text{research INPUT}} \]

Research OUTPUT is measured by all the effects of the research activities on industry and society, while research INPUT consists of the financial and manpower investments in the specific field. Of course both quantities are difficult to assess if at all\(^1\). However, some measures of research output could be envisaged to be

1) number of publications in a specific field (citation index)
2) savings in costs of industrial operations in a specific field
3) the licencing/know-how balance, etc.

In general, however, even a qualitative assessment of the REF, will suffice to judge the value of a specific research effort. At least it should be a better yardstick than none at all.

\(^1\)It is important to note that research OUTPUT and INPUT values must belong to different categories of measuring values. Otherwise the definition becomes meaningless. The REF can also be seen as the differential of the knowledge-growth curve.
The REF will vary in value from zero to values larger than one. In stage I - the lag phase of a scientific development - research input is much larger than output and therefore the REF is much smaller than one. The same can be true - for stage III - the obsolescence phase or the asymptotic phase, where a large amount of research with enormous financial expense is sometimes required to further the knowledge in a field. Therefore in this stage the tendency for the REF is to become smaller than one (REF 1).

Only in phase II thus - i.e. in the logarithmic growth phase of a specific knowledge - the REF is larger than one (REF 1).

This behavior is illustrated by Fig. 9 which shows the different stages and the curves for the specific knowledge as well as for the REF.¹)

We thereby have obtained at least a qualitative criterion for research effectiveness. What should be especially worth considering is, that with this measure we have been able

¹) In previous discussions on this point (Ref. 14) it was argued that from industrial experience it emerges that the REF would always be larger than 1. This would require an almost linear knowledge growth curve with a positive slope. This is unlikely to occur over longer periods of time. The difference in opinion can possibly be explained by the period of time which is considered. For relatively short time intervals, applicable to industrial process lives the REF may.
to distinguish clearly between the several stages of the development of knowledge in a certain field.

It is interesting to note, that - again qualitatively - we could assess the influence of the research expenses on our research efforts with time i.e. with the development of the growth curve. This is schematically shown in Fig. 10. Research expenses - low in stage I - rise exponentially to stage III, where they level off only in case of obsolescence i.e. when a specific field is neglected and no further research is being carried out.

To summarize: this all may seem - and it certainly is - a rather crude way of judging research effectiveness. However, although the entire picture was presented on a qualitative bases, it should allow us to draw some qualitative conclusions from it, which can be stated as follows:

1) It we accept that scientific knowledge does not accumulate linearly, but rather increases by steps as a biological growth curve, then we should always differentiate in our research efforts the stage - lag, log or asymptotic - we are working in. We should - doing this - be better able to ask us, what do we want to achieve in this stage? How do we go about our research?

I have often wondered in going through our chemical engineering publications the last twenty years e.g. how many more diagrams on the gas/liquid flow in packings there will be presented, or what new correlations in tray efficiencies etc.etc.etc. will

1) Indeed be larger than 1. However, considering longer periods, in the order of 50 to 100 years, the knowledge growth curve will most likely follow the indicated curve.
add to the practical knowledge for the design of chemical plants. Are we not - with insufficient coordination and differentiation - doing research in some fields over and over again? The important point, that should be made here is - research is not equally effective in all stages of the development of the knowledge in a specific field i.e. in the field of a specific unit operation.

2) Research is especially effective in stage II - the logarithmic growth phase. Of course this can be considered the "jumping the band wagon" situation. A field that shows promising returns is where everybody wants to join in.

3) The stage III - the deterioration or obsolescence phase or even the asymptotic growth phase seems the last attractive research phase. And it is the point I would like to make here, that we should be more aware of the high expenses and low returns to be expected there. So the indication for this phase would be: Let's see where we are, and if no special reward seems likely - let's get out of this field and rather start a new one (or several new ones, for the same amount of money). Of course, there is a danger here which so far I have not mentioned. If we reconsider Fig.7 - the KUHN theory - we see that out of the stagnation phase - or the rigid paradigm as KUHN calls it, i.e. of normal conventional scientific effort - comes, through the anomalies - the new paradigm, which brings knowledge to a new height.

Therefore, one cannot - or rather should not say - let's all get out of that field because, there may and certainly in due course will be, a new growth even in a field of
stagnation\textsuperscript{1}).

4) The most intriguing phase of research is – of course – phase I. Small financial resources are required and the chance to pass into a logarithmic growth phase is there. It is surprising – if one overviews the research efforts in chemical engineering in the past, how little interest these lag phases of research have obtained from scientists. Especially in times – as we have now – where great problems in energy conservation, raw material conservation etc. present themselves, we probably – as individuals and as industrial companies – would be alert to these new fields of promising growth more than we are at present. It is evident also, however, that not all research projects started in this phase will be successful. But this is the normal risk factor involved.

\textsuperscript{1) Another possibility would be that a new paradigm develops side by side with the older paradigm. This situation applies e.g. to the concept of transport phenomena as against the concept of unit operations. A similar situation occurs in the field of thermodynamics were at present several paradigm exist simultaneously side by side.
Conclusions

For many years there seems to prevail in academic circles of the chemical engineering profession a tendency to work along established lines of research and thereby neglect to a large extent the practical needs of the chemical engineers in process development and plant design. This tendency could be described as "science for science's sake". However, it has rightly been pointed out that science comes to an end, when the results of scientific effort are correct but not of much value. The reasons for this discrepancy between academic efforts and practical needs are attributed to the following reasons:

- existing academic standards
- prevailing research methodology
- shortcomings in communication between academic and practicing chemical engineers
- shortcomings in publication practice

As regards the academic standards it is felt that the standard of academic achievement, which can be characterized by the slogan "publish or perish" is detrimental to science. It is one of the reasons for the flood of publications which to a large extend are left unnoticed or undigested. Quality of work rather than quantity should be more observed. Also the call for "originality" of academic work needs reconsideration. To compare, scrutinize and summarize should be considered and certainly is of equal academic interest and even greater value to the scientific community than are original publication on trivialities.

In some universities it seems to be preferred that many young scientists start to work on their own scientific projects.
This situation has certainly some advantages especially for the person in probably would be better to concentrate a team of scientists to tackle a major unsolved problem rather than to scatter the efforts.

In research methodology it seems important to adhere to certain rules of work among which - comparison of the experimental results with an hypothesis and with other existing theories are outstanding. Too many publications seem to neglect especially the comparison with other existing theories or shortcut it. Thereby an ever increasing number of new formulae, theories and results is produced whereby hardly anybody can distinguish the value and importance of such results. There are at least ten to twenty formulae for the calculation of pressure drops through packed beds, etc.etc. However, a scrutinizing comparison and proposal which of these formula is considered the best under which conditions - such information is mostly lacking or only available to the person, who dealt with the one subject for a longer period.

Shortcomings in communication between academic and practising chemical engineers become obvious in international meetings of smaller size, where personal communication is still possible. From such meetings the vast areas which would require special attention of academic research could be and should be established. As an example for the way in which such areas for further work can be determined, the PRATT-Report (Ref.7) can be mentioned.

At last some shortcomings in the publication practice of papers should be mentioned. Some years ago several journals regularly produced annual summaries and reviews of the
work in certain areas. Lately, however, such publications can hardly be seen, although some editors seem to encourage such reviews. The importance of summaries and review papers can hardly be overstressed. Every effort should therefore be made by editors and publishers to encourage such work. Also the writing of books especially in a time when a large part of the chemical engineering science seems to have reached some point to maturity is to be encouraged.

Summarizing thus we can say that besides the improvement in research methodology and effectiveness also the academic standards and the standards of the scientific community as regards publication and review practice need reconsideration. In a situation as described in the foregoing one has basically two alternatives to follow: the one is to start thinking how the situation can be improved and then do something or the other alternative - do nothing and wait until somebody else will take the helm. This could and would be the respective governments that will have to drastically reduce research and educational expenditures. Personally I always was in favor to not wait for somebody also to tell me that I should do.
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List of figures

Fig. 1/2 Priorities of Work from PRATT-Report for Distillation and Absorption

Fig. 3 Comparison of BACON's and POPPER's Theory of Science

Fig. 4 Flow scheme of the general working method in scientific research

Fig. 5 Modelling in Biokinetics

Fig. 6 Cybernetic Model

Fig. 7 KUHN's Theory of growth of scientific knowledge

Fig. 8 The Paradigm of Chemical Engineering

Fig. 9 The knowledge - growth curve of a typical unit operation

Fig. 10 The Research Effectiveness Factor (REF)

Fig. 11 Research Expenses vs. Time
<table>
<thead>
<tr>
<th>DISTILLATION</th>
<th>PRIORITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Equilibrium and enthalpy data for hydrocarbons near critical point</td>
<td>5</td>
</tr>
<tr>
<td>(ii) Prediction of liquid phase interaction constants</td>
<td>4</td>
</tr>
<tr>
<td>(iii) Plate column hydrodynamics (excluding UMIST programme)</td>
<td>2</td>
</tr>
<tr>
<td>(iv) Improved plate designs</td>
<td>3</td>
</tr>
<tr>
<td>(v) Packed column hydrodynamics</td>
<td>1</td>
</tr>
<tr>
<td>(vi) Factors influencing binary plate efficiency</td>
<td>4</td>
</tr>
<tr>
<td>(vii) Multicomponent plate efficiency</td>
<td>4-5</td>
</tr>
<tr>
<td>(viii) Packed column performance (binary and multicomponent)</td>
<td>2</td>
</tr>
<tr>
<td>(ix) Development of improved low density packings</td>
<td>3</td>
</tr>
<tr>
<td>(x) Dynamic modelling and control</td>
<td>3-4</td>
</tr>
<tr>
<td>(xi) Energy conservation</td>
<td>5</td>
</tr>
<tr>
<td>(xii) Energy conservation (azeotropic and extractive distillation)</td>
<td>3</td>
</tr>
<tr>
<td>(xiii) Distillation with chemical reaction</td>
<td>1-2</td>
</tr>
</tbody>
</table>

Ref. PRATT-Report (Ref. 7)

Priorities: 5 = very high
             1 = very low

Fig. 1    PRIORITIES FROM PRATT REPORT
<table>
<thead>
<tr>
<th>GAS ABSORPTION</th>
<th>PRIORITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Equilibria, hydrodynamics and performance</td>
<td>3</td>
</tr>
<tr>
<td>(ii) Simultaneous heat and mass transfer: exact solution, including effects of &quot;fogging&quot;</td>
<td>3</td>
</tr>
<tr>
<td>(iii) Cooling towers, etc: mass transfer rates</td>
<td>3</td>
</tr>
<tr>
<td>(iv) Cooling towers: air flow in natural circulation type</td>
<td>3</td>
</tr>
<tr>
<td>(v) Condensation of mixed vapours, without and with non-condensables present</td>
<td>3</td>
</tr>
<tr>
<td>(vi) Design of columns for absorption-reaction systems</td>
<td>3</td>
</tr>
<tr>
<td>(vii) Fractional absorption: potential applications (including O₂ separation from air)</td>
<td>4</td>
</tr>
<tr>
<td>(viii) Supercritical absorption - potential applications</td>
<td>3</td>
</tr>
</tbody>
</table>

Ref. PRATT-Report (Ref. 7)
INDUCTIVE METHOD
F. BACON [1561 – 1626]

Problem
(Working Hypothesis)

Experiments
Hypothesis
Comparison
Experiments/Hypothesis

LOGICAL INDUCTION

DEDUCTIVE METHOD
K. POPPER [1902 – ]

Problem
Hypothesis
Testing
Experiments
Comparison
Theory/Exp.

Verification/
Falsification

LOGICAL
INDUCTIVE-DEDUCTIVE STEPS

INTUITIVE STEPS

THEORIES OF SCIENCE
TU GRAZ
1981

FIG.: 3
EXPERIMENTS

PLANNING OF EXPERIMENTS

EVALUATION OF EXPERIMENTS

SETTING UP OF FUNCTIONAL RELATIONSHIPS

HYPOTHESIS

PROBLEM

EXISTING THEORIES [MODELS]

PARADIGM

CONSISTENT WORKING METHOD

UNSATISFACTORY WORKING METHOD

FIG.: 4

METHODOLOGY OF SCIENCE

TU GRAZ 1981
EXPERIMENTS

x = PROCESS-VARIABLES \([p_H, T, S, X, O_2 etc]\)

k = MODEL-PARAMETER \([\mu_{max}, k_s]\)

PLANNING OF EXPERIMENTS \([x]\)

ANALYSIS

TRANSPORT-PHENOMENA

KINETICS

HYPOTHESIS for SUBMODEL \([f]\)

IDENTIFICATION OF SUBMODEL

PARAMETER EVALUATION \([k]\)

MODIFICATIONS \(f, x, k\)

INTERACTIONS

MODEL TESTING

PROCESS MODEL

FIG.5: BIOKINETIC MODELLING ACC. TO REF 3 TU GRAZ 1981
INDUCTION

PROBLEM

DEDUCTION

SUBJECT

INTER-SUBJECTIV INFORMATION

OBJECT

EXPERIMENTAL MODEL

ACTION

DECISION

PRELIMINARY RESULTS

1. MODEL

2. MODEL

3. MODEL

xth MODEL

FIG. 6 CYBERNETICAL MODEL TU GRAZ 1982
FIG. 7: Kuhn's Theory of Growth of Scientific Knowledge

NORMAL SCIENCE | EXTRAORDINARY SCIENCE | NORMAL SCIENCE
---|---|---
PRE-PARADIGM PHASE | PARADIGM I | PARADIGM II
ANOMALIES | CRISIS | DIE-OUT OF OLD PARADIGM
PARADIGM FORMATION

TIME

TU GRAZ 1981
PARADIGM CRITERIA

1) Constellation organized and accepted Theories and Knowledge.
2) Effective Methodology and Tools.
3) Past Achievements and Applications.
4) Standards and Values.
5) Curricula and Textbooks.

THOMAS S. KUHN, 1962

EXAMPLES IN CHEMICAL ENGINEERING

Unit operations
Transport - Phenomena

EXAMPLES OF PRE-PARADIGM AREAS

Optimisation
Catalyst Preparation
Solids Handling

FIG. 8:
THE PARADIGM OF CHEMICAL ENGINEERING
TU GRAZ 1981
FIG. 9: KNOWLEDGE-GROWTH-CURVE FOR TYPICAL UNIT OPERATION

STAGE I
- lag phase

STAGE II
- log phase

STAGE III
- a) asymptotic approach
- b) obsolescence

TIME [YEARS]
- 20 - 40
- 20 - 60

SPECIFIC KNOWLEDGE
- 0%
- 100%

THE RESEARCH EFFECTIVENESS FACTOR [REF]  

\[
\text{DEF } \text{REF} = \frac{\text{OUTPUT}}{\text{INPUT}}
\]

1  \quad \text{INPUT} = \text{OUTPUT}  

\gg 1 \quad \text{OUTPUT} \gg \text{INPUT}  

\ll 1 \quad \text{INPUT} \gg \text{OUTPUT}  

\text{PHASES} \quad \text{STAGES}

II  

LOG PHASE  

LAG PHASE  

I / III

FIG.: 10  

TU GRAZ 1980
RESEARCH EXPENSES VS. TIME

STAGE I       STAGE II       STAGE III

TIME

FIG.:11

RESEARCH EXPENSES VS. TIME

TU GRAZ 1980
SESSION A:
PHASE EQUILIBRIA AND FLUID PHASE PROPERTIES
Section A

PHASE EQUILIBRIA AND FLUID PHASE PROPERTIES

Introductory Lecture

by

Peter Rasmussen
PROLOGUE

Professor F. Moser and the organizing committee has bestowed upon me the great honour to act as chairman for this section and to present a review lecture at the beginning. I have accepted these two challenges with thanks, not realizing the difficulties as regards the review lecture. It is totally impossible within the given limits of time and paper to present an overview over all the important developments that have taken place during the last few years within the area of phase equilibria and fluid phase properties. It has therefore been necessary to be highly selective about the topics to cover. Judging from the abstracts to this meeting it was clear that the main interests of the audience would be within the area of phase equilibria.

The review will hence pertain to phase equilibria. This is however still such a large field that neither my knowledge nor my experience nor the time will allow me to cover more than well defined, subjectively chosen corners for this lecture.

More general reviews may f.ex. be found in the proceedings from two conferences on Phase Equilibria and Fluid Properties in the Chemical Industry (1977, 1980).
CONDITIONS OF PHASE EQUILIBRIUM

The necessary and sufficient condition for equilibrium in a closed system at fixed pressure P and temperature T is that the total Gibbs function, G, is at minimum. A differential disturbance will therefore not produce any change at equilibrium of the Gibbs function and we may write

\[(dG = 0)_{P,T}\]  \hspace{1cm} (1)

The criterion presented by equation (1) is a necessary, but not sufficient condition of equilibrium. Equation (1) does not help us in distinguishing between a maximum, an inflection point, and a minimum. For vapor-liquid equilibria (VLE), gas-liquid equilibria (GLE) and solid-liquid equilibria (SLE) equation (1) may be used without adverse effect. For liquid-liquid equilibria (LLE) extensive calculations by Sorensen et al. (1979) have revealed that difficulties and erroneous results may arise from using equation (1).

For a system containing N components and a number of phases a, b, \(\gamma\),..., equation (1) may be expressed by means of fugacities

\[f_a^i = f_b^i = f_\gamma^i = \ldots \]  \hspace{1cm} i = 1, 2, ..., N  \hspace{1cm} (2)

The condition for equilibrium between two phases a and \(B\) is thus that the fugacity of each component \(i\) is the same in phases a and \(B\).

For practical purposes the fugacities are normally rewritten in terms of a number of variables. In this review we will only consider vapor (or gas) and liquid phases and we will therefore only look at expressions for such phases.

The vapor-phase fugacity \(f_V^i\) may be rewritten by defining the fugacity coefficient \(\phi_V^i\).

\[f_V^i = \gamma_i \phi_V^i \]  \hspace{1cm} (3)

where \(\gamma_i\) is the vapor-phase mole fraction.

The liquid-phase fugacity \(f_L^i\) is normally rewritten in one of three possible ways:
1) by means of the fugacity coefficient $\phi_i^L$ and the liquid-phase mole fraction $x_i$

$$f_i^L = x_i \phi_i^L p$$

(4)

2) by means of the activity coefficient $\gamma_i^L$ and the standard state or reference fugacity $f_i^0$

$$f_i^L = x_i \gamma_i f_i^0$$

or

3) by means of the activity coefficient $\gamma_i^m$ and the Henry's constant $H_i,m$

$$f_i^L = x_i \gamma_i^m H_i,m$$

(6)

Equations (3) and (4) form the basis for calculating VLE and GLE from equations of state (SRK, PFGC etc.).

Equations (3) and (5) form the basis for calculating VLE (and GLE) from molecular activity coefficient models (UNIQUAC, Wilson etc.) and from group-contribution models (UNIFAC, ASOG and others). The reference fugacity $f_i^0$ of pure components $i$ in equation (5) may be calculated as follows

$$f_i^0 = P_i^S \phi_i^S \text{POY}_i$$

(7)

where $P_i^S$ is the vapor pressure of pure component $i$ at the temperature of the system, $\phi_i^S$ is the fugacity coefficient at saturation of pure component $i$ and POY$_i$ is the Poynting correction factor.

The pure component vapor pressures $P_i^S$ are often calculated by means of the Antoine equation

$$\log P_i^S = A_i - B_i/(T + C_i)$$

(8)

Extensive tables with Antoine constants $A_i$, $B_i$ and $C_i$ may be found f.ex. in Boublik et al. (1973), Ohe (1976), Reid et al. (1977) and Dykyj and Reţas (1979). Methods for the prediction of pure component vapor pressures from structural information alone have been developed in recent years by Smith et al. (1976), Edwards et al.
At low to moderate pressures (up to about 10 bars) the values of \( \phi_1 \) (equation 3) and \( \phi_i^S \) (equation 7) may be estimated from the virial equation of state truncated after the second term.

\[
\frac{P_v}{RT} = 1 + \frac{BP}{RT}
\]

Experimental values of the second virial coefficients \( B \) may be found f.ex. in Dymond and Smith (1980) and in Warowny and Stecki (1979). Usually it is not possible to find the desired virial coefficients in the literature and one has to rely on predictive methods like the methods by Hayden and O’Connell (1975) or Tsonopoulos (1974, 1975, 1978, 1979).

At such conditions where equations (3) and (5) are used, the Poynting correction factor is often near unity and may be neglected.

Equations (3), (5) and (6) form the basis for calculating GLE for systems in which one or more compounds are supercritical i.e. the equilibrium temperature is higher than the critical temperature of one or more compounds. There is quite often a little confusion about the pressure conditions for the Henry’s constant \( H_{i,m} \).

Let us consider a gas 2 dissolved in a liquid 1. The vapor pressure of the pure liquid 1 is \( P^S_1 \). The Henry’s law constant may then be written as

\[
H_{2,1} = H_{2,1}(P^S_1) \exp \left\{ \int_{P^S_1}^P \frac{\tilde{v}_2}{RT} dP \right\}
\]

where \( H_{2,1}(P^S_1) \) is the Henry’s constant at pressure \( P^S_1 \) and \( \tilde{v}_2 \) is the partial molar volume of the gas dissolved at infinite dilution in the liquid. It may be shown that \( H_{2,1}(P^S_1) \) is the limit value calculated from experimental solubility data as follows

\[
H_{2,1}(P^S_1) = \lim_{x_2 \to 0} \left( \frac{f^V}{x_2} \right)_2
\]

where \( x_2 \) is the solubility in the liquid corresponding to a vapor-phase fugacity \( f^V_2 \).
The value of $y_2$ at infinite dilution ($x_2 = 0$) is equal to unity. This is called the unsymmetrical convention.

**PHASE STABILITY**

Before we discuss various procedures for the calculation of fugacities for systems with equilibrium between different phases it is appropriate to present the conditions for stability of a single phase.

Michelsen (1982 a, b) has most recently carried out an elegant analysis of the thermodynamic stability of a mixture. The analysis is of fundamental interest and it provides a procedure which is of great importance in flash calculations.

The analysis is based on Gibbs' tangent plane criterion and it will be briefly described for the simple case of a binary mixture, which may or may not split into two phases I and II. Michelsen has treated the general case of a multicomponent mixture which may split into several phases, and he has shown how the criterion may be computationally implemented.

Consider a binary mixture at pressure $P$ and temperature $T$. The mixture contains $n_1$ and $n_2$ moles of components 1 and 2. The total Gibbs function of the mixture is

$$G_0 = n_1 \mu_1^0 + n_2 \mu_2^0$$

(11)

$\mu_1^0$ and $\mu_2^0$ are the chemical potentials of components 1 and 2 corresponding to $P$, $T$ and the mole fractions $z_1$ and $z_2$, where $z_i = n_i / (n_1 + n_2)$, $i = 1, 2$.

Let us assume that the mixture is divided into two phases I and II. The amount of phase II is infinitesimal, it contains $\epsilon$ moles and its composition in mole fractions is $(y_1, y_2)$. The total Gibbs function of phase II is

$$G_{II} = \epsilon (y_1 \mu_1 + y_2 \mu_2)$$

(12)

where $\mu_1$ and $\mu_2$ are the chemical potentials corresponding to the composition $(y_1, y_2)$. 
The total Gibbs function of phase I may be expanded by a Taylor series. Discarding second and higher order terms one gets

\[ G_I = G_0 - \epsilon y_1 \left( \frac{\partial G_0}{\partial n_1} \right) n_2 - \epsilon y_2 \left( \frac{\partial G_0}{\partial n_2} \right) n_1 \]

\[ = G_0 - \epsilon y_1 \mu_1 - \epsilon y_2 \mu_2 \]  

(13)

The change in the Gibbs function due to the phase splitting is

\[ \Delta G = G_I + G_{II} - G_0 \]  

(14)

Insertion of equations (11), (12) and (13) in equation (14) gives

\[ \Delta G = \epsilon \lambda y_1 (\mu_1 - \mu_1^0) \quad i = 1, 2 \]  

(15)

The total Gibbs function would have been at a global minimum, if the original mixture had been stable, and no phase splitting could occur spontaneously. This means that for a stable mixture

\[ \Delta G > 0 \]  

(16)

The necessary and sufficient criterion for stability of the original mixture is therefore

\[ F = \lambda y_1 (\mu_1 - \mu_1^0) \geq 0, \quad i = 1, 2 \]  

(17)

for all possible trial values of \( y_1 \).

Figure 1 shows the molar Gibbs function of mixing \( \Delta g_m \) as a function of composition. The tangent is drawn to a point corresponding to a mole fraction \( z_1 \). The vertical distance between the \( \Delta g_m \) curve and the tangent is equal to \( F \). It is seen that stability requires that the tangent at no point lies above the \( \Delta g_m \) curve.

**EQUATIONS OF STATE**

Using an equation of state for calculating the fugacities in both the vapor \( \phi_1^V \) and the liquid \( \phi_1^L \) phase has several advantages. Equations (3) and (4) may be combined to equation (18).
which does not require the specification of any extra functions or variables like $f_i^0$ and $y_i$ for the calculation of VLE. Equation (18) guarantees continuity at the critical point, all needed thermodynamic properties may be derived from the same model, and the presence of noncondensable gases causes no additional complications. It is therefore understandable that so much effort is invested in the development of equations of state and literally hundreds of equations have been published since van der Waals proposed his equation in 1873. A recent monograph edited by Chao and Robinson (1979) presents a most informative state of the art review.

Cubic Equations

Many cubic equations of state similar to that of van der Waals have been proposed. An excellent survey is presented by Martin (1979). They express the pressure by means of two terms, one for the repulsive forces and one for the attractive forces. One form (Schmidt and Wenzel, 1980) for such an equation of state is

\[
P = \frac{RT}{v-b} - \frac{a}{\sqrt{v^2 + ubv + wb^2}}
\]

(19)

where $a$, $b$, $u$ and $w$ are parameters, which may or may not be treated as functions of temperature. The values of $a$ and $b$ for mixtures are calculated from pure component values and binary interaction parameters following various mixing rules. Dependent on the values of $u$ and $w$ one may reduce equation (19) to other equations of state as shown in Table 1.

Table 1. Some equations of state derived from equation (19)

<table>
<thead>
<tr>
<th>$u$</th>
<th>$w$</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>Van der Waals</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>Soave-Redlich-Kwong (1972) (SRK)</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>Peng-Robinson (1976)</td>
</tr>
<tr>
<td>3</td>
<td>-2</td>
<td>Harmens (1977, 1980)</td>
</tr>
<tr>
<td>$u$</td>
<td>1-u</td>
<td>Heyen (1981)</td>
</tr>
</tbody>
</table>
Schmidt and Wenzel (1980) present values of the critical compressibilities from various equations of state. They show that the more recent modifications of the van der Waals equation give smaller values of the critical compressibility factors than the earlier modifications: \( z_c = 0.333 \) for the Redlich-Kwong (1949) equation and \( z_c = 0.286 \) for the Hamens (1977) equation.

Cubic equations are popular because of their simplicity and general applicability. They may be used for PVT as well as for phase equilibrium calculations, but they cannot represent accurately a wide density range, and they are not very accurate for polar substances. Much work has therefore been carried out to extend the range of applicability both with respect to density range and with respect to types of tractable compounds:

1) Vidal (1978) and Huron and Vidal (1979) have interesting discussions on the relationship between mixing rules for the parameters \( a \) and \( b \) and expressions for the excess Gibbs function. They show that using the classical mixing rules usually associated with cubic equations greatly reduces their use. Successful extensions of the cubic equations to mixtures with polar components should emphasize the development of new mixing rules. An example of this approach is presented by Heyen (1981), who uses two binary interaction parameters for the calculation of \( a \) for a mixture. Even for a strongly polar system like butanol-water which exhibits a miscibility gap it is possible for Heyen to get a good agreement between experimental and calculated VLE data.

2) Another approach is provided via a combination of an equation of state and chemical theory (Baumgärtner et al., 1979a, 1979b).

3) A most recent and interesting possibility of extending the application of cubic equations of state to strongly polar mixtures has been proposed by Mollerup (1981). Mollerup derives equations of state from van der Waals fluid theory and the local composition concept. The equations contain in the high-density limit the well-known activity coefficient models like NRTL, Wilson and UNIQUAC which can represent polar mixtures.

4) It is well-known that some of the cubic equations like the Soave-Redlich-Kwong (SRK) equation may very well represent VLE but unfor-
Fortunately they give a rather poor representation of PVT properties. Peneloux and Rauzy (1982) have proposed a simple correction to the SRK equation which in some cases improves the possibility for calculating densities without changing the equations needed for phase equilibrium calculations. This means that the correction may easily be implemented into existing computer programs using the SRK equation. The basic change in the SRK equation is a linear translation along the volume axis

\[ v = v - \sum_{i=1}^{N} c_i x_i \quad i = 1, N \quad (20) \]

where the new parameters \( c_i \) are calculated from critical properties.

5) It is difficult to calculate VLE for multicomponent mixtures with an equation of state in the near critical region. The reason is that it is not known in advance during a calculation whether a given set of specifications corresponds to a single solution, to multiple solutions or no solution at all. The computational procedures have recently been improved significantly. Michelsen (1980) describes a procedure for a rapid construction of the complete phase envelope for a specified total composition and phase ratio. The SRK equation of state is used in the form presented by Christiansen et al. (1979). Accurate and rapid calculations of critical points are also described by Heidemann and Khalil (1980) and by Michelsen and Heidemann (1981).

At the end of this section it should be mentioned that several papers have been published lately on specific problems and applications of cubic equations. A few examples for the popular SRK equation are: calculation of binary interaction parameters (Paunovic et al., 1981), calculation of pure component parameters (Soave, 1980) and avoidance of trivial roots and spurious derivatives (Poling et al. 1981).

Other Equations

The cubic equations mentioned above have preserved the repulsive term of the van der Waals equation (see equation (19)). This is a disadvantage since it does not allow a very good representation of high pressure PVT and VLE data. Several attempts have been made to replace the term with a physically more correct term representing the behavior
of hard bodies. The first proposal was the one by Carnahan and Starling (1969). A recent example of these perturbed hard body equations of state is presented by Ishikawa et al. (1980). The equations give excellent results for natural gas and petroleum type mixtures. Gmehling et al. (1979) used chemical theory to calculate the concentrations of the "true" species. These "true" species were then treated with a perturbed hard body equation of state. The chemical equilibrium constant was an extra parameter which allowed Gmehling et al. (1979) to describe very well methanol-water and ethanol-water in the pressure range 1-100 bar.

Other equations of state are similar in form to the virial equation. The compressibility factor is thus presented as a polynomial in density \( \rho \). An early example of these types of equations is the well-known BWR equation. A more recent example is the Bender (1975) equation.

\[
P = \rho T(R+B\rho+C\rho^2+D\rho^3+E\rho^4+F\rho^5+(G+H\rho^2)\rho^2 \exp(-Y\rho^2))
\]  

(21)

The constants B through H are functions of temperature. The total number of pure component parameters is twenty and for the binary interaction between each pair of components in a mixture three more parameters are needed. Sievers and Schulz (1980) have presented new parameters for methane covering the temperature range 91-625 K and pressures up to 500 bar with high accuracy.

Many modifications of these many-parameter equations have been proposed. Two recent examples are: 1) Nishiumi (1980): a generalized BWR equation applicable to high boiling hydrocarbons, \( C_{10}-C_{20} \), and for mixtures of these compounds and for pure component properties of polar substances. 2) Vetere (1982): a new eight-parameter equation applicable for pure polar and nonpolar compounds. The equation is simple and it seems fairly accurate even in the range of the critical isotherm and at high densities.

Deiters (1981a, b and 1982) has developed a promising semiempirical equation of state for nonpolar and weakly polar substances. The equation is derived from the square well model of the intermolecular pair potential. It contains three adjustable parameters per pure component.
and two interaction parameters for a binary mixture. It can describe phase equilibria in binary systems also at very high pressures (beyond 1000 bar) with reasonable accuracy.

This short paper does not allow the mention of all types of equations of state. One important area has for example been left out, namely the corresponding states theories. Thorough reviews are given by Mentzer et al. (1980, 1981).

For an overall orientation on the whole area of equations of state reference is again given to Chao and Robinson (1979).

**ACTIVITY COEFFICIENT MODELS**

For systems containing polar components or polymers it is as seen above difficult to find an equation of state that will allow the calculation of liquid phase fugacities. Such systems are most common and are often of interest for VLE and LLE calculations at low to moderate pressures. The liquid phase fugacity is then calculated according to equation (5). The calculation of the reference fugacity \( f_\text{id} \) has been explained previously while the calculation of activity coefficients \( \gamma_i \) will be the topic of this and the following section.

The liquid phase activity coefficients are related to the molar excess Gibbs function \( \bar{g}^E \) as follows

\[
\bar{g}^E = RT \sum_{i=1}^{N} x_i \ln \gamma_i
\]

and

\[
RT \ln \gamma_i = \frac{\bar{g}^E}{\bar{g}^E_i}
\]

where \( \bar{g}^E_i \) is the partial molar excess Gibbs function. The molar excess Gibbs function \( \bar{g}^E \) is defined as

\[
\bar{g}^E = g - g^{id}
\]

where \( g \) is the molar Gibbs function of a mixture, at a given temperature \( T \), pressure \( P \) and composition \( x_i \), while \( g^{id} \) is the molar Gibbs function for the mixture at the same conditions assuming ideality.

Many different models for \( \bar{g}^E \) and hence for \( \gamma_i \) have been used over the years like the Margules, VanLaar, Redlich-Kister, Scatchard-
Hildebrand and Flory-Huggins equations. G.M. Wilson introduced in 1964 the local composition concept which has opened for the development of some of the most popular models today like the Wilson, NRTL and UNIQUAC models. Many of the problems related to these local composition models may be illustrated via a description of the UNIQUAC model and of some of the attempts to improve the model.

The UNIQUAC model was derived by Abrams and Prausnitz (1975) from statistical mechanical arguments as a generalization of the quasichemical lattice theory developed by Guggenheim (1952). In 1978 the model was rederived by Maurer and Prausnitz using phenomenological arguments based on two-liquid theory.

In UNIQUAC the molar excess Gibbs function is given by two terms

\[ g^E = g^E(\text{combinatorial}) + g^E(\text{residual}) \] (25)

The **combinatorial term** takes into account liquid phase nonidealities due to differences in molecular size and shape and may be written as follows

\[ g^E(\text{combinatorial}) = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} \] (26)

where \( \phi_i \) and \( \theta_i \) are volume and area fractions calculated from pure-component volume and surface area parameters \( r_i \) and \( q_i \) and from mole fractions \( x_i \). \( z \) is the coordination number and is normally set equal to ten.

The **residual term** takes into account nonidealities due to intermolecular interactions. It may be written as follows

\[ g^E(\text{residual}) = -\sum_i q_i x_i \ln \left( \sum_j \tau_{ji} \right) \] (27)

The summations in equations (26) and (27) should be taken over all components. The values of \( \tau_{ji} \) are calculated from the following equation

\[ \tau_{ji} = \exp(-\frac{a_{ji}}{RT}) \] (28)

where \( a_{ji} = \frac{z}{2} \frac{U_{ji} - U_{ii}}{RT} \) (29)
The values of $U_{ji}$ characterize the energy of interaction between sites $i$ and $j$ on the lattice.

The UNIQUAC model has turned out to be a flexible and reliable model which allows good representation of VLE and LLE. Multicomponent systems can be described by means of parameters estimated from experimental data for the relevant binary mixtures. The DEHEMA Chemistry Data Series for VLE (Gmehling and Onken, 1977) and LLE (Sørensen and Arlt, 1979) give volume and surface area parameters $r_i$ and $q_i$ for many substances and also interaction parameters $a_{ji}$ for thousands of different mixtures.

Any liquid phase model for $g^F$ that also describes correctly the temperature variation of $g^F$ can be used to simultaneously correlate heats of mixing data, $h^E$, and $g^F$ data according to the Gibbs-Helmholtz equation

$$h^E = -RT \frac{\partial (g^F/RT)}{\partial T}$$

This means that parameters estimated from $h^E$ data should be applicable for the representation of $g^F$ data and vice versa. It is not possible with the UNIQUAC model to make a such simultaneous correlation.

Skjold-Jørgensen et al. (1980) modified the model by letting the coordination number be a generalized function of temperature

$$z(T) = 35.2-0.1272T + 0.00014T^2$$

This modification improved the capabilities of UNIQUAC significantly for nonassociating systems. It should be noted that $z$ is included in both equations (26) and (29).

The $r_i$ and $q_i$ values used in the UNIQUAC model are calculated from the van der Waals volumes and surface areas presented by Bondi (1968). The van der Waals values are normalized by means of the volume and surface area of a methylene group in polyethylene. This may not always be the best normalizing factors as indicated by Skjold-Jørgensen et al. (1982) who find that for many systems it would be advantageous to double the $r_i$ and $q_i$ values. It should be noticed that $q_i$ enters as a factor in both the combinatorial and the residual term for $g^F$. Nagata and Katoh (1980/81) have in a new modification partly avoided
the normalization problems by letting \( q \) in equation (27) have the value of unity.

Sayegh and Vera (1980) discuss expressions for the combinatorial term and they propose a rigorous method for calculating \( q \) values which are independent of an arbitrary choice of a normalization factor like the surface area of a methylene group.

Kikik et al. (1980) also discuss the expression for the combinatorial term. They propose a simple modification allowing a much better representation of infinite dilution activity coefficients.

The basic ideas in the local composition models are 1) that the concentrations at the molecular level may be different from the overall concentrations and 2) that it is possible to write expressions for the local concentrations as functions of the overall concentrations and of the interaction energies between the various types of components in a mixture. For the local surface area fraction \( \theta_{21} \) of component 2 around a central 1-molecule in a binary mixture we may thus write for the UNIQUAC model

\[
\theta_{21} / (1 - \theta_{21}) = (\theta_2 / \theta_1)^{\tau_{21}}
\]

(32)

This equation may lead to some inconsistencies when \( \tau_{21} \) as given by equation (28) is considered to be independent of concentration. This has been pointed out in several publications and it has quite recently been discussed by Panayiotou and Vera (1981). The same authors have in 1980/81 proposed a modified quasichemical model for \( g^E \) which does not possess these inconsistencies. Kemény and Rasmussen (1981) have on the other hand shown that local composition expressions like equation (32) may be derived from two-fluid theory. The discussion about the basic local composition concept is not yet finished and it will hopefully lead to new and better \( g^E \) models.

The UNIQUAC model does represent VLE and LLE very well but not simultaneously (Malanowski et al. 1981). In an attempt to solve this problem Skjold-Jørgensen et al. (1982) have introduced a concentration dependence of the interaction energy \( U_{ij} \)

\[
U_{ij} = U^\infty_{ij} + a_i \delta_j + \sum_k b_{jk} \theta_k
\]

(33)
The term \( U_{ij} \) is a reference quantity. Association-like effects are taken into account by means of the term \( a_j \beta_j^e \) where \( a_j \) is a fitting parameter and \( \varepsilon = 0.25 \). Solvation-like effects are taken into account by means of the term \( E_{ij}^k \beta_k \) where \( \beta_{ij}^k \) are fitting parameters. Significant improvements in the simultaneous representation of VLE and LLE have been obtained.

Association and solvation effects have been approached by others by means of chemical theory. A recent example are the papers by Nath and Bender (1981a and b). At the end of this section it may be said that many other fascinating ideas and types of \( g \) models have been described in the literature and that the whole area of \( g \) models seems to be in a period with much progress and promising activity.

GROUP-CONTRIBUTION MODELS

The activity coefficient models mentioned until now can only be applied if we have the necessary parameters for the individual components and for the interactions between the components. Such parameters are obtained from experimental phase equilibrium data.

Group-contribution methods allow for the prediction of liquid phase activity coefficients for binary and multicomponent mixtures for which little or no experimental information is available. The methods are based on the solution of groups concept. The groups are structural units such as \( CH_3, OH \) and others which when added form the parent molecules. Instead of considering a liquid mixture as a solution of molecules, the mixture is considered as a solution of groups. The activity coefficients are then determined by the properties of the groups rather than by those of the molecules. This is a great advantage. The number of different components of interest in chemical technology is thus very large while the number of different groups that build these components is relatively small. The activity coefficients of a large number of very different mixtures may hence be calculated from characteristic parameters representing a few groups and the energetic interactions between the groups.

At the 1980 conference on Phase Equilibria and Fluid Properties in the Chemical Industry a review on group-contribution methods was presented by Rasmussen and Skjold-Jørgensen. Only the fundamentals
of ASOG and UNIFAC and some quite recent developments of these models will therefore be presented here.

ASOG and UNIFAC are the most established group-contribution models to date for the prediction of liquid phase activities in nonelectrolyte mixtures. In both methods the activity coefficients are calculated from two terms

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (34)$$

The combinatorial term $\ln \gamma_i^C$ takes into account differences in size and shape of the molecules and the residual term $\ln \gamma_i^R$ describes the nonidealities due to energetic interactions between the groups.

**Analytical Solution of Groups (ASOG)**

Kojima and Tochigi have in 1979 presented a comprehensive treatment of the ASOG method for VLE calculations. The necessary equations are shown in Table 2. The combinatorial term is calculated by an equation similar to the Flory-Huggins equation which means that only differences in size of the molecules are taken into account. The residual group activity coefficients are calculated according to the Wilson (1964) equation with concentrations given by group fractions instead of mole fractions. Kojima and Tochigi (1979) have included 31 groups and they have estimated parameters representing 143 out of the 465 possible group interactions in the temperature range 303 to 423 K.

The group interaction parameters $a_{kl}$ between groups $k$ and $l$ are considered to be functions of temperature

$$\ln a_{kl} = m_{kl} + n_{kl}/T \quad (35)$$

where $m_{kl}$ and $n_{kl}$ are temperature independent parameters. This gives four parameters per pair of groups $(m_{kl}, m_{lk}, n_{kl}, n_{lk})$. Tochigi et al. (1981) have modified equation (35) to

$$\ln a_{kl} = \ln \frac{v_l}{v_k} - b_{kl}/T \quad (36)$$

where $v_l$ and $v_k$ are the number of non-hydrogen atoms in groups $l$ and $k$. This modification reduces the number of parameters to two per pair of groups $(b_{kl}$ and $b_{lk})$. 
### Table 2. ASOG equations for the prediction of liquid-phase activity coefficients

\[
\ln \gamma_i^C = \ln \phi_i^C + \ln \gamma_i^R
\]

\[
\ln \gamma_i^C = \ln \phi_i^C \cdot \gamma_i^R
\]

\[
\phi_i = \frac{x_i S_j}{\sum_j x_i S_j}
\]

\[ j = 1, 2, \ldots, N \]

- \( S_i \) = number of atoms (other than hydrogen) in molecule \( i \)
- \( x_i \) = liquid mole fraction of component \( i \)
- \( N \) = number of components

\[
\ln \gamma_i^R = \sum_{k=1}^{M} v_{ki} \ln r_k^* - \ln r_k^{(1)}
\]

\[
v_{ki} = \text{number of atoms (other than hydrogen) in groups } k \text{ in molecule } i
\]

- \( r_k \) = group activity coefficient of group \( k \)
- \( r_k^{(1)} \) = group activity coefficient of group \( k \) in pure component \( i \)
- \( M \) = number of groups

\[
\ln r_k = - \ln \left( \sum_i a_{ki}^* x_i \right) + 1 - \sum_i \frac{x_i a_{kk}}{\sum_m a_{km}}
\]

- \( a_{ki}^* \) = group interaction parameter characteristic of groups \( k \) and \( i \) \((a_{ki}^* \neq a_{kk})\)
- \( X_k \) = group fraction of group \( k \)
- \( \gamma_i^R = \frac{x_i V_{ki}}{\sum_k x_i V_{ki}} \)

\[ k = 1, 2, \ldots, M \; ; \; i = 1, 2, \ldots, N \]
The ASOG method has been applied by Tochigi et al. (1980) to predict LLE for ternary systems with reasonable success considering the fact that the parameters used were those estimated from VLE data by Kojima and Tochigi (1979). The method has most recently been used to predict SLE with good accuracy (Ochi et al., 1982).

An interesting publication by Kawaguchi et al. (1981) shows the application of ASOG in conjunction with a hydration model for the estimation of water activity in aqueous electrolyte solutions. The publication has been followed up in 1982.

Ashraf and Vera (1980) have proposed a simplified group-contribution method similar to ASOG. The method called SIGMA has been tested with the same temperature independent parameters for the prediction of VLE and heats of mixing data of binary and ternary systems containing CH₂, OH and Cl groups. The method seems to provide a rather simple approach for approximate calculations for systems with strongly interacting molecules.

UNIQUAC Functional-Group Activity Coefficients (UNIFAC)

Fredenslund et al. have in 1977 presented a comprehensive treatment of the UNIFAC method. The necessary equations for the prediction of activity coefficients from UNIFAC are shown in Table 3. The UNIFAC method is based on the UNIQUAC model, which means that the equations and the problems are similar to those of the UNIQUAC model.

The parameters needed for the use of UNIFAC are group volumes (R_k), group surface areas (Q_k) and group interaction parameters (a_{mn} and a_{nm}). Extensive tables with revised and updated values for these parameters for 40 groups have been presented by Gmehling et al. (1982). Parameters representing 346 out of the 780 possible group interactions have been estimated. These parameters can be used to predict VLE data for non-electrolyte binary and multicomponent mixtures in the temperature range 300 to 425 K. Parameters for some special groups as for example lactames and silicones may be found in Hauthal et al. (1980), Kato (1980) and Herskowitz and Gottlieb (1981). The group interaction parameters have been estimated from experimental VLE data. Predictions of LLE and heats of mixing (H^E) based on these parameters are
Table 3. UNIFAC equations for the prediction of activity coefficients

\[
\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R
\]

\[
\ln \gamma_i^C = (\ln \phi_i / x_i + 1 - \phi_i / x_i) - \frac{1}{2} z q_i (\ln \phi_i / \theta_i + 1 - \phi_i / \theta_i)
\]

\[
\phi_i = \frac{x_i r_i}{\sum_{j} x_j r_j}
\]

\[
\theta_i = \frac{x_i a_i}{\sum_{j} x_j a_j}
\]

Summation over all components

\[
r_i = \sum_{k} v_{ki} R_k
\]

\[
q_i = \sum_{k} v_{ki} Q_k
\]

Summation over all groups

\[
R_k = \text{volume parameter for group } k
\]

\[
Q_k = \text{surface area parameter for group } k
\]

\[
v_{ki} = \text{number of groups of type } k \text{ in molecule } i
\]

\[
x_i = \text{liquid mole fraction of component } i
\]

\[
z = \text{coordination number } = 10
\]

\[
\ln \gamma_i^R = \sum_{k} v_{ki}(\ln r_k - \ln r_k^{(i)})
\]

Summation over all groups

\[
\ln r_k = Q_k [1 - \ln(\sum_{m} v_{mk} x_m) - \sum_{m} \psi_{mn}^{m} \psi_{mn}^{n}]
\]

\[
\psi_{nm} = \exp(-a_{nm}/T)
\]

\[
\theta_m = Q_m \left[ \sum_{n} v_{mn} x_m \right]
\]

\[
x_m = \frac{\sum_{n} v_{mj} x_j}{\sum_{n} v_{nj} x_j}
\]

\[
a_{mn} = \text{group interaction parameter for the interaction between groups } m \text{ and } n
\]
qualitatively reasonable, while a quantitative and simultaneous representation of both VLE and LLE from the same parameters is not feasible. The problems are the same as described for the UNIQUAC model. A parameter table explicitly for LLE predictions has therefore been developed (Magnussen et al., 1981, see also Arlt et al., 1981) and the previously described modifications of UNIQUAC by Skjold-Jørgensen et al. (1980), Kikic et al. (1980) and Skjold-Jørgensen et al. (1982) are also directed towards improvement of the UNIFAC method. Work is in promising progress in our group to combine the various UNIQUAC/UNIFAC modifications into one model that will allow, with the same parameters, a simultaneous correlation of VLE, LLE and $H^E$ data.

The UNIFAC method has become a most popular method for the prediction of liquid phase activity coefficients, Gmehling et al. (1980). It has been used not only for direct phase equilibrium calculations of VLE, LLE and SLE but also other applications have been reported. Examples are: Estimation of solvent effects on chemical reaction rates (Lo and Paulaitis, 1981, and Gmehling and Fellensiek, 1980); Estimation of flash points of flammable liquid mixtures (Gmehling and Rasmussen, 1982) and Choice of solvent for extraction purposes (Tegtmeier and Misselhorn, 1981). The method has also been used to describe phase equilibria of polymer solutions (Oishi and Prausnitz, 1978, Hützsch and Glinnemann, 1979, Arai and Iwai, 1980, and Gottlieb and Herskowitz, 1981).

The UNIFAC group-interaction parameters have been determined almost exclusively from experimental VLE data. Lack of reliable experimental data has prevented the estimation of some parameters. Since it is a time-consuming and difficult task to measure VLE data in the whole concentration range of the many mixtures of interest, one has to look for other types of experimental information. One such possibility is to use infinite dilution activity coefficients calculated from gas-liquid-chromatographic data. Alessi et al. (1981) have shown that it is indeed possible to estimate UNIFAC parameters from infinite dilution activity coefficients. In this context it can be mentioned that Rizzi and Huber (1981) have made a comparative study of the prediction of infinite dilution activity...
coefficients by means of various group-contribution methods.

Other Group- Contribution Methods

ASOG and UNIFAC are related to the lattice theory of liquids and they can only be used to predict liquid phase properties. That is also the case for some other recently developed group-contribution methods: 1) Nagata and Koyabu (1981), 2) Kehiaian (1979, 1980), 3) Chien et al. (1981) extension of the Nitta et al. (1977) paper, and 4) Dohnal et al. (1981). A group-contribution model which can predict simultaneously the thermodynamic properties of liquid and vapor phases would be a decided improvement. The PFGE equation (Moshfegian et al., 1979) represents such a model. It may be used for hydrocarbon systems over a wide range of pressures and with components ranging from C\textsubscript{1} to C\textsubscript{32}. The systems may also include polar components. Ishizuka et al. (1980) have proposed a similar group-contribution model based on hole theory for alkanes and aromatics. Pure component properties like molar volumes and heats of vaporization are represented very well in the reduced temperature range 0.3 to 0.8. Also VLE and SLE data may be predicted with good accuracy.

CONCLUSION

There has been much progress within the area of phase equilibrium calculations during the last few years. Many types of computations are possible today which were unthinkable just a few years ago. It seems reasonable, considering the present rate of progress, to express the hope that it will soon be possible also to make good correlations and predictions for systems of electrolytes, for mixtures with polymers, for high pressure equilibria between polar/nonpolar gases and liquids and for high boiling petroleum fractions.
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Figure 1. Molar Gibbs function of mixing for binary mixture showing tangent at mole fraction $z_1$ and $F$ at mole fraction $y_1$. 
REPRESENTING BOTH THE VAPOR AND LIQUID PHASES BY A GENERALIZED REDLICH-KWONG EQUATION OF STATE WITH SEPARATE SETS OF PARAMETERS FOR EACH PHASE

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SUMMARY

The separate sets of parameters in the Redlich-Kwong equation of state were evaluated from vapor pressures and saturated liquid and vapor densities and fugacities of pure substances. The parameters were further generalized in terms of $T$, $w$ and $Z$. Comparisons of predicted vapor pressures, enthalpies of vaporization, densities and enthalpy departures of saturated phases with literature data are given, demonstrating the advantages of the proposed modification when the saturated line of pure nonpolar and moderately polar substances is of principal interest. The proposed equation can be successfully extended to compressed liquid and superheated vapor of pure components as well as to multicomponent mixtures.

Some illustrative examples of experimental and calculated vapor-liquid equilibria are also presented to demonstrate the applicability of the new modification to VLE predictions, with the exclusion of the critical region.
INTRODUCTION

The modifications of the most successful two-parameter equation of state, formulated 1949 by Redlich and Kwong, have been abundant. The most useful to the chemical engineer are those equations of state which are generalized, along with the equal fugacity criterion ($f^L = f^V$) incorporated /1-4/.

However, none of the available generalized modifications of the Redlich-Kwong (RK) equation of state is adequate as to represent both the vapor and liquid phases. Therefore, it seems worthwhile to follow the idea of two different sets of values for the RK equation parameters for the liquid and vapor phase, mutually related by the equal fugacity criterion, which is suggested by Zudkevitch and Joffe (1970). The aim of the present work is to develop the generalized expressions for the separate sets of the temperature-dependent RK parameters for the liquid and vapor phase, which enable accurate representing of both phases of nonpolar and slightly polar substances.

PROPOSED MODIFICATIONS

The RK equation for a pure substance is given by the following equation:

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)}$$  \hspace{1cm} (1)

where

$$a = \Omega_a R^2 T_c^2.5 / P_c$$  \hspace{1cm} (2)

$$b = \Omega_b R T_c / P_c$$  \hspace{1cm} (3)

or, in terms of the compressibility factor $Z$,

$$Z^3 - Z^2 + B(A-1-B)Z - AB^2 = 0$$  \hspace{1cm} (4)

where

$$Z = P_v / RT$$  \hspace{1cm} (5)

$$A = \Omega_a R^{1.5} / T$$  \hspace{1cm} (6)

$$B = \Omega_b P_v / T$$  \hspace{1cm} (7)

$$\Omega_{ab} = \Omega_a / \Omega_b$$  \hspace{1cm} (8)
The criteria

\[ Z_{\text{cal}}^S = Z_{\text{exp}}^S \quad (9) \]
\[ \psi_{\text{cal}}^S = \psi_{\text{exp}}^S \quad (10) \]

when applied to each saturated phase independently of the other phase, may produce two separate pairs of the parameters \( \Omega_{ab} \) and \( \Omega_b \) for a given temperature (Zudkevitch and Joffe, 1970). The authors presented the appropriate computing procedure which they had tried on several hydrocarbons. As reported, the solutions for the vapor phase tend to take an erratic course and become negative after passing through a maximum, when temperature is lowered. The failure of the procedure seems to be caused by a rapid decreasing of the sensitivity of the calculated \( Z_v \) values to the \( \Omega_b \) variations, along the saturation line. The sensitivity defined as:

\[ \alpha = \frac{\partial \ln Z_{\text{v,cal}}}{\partial \ln \Omega_{b,v}} \quad (11) \]

can be derived from Eq. (4):

\[ \alpha = \frac{Z_3^2 - Z_2^2 + B^2(A+Z)}{2Z_2^2 - Z_2^2 + B^2A} \quad (12) \]

In Eq. (12) \( Z \) stands for \( Z_{\text{v,cal}}^S \) being the largest real root of Eq. (4), for a given temperature \( T \) and the corresponding vapor pressure \( P_v^S \). At sufficiently low temperatures \( Z \) is almost unit allowing for the approximation:

\[ \alpha = \frac{B^2A}{A+ B^2A} \quad (13) \]

By incorporating into Eq. (13) the Clausius exponential temperature function for vapor pressure, one can readily show that \( \alpha \) approaches zero as temperature lowered. By the presented observation the replacement of the local criterion (9) by a mean-squares one:

\[ \Sigma\left( Z_{\text{v,cal}}^S - Z_{\text{v,exp}}^S \right)^2 = \text{minimum} \quad (14) \]

is imposed.

Some preliminary calculations based on criterion (14) combined with the condition (10) were tried,
assuming the $\Omega_{b,v}$ parameter temperature independent. The tests were successful up to $T_r = 0.95$. In the critical region the problem arises - the largest real root of the cubic Eq. (4) dissappears in the course of the summ of squares (14) reduction. The Zudkevitch and Joffe calculation scheme is tried in that region, both the $\Omega_{ab,v}$ and $\Omega_{b,v}$ being temperature dependent. However, the calculations were often frustrated by the dissappearance of the vapor-like root of state equation (1). An attempt is made to overcome this difficulty by introducing the third parameter $c$ in the critical region:

$$P = \frac{RT}{v - b + c} - \frac{a}{T^{1.5}(v+c)(v+b+c)}$$  \hspace{1cm} (15)

$$c = \frac{\Omega_c RT_c}{P_c}$$  \hspace{1cm} (16)

Retaining the original value 0.08664 for the RK parameter $\Omega_p$, the test calculations, for fourteen substances, of the constant values of $\Omega_c,v$ and temperature dependent values of $\Omega_{ab,v}$ were successful in the interval $0.93 < T_r < 0.995$. It remains adopt the method of extrapolating parameter values to the critical point.

As far as the low temperature region is considered, it is observed that the $\Omega_{ab}$ values evaluated from the criteria:

$$Z_1,\text{cal} = Z_1,\text{exp}$$  \hspace{1cm} (17)

$$\gamma_1,\text{cal} = \gamma_1,\text{exp}$$  \hspace{1cm} (18)

along with the condition:

$$\Omega_{b,v} = \text{constant}$$  \hspace{1cm} (19)

may provide the correct estimates for both the saturated vapor fugacity and compressibility factor up to $T_r = 0.65$. As the result of solving Eqs. (17) and (18), retaining the upper temperature interval value for $\Omega_{b,v}$, the common values of $\Omega_{ab}$ for both phases are obtained, as well as the values of $\Omega_{b,1}$.
The values of the parameter obtained for a number of nonpolar and slightly polar substances are further correlated in terms of $T_r$, $w$ and $Z_c$. The resulting equations are presented in /6/.

RESULTS

Pure substances

Vapor pressures. Above the boiling point temperatures, the proposed correlation performs similarly as the other generalized modifications of the RK state equation formulated on the basis of the equal fugacity criterion /1-4/, providing the good estimates (average absolute deviation is about 1%). Below the boiling point, however, any of the equations analysed is much less successful. The average absolute deviations of vapor pressures of n-alkanes $C_2-C_{10}$, from their triple to their boiling points, obtained with the new correlation, the Soave equation (SRK) /1/ and the equation by Hamam et al. (HCEL) /2/, are 3.3%, 4.7% and 16%, respectively. Instead of the experimental vapor pressure data, the smoothed values were used for comparison, generated from the Clausius /7/ or the Antoin /8/ equation.

Densities. Both the new and HCEL modifications produce accurate liquid density estimates, the former being more reliable in the compressed liquid region. As far as the saturated vapor densities are concerned, it may be stated that the proposed equation offers better estimates than the SRK modification, especially in the critical region. A comparison is presented in Table 1, the values in the brackets corresponding to the critical region, $T_r > 0.95$.

Heats of vaporization. Having in mind the relation between heat of vaporization, densities of saturated phases and vapor pressure (the Clapeyron equation), one can expect good predictions from the new correlation. Thus, the average absolute deviations obtained for 25 pure substances are 1.1% and 4.5% below, and in the critical region, respectively. This compares favorably with the deviations obtained by the
SRK equation (1.7% below and 10.7% in the critical region) and the HCEL equation which gives very poor results both in the lowest temperature interval and in the critical region.

Table 1.- Comparison of Saturated Vapor Density Predictions

<table>
<thead>
<tr>
<th>Substance</th>
<th>No. of data points</th>
<th>Reduced temperature range</th>
<th>This work</th>
<th>SRK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>23(9)</td>
<td>0.625-0.999</td>
<td>0.49(1.86)</td>
<td>1.52(2.21) /9/</td>
</tr>
<tr>
<td>Butane</td>
<td>15(19)</td>
<td>0.641-0.998</td>
<td>1.52(2.73)</td>
<td>0.79(7.25) /10/</td>
</tr>
<tr>
<td>i-Butane</td>
<td>12(18)</td>
<td>0.640-0.998</td>
<td>0.65(9.71)</td>
<td>1.13(10.6) /11/</td>
</tr>
<tr>
<td>Pentane</td>
<td>14(15)</td>
<td>0.658-0.999</td>
<td>0.43(5.09)</td>
<td>2.27(11.68)/12/</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>15(15)</td>
<td>0.654-0.997</td>
<td>0.39(4.24)</td>
<td>1.97(10.6)/13/</td>
</tr>
<tr>
<td>neo-Pentane</td>
<td>13(12)</td>
<td>0.651-0.998</td>
<td>0.40(1.35)</td>
<td>2.04(5.79)/14/</td>
</tr>
<tr>
<td>Ethylene</td>
<td>18(10)</td>
<td>0.600-0.992</td>
<td>1.33(3.58)</td>
<td>3.25(7.73)/15/</td>
</tr>
<tr>
<td>Cyclo-Butane</td>
<td>16(6)</td>
<td>0.736-0.987</td>
<td>1.01(5.91)</td>
<td>2.36(8.11)/16/</td>
</tr>
<tr>
<td>CO₂</td>
<td>14(5)</td>
<td>0.711-0.999</td>
<td>1.15(2.23)</td>
<td>1.34(4.25)/15/</td>
</tr>
<tr>
<td>H₂S</td>
<td>8(5)</td>
<td>0.744-0.999</td>
<td>1.58(3.76)</td>
<td>2.92(5.41)/17/</td>
</tr>
<tr>
<td>Overall:</td>
<td>144(114)</td>
<td></td>
<td>0.86(4.39)</td>
<td>1.95(8.13)</td>
</tr>
</tbody>
</table>

The values in brackets correspond to the critical region $T_r > 0.95$

Enthalpy departures. The calculated enthalpy departures of saturated phases has been compared with the experimental values for methane, propane, cyclohexane, benzene and nitrogen. For a total of 63 data points, 20 of which lie in the critical region, the overall absolute deviations in kJ/kg are 3. and 7.1 below the critical region, and 4.8 and 22.5 in the critical region, for the new and the SRK equation, respectively. The improvement resulting from the new correlation is evident. However, it is to say that the two equations generate enthalpy values of about the same reliability, outside the saturation region. Furthermore, in the limited region defined as $T_r > 0.95$ along with $P_r > 2$, the SRK equation generates definitely better estimates for the liquid phase, the new one giving deviations greater than 10%.
Mixtures

PVT and enthalpy calculations. The comparisons have shown that, in general, the new and the Soave equation give similar results, except that the new equation gives considerably better liquid density predictions, and on the other hand, that the Soave equation gives more reliable values for liquid enthalpies in the region $T_r > 0.95$, $P_r > 2$.

VLE calculations. The calculations were performed for a number of systems /6/. With the exclusion of the critical region, the new equation provides the reliable results. As an example, for the total of 21 data points for the methane-ethane-propane system, examined by Wichterle and Kobayashi (1972) and reproduced by Mollerup /18/, the average absolute deviations obtained in the bubble point pressure calculations are as follows:

<table>
<thead>
<tr>
<th></th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$K_2$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Eq.</td>
<td>1.3</td>
<td>4.3</td>
<td>6.8</td>
<td>3.3</td>
</tr>
<tr>
<td>SRK</td>
<td>1.6</td>
<td>5.3</td>
<td>7.4</td>
<td>2.1</td>
</tr>
</tbody>
</table>

The VLE calculations with the separate RK parameters may not converge in the critical region. In order to test the behavior of the new correlation in this region, both the bubble and the dew point calculations were performed for the 6-component natural gas mixture /19/. In contrast to the Soave method, that converged at all of the 8 points lying in the vicinity of critical point, the new one failed to converge at two points. For the rest of 6 points the average percent deviations obtained are:

<table>
<thead>
<tr>
<th></th>
<th>Bubble</th>
<th>Dew</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P$</td>
<td>$T$</td>
</tr>
<tr>
<td>New Eq.</td>
<td>0.84</td>
<td>0.23</td>
</tr>
<tr>
<td>SRK</td>
<td>2.59</td>
<td>0.69</td>
</tr>
</tbody>
</table>

CONCLUSIONS

In this investigation, generalized correlations for the se-
parate sets of the RK parameters for the liquid and the vapor phases were established. The comparisons with the other modifications of the RK equation indicates that the proposed equation represents a good improvement in the region of the saturated phases of a pure substance. The proposed correlations offer also good multicomponent VLE predictions, with the exclusion of the critical region.

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AN EFFICIENT METHOD TO AVOID TRIVIAL SOLUTIONS IN BUBBLE POINT PRESSURE CALCULATIONS FROM A CUBIC EQUATION OF STATE

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SUMMARY

The appearance of the so called trivial solutions i.e. the false unit equilibrium constants is associated with producing unrealistic values of vapor and liquid densities by means of a state equation.

A simple and reliable method is presented to avoid trivial solutions when a cubic equation of state is used for calculating pressure and equilibrium constants at the bubble point of a mixture. The failure is prevented by generating artificial density values leading to a correct solution.

The method's utility is demonstrated with some illustrative calculations, based on the use of Soave modifications of Redlich-Kwong equation of state.
INTRODUCTION

A suitable equation of state when applied to both phases provides good results in the prediction of vapor-liquid equilibrium (VLE). However, in the vicinity of critical point, the so called trivial solutions (TS), followed by false unit equilibrium constants, frequently appear.

In the last few years, several authors have suggested some ideas for avoiding TS, the problem being stated by Harmsen firstly /1/. Huron et al. /2/ have proposed a step by step procedure of searching pressure interval where equation of state has three real roots. The procedure seems to be time consuming and unreliable, as reported. Asselineau et al. /3/ have proposed a versatile and reliable algorithm for calculation of VLE up to the critical point, which, in return, is rather cumbersome and seems unreasonable for chemical engineering purposes. Recently, Polling et al. /4/ have presented a simple method to find and avoid TS for a cubic equation of state. The authors have suggested pressure reduction to generate vapor phase properties and adjustment of composition for the liquid phase. No recommendations for a magnitude of corrections have been presented. The effect of pressure reduction has not been studied in the light of possible simultaneous disappearance of liquid phase properties, as well.

The scope of this work is to develop a simple and reliable method for avoiding trivial roots in bubble point pressure determination, suitable for use in chemical engineering calculations. The utility of the proposed procedure is demonstrated for Redlich-Kwong-Soave equation of state /5/, which may be rewritten as:

\[ f(z) = z^3 - z^2 + B(A-1-B) - AB^2 = 0 \]  
(1)

where \( z \) is the compressibility factor and \( A \) and \( B \) are given by:
The appearance of TS is affected by producing unrealistic values of vapor and/or liquid densities from a state equation.

Figure 1. Possible forms of $f(z)$
The possible cases regarding number and types of the real roots of eq (1) are presented in Figure 1. Evidently, the problem arises when the vapor compressibility factor $z^V$, is to be predicted from the curves IV and V. The similar situation appears for liquid phase with cases I and II. It is to be noted that a liquid compressibility factor value for a mixture $z^L$, predicted as a single real root of the curves I and II, might be considered satisfactory, as well. This calls for an appropriate criterion. A loose empirical criterion has been proposed by Rolling et al. /4/.

The following four actions for controlling and avoiding trivial roots are presented here:

(a) Adjustment of the starting bubble point pressure values

(b) Generation of artificial density values by the local extrema in $f(z)$

(c) Temporary conservation of liquid phase density values

(d) Pressure correction to produce artificial vapor density values

(a) Starting pressure value. In order to separate starting $z^V$ and $z^L$ values, it is recommended to reduce pressure until the condition

$$\frac{z^V}{z^L} > 1.2$$

is met.

(b) Artificial density values. In early iterations of the bubble point pressure computation procedure, cases IV and II for vapor and liquid phase, respectively, may occur. It is suggested to use artificial compressibility factor values obtained as follows.

The local minimum (maximum) $z$ value, $z^V_m$ ( $z^L_m$), is adopted as the temporary vapor (liquid) compressibility factor (Figure 1.). By the numerous tests, it is indicated that, in the course of iterations, the curve IV transforms to form III, II or I, leading to a real final value $z^V$. Similarly, the evolution of the form II to
III, IV or V leads to "liquid like" $z^L$ value less than $1/3$. A problematic case of a transition from the form II to the form I, will be discussed in the point (c).

When applying some of the derivatives exploiting methods for bubble point pressure calculation, spurious derivative values ($\alpha f/\alpha z$) produced by artificial $z$ values may be prevented by replacing them by inconsistent $z$ values obtained from somewhat higher (for vapor phase) or lower (for liquid phase) $z$ values.

(c) Conservation of liquid phase density values. The transition of the form II (or the form V) to the form I (Figure 1.), may lead to the "vapor like" TS. In order to avoid the failure, the assumption of the liquid incompressibility (although it is not valid in the critical region) is adopted. The $z_m^L$ value obtained from the curve II (or the $z^L$ value obtained from the curve V) is conserved until a prescribed value of the loose convergence criterion is reached. Further on, the true root of the state equation is taken for $z^L$ value. By the procedure described, the correct final solution with $z^L$ value greater than $1/3$ is usually attained. However, retaining of an unrealistic $z^L$ value, through intermediate iterations, may sometimes give rise to a "vapor like" TS followed by the high value of calculated pressure. At this point, the bubble point calculation is repeated, including reduction of the starting pressure value (a), but with no adjustment of the liquid phase.

(d) Producing artificial vapor density values. If the local extrema are absent (curve V), it is necessary to find out conditions for generating them, i.e. for the transition of the curve V to the curve IV. In this work, the pressure correction is proposed via the necessary condition for the existence of three real roots of a cubic equation. For the eq (1) the necessary condition is stated as follows:

$$1 - 3B(A-1-\beta) > 0$$

(4)
If the term \(3B^2\) is neglected, the relation (4) may be replaced by:

\[
B = \frac{1}{3(A-1)}
\]  

(5)

Thus, the corrected pressure value can be explicitly found as:

\[
P = \frac{RT}{3b(A-1)}
\]  

(6)

Similar expressions for other cubic equations of state can be easily derived.

It should be noted that the pressure reduction may cause the loss of the proper liquid phase density values. The simultaneous inclusion of the action (c) is imposed.

RESULTS

The techniques discussed above were applied to ten binary systems, the selected data lying in the vicinity of the critical points.

The bubble point pressure problem is solved by the decomposition scheme of Chao and Sender /6/. The starting estimates of equilibrium ratio \(K_i\) values were obtained from experimental data when available. Otherwise, the Starlings/7/ correlations for an ideal system \(K_i\) values were used. All computations were carried out with zero binary interaction parameter \(C_{ij}\) values.

With the standard algorithm, the TS have occurred at 75% of the tested points, when starting from the experimental bubble point pressures.

The reliability of the proposed techniques is demonstrated in Table 1. The two TS indicated, are suspected to occur due to the Soave model. Namely, the comparison of calculated and experimental \(K_i\) values shows that, when approaching the critical point, the calculated results converge to the unit values considerably faster than the experimental data.
Table 1. Results of bubble point pressure calculations

<table>
<thead>
<tr>
<th>System, Number of data /Ref./</th>
<th>Starting pressure $(r_{o}/r_{exp})$</th>
<th>Number of points at which the actions were applied</th>
<th>Number of TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane-Butane, 25 /8/</td>
<td>0.5 7 25 0</td>
<td>15 1 0</td>
<td></td>
</tr>
<tr>
<td>Methane-Pentane, 15 /9/</td>
<td>0.5 0 3 0</td>
<td>1 0</td>
<td></td>
</tr>
<tr>
<td>Isobutane-Butane, 19 /10/</td>
<td>1 0 13 0</td>
<td>9 15</td>
<td></td>
</tr>
<tr>
<td>Butane-Decane, 2 /11/</td>
<td>1 1 0 0</td>
<td>0 1</td>
<td></td>
</tr>
<tr>
<td>Methane-H2S, 15 /12/</td>
<td>0.5 0 9 0</td>
<td>3 0</td>
<td></td>
</tr>
<tr>
<td>Isobutane-H2S, 16 /13/</td>
<td>1 0 0 14</td>
<td>0 7</td>
<td></td>
</tr>
<tr>
<td>Isobutane-H2S, 12 /14/</td>
<td>0.5 2 15 0</td>
<td>7 0</td>
<td>2</td>
</tr>
<tr>
<td>CO2-N2, 8 /15/</td>
<td>0.5 0 8 0</td>
<td>0 0</td>
<td></td>
</tr>
<tr>
<td>Butane-CO2, 16 /16/</td>
<td>0.5 0 14 0</td>
<td>5 0</td>
<td></td>
</tr>
<tr>
<td>Nitrogen-Methane, 19 /17/</td>
<td>0.5 0 19 0</td>
<td>4 0</td>
<td></td>
</tr>
</tbody>
</table>
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PREDICTION OF SECOND VIRIAL COEFFICIENTS OF POLAR FLUIDS BY AN IMPROVED CORRESPONDING STATES METHOD

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Summary

Second virial coefficients are calculated combining the Kihara spherical core potential with a term accounting for polar interactions. The resulting potential is rearranged in the form required by the corresponding states theorem, introducing temperature-dependent effective potential parameters.

The "true" molecular parameters are related to the critical constants and the hard-core diameter is related to the gyration radius of the molecule. The latter correlation depends on the molecular shape.

In order to test the accuracy of the proposed method, comparisons are carried out with experimental data for several fluids.
Introduction

Several correlations proposed in the past to evaluate the second virial coefficients $B$ are based on the corresponding states theorem (CST)\textsuperscript{1-3}. The extension of CST to fluids with non-spherical molecules is, commonly, made by means of the acentric factor $\omega$.

Recently some correlations of $B$ have been proposed which use the gyration radius $R$ instead of $\omega$\textsuperscript{4-6}. The advantage of using $R$ as asphericity parameter is the fact that $R$ is defined strictly in terms of molecular structure. Therefore it does not include polarity effects and differs, in this respect, from other third parameters based on macroscopic properties.

In this paper the radius of gyration is used as a third parameter and the polarity effects are taken into account by adding electrostatic and induction contributions to the dispersion forces. The Kihara potential for a spherical core is assumed as dispersion term. Shape effects are characterized by associating, to each molecule, a pseudo-sphere with a hard-core diameter depending on the shape of the molecule as well as on its size.

Second virial coefficients

The expression of $B$ deriving from the Kihara spherical potential is:

$$B = \frac{B}{r} = \frac{1}{2\pi N_A Q_0^3} \varepsilon T^{3/2}(T_r) + \frac{1}{3} a F_2(T_r) + \frac{1}{6} a F_1(T_r) + \frac{1}{6} \frac{a^2}{r} F_1(T_r) + \frac{a^3}{r}$$  

(1)

where $N_A$ is the Avogadro's number, $T = kT/\varepsilon$ is the reduced temperature, $k$ is the Boltzmann's constant and $a = 2a/Q_0$ is the reduced diameter of the hard-core. The functions $F_1$, $F_2$ and $F_3$ are tabulated by Kihara\textsuperscript{7} and can be fitted by analytical expressions.

The molecular parameters $Q_0$, $\varepsilon$ and $a$, which appear in eq.(1),
are commonly obtained by fitting experimental values of either $B$ and/or the viscosity. Therefore this procedure does not allow predictions of $B$; furthermore, in the case of polar fluids, fitting $B$ by eq.(1) gives parameters which include polarity effects. A method based on the CST is proposed to calculate potential parameters from critical constants and the radius of gyration. In the case of polar fluids dipole moments and polarizabilities are required further on.

**Non-polar fluids**

The reduced hard-core diameter $a_r$ of non-polar fluids can be related to $R$. Empirical correlation $a_r$ vs. $R$ obtained with the few experimental data of $a_r$ available in the literature $^8,9$, shows a linear dependence of $a_r$ on $R$. The quality of the correlation improves if a different straight line is used for each molecular shape. The correlations obtained with $R$ taken from Reid et al. $^10$ and $a_r$ deduced from $B$ are:

<table>
<thead>
<tr>
<th>Molecular shape</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherocylinders</td>
<td>$a_r = 0.2966 R - 0.2026$</td>
</tr>
<tr>
<td>Regular tetrahedrons</td>
<td>$a_r = 0.1346 R + 0.1345$</td>
</tr>
<tr>
<td>Thin rods</td>
<td>$a_r = 1.1663 R - 0.5253$</td>
</tr>
<tr>
<td>Planes</td>
<td>$a_r = 0.4012 R - 0.6172$</td>
</tr>
</tbody>
</table>

These correlations allow us to represent molecules of arbitrary shape by equivalent spherical molecules with a suitable hard-core diameter.

The other two parameters, $\varepsilon/k$ and $Q_0$, can be obtained straightforward from the three parameters CST. From the critical conditions $^11$ follows:

$$T_{c,r} = \frac{T_c}{(\varepsilon/k)} = f_r(a_r)$$  \hfill (2)
Eqs. (2) and (3), with \( a = 0 \), give constant values of the reduced critical quantities. The use of the Lennard-Jones potential \( (a = 0) \) gives \( T = 1.29 \), \( P = 0.133 \). Fitting \( T_{c,r} \) and \( P_{c,r} \) with \( a \) of several non-polar fluids, with the constraints for \( a = 0 \), produces the following expressions:

\[
\begin{align*}
        f_T(a_r) &= 1.29 \exp(-2.343a_r + 3.771a_r^2 - 2.661a_r^3) \\
        f_P(a_r) &= 0.133 \exp(-7.498a_r + 10.9396a_r^2 - 7.5396a_r^3)
\end{align*}
\]

These equations can be used to express the parameters \( \epsilon/k \) and \( \phi_0 \) by means of the critical values and the size-shape factor \( a_r \).

Replacing eqs. (4) into eq. (1) one obtains \( B \) reduced by means of macroscopic quantities:

\[
B_R = \frac{BP_c}{RT_c} = \frac{2}{3} \frac{f_P(a_r)}{f_T(a_r)} \frac{B(a_rT_R)}{R(a_rT_R)}
\]

where \( T_R = T/T_{c,r} = T/T \) and \( a = c_R + c_z \). Eq. (5) is an universal function of \( T_R \), \( R \) and the molecular shape.

Fig. 1 shows the results of the calculations for some non-polar compounds of different molecular shape.

**Polar fluids**

For polar molecules, the potential includes the dipole-dipole and dipole-induced dipole interactions. If the angle-averaged terms are used for polar interactions the potential energy of a pair of molecules is:
\[ \varphi(r) = 4 \varepsilon \left[ \left( \frac{\theta_0}{\theta} \right)^{12} - \left( \frac{\theta_0}{\theta} \right)^6 \right] - \frac{1}{\theta^6} \left( \frac{\mu^4}{3kT} + 2a\mu^2 \right) \] (6)

where \( \mu \) is the dipole moment and \( a \) is the polarizability.

Fig. 1 - Second virial coefficients of non-polar gases.
Rearranging eq. (6) produces:

\[ \varphi(r) = 4 \epsilon' \left[ \left( \frac{q_0'}{q} \right)^{12} - \left( \frac{q_0'}{q} \right)^6 \right] \]

(7)

where

\[ \epsilon' = \epsilon F^2(T) \]

(8)

\[ q_0' = q_0 / F^{1/6}(T) \]

(9)

F(T) = 1 + \mu_r^2 \frac{\epsilon/k}{3T} + \alpha_r \mu_r

and

\[ \mu_r = \frac{\mu^2}{(2\epsilon q_0^3)} \]

(10)

\[ \alpha_r = \alpha / q_0^3 \]

Eq. (7) has the same form of the eq. (1) with the pseudo-parameters \( \epsilon' \) and \( q_0' \) dependent on the temperature. This means that pseudo-non-polar substance can be associated to any polar fluid with microscopic parameters defined by eqs. (8). Therefore eq. (1) can be used to calculate \( B_r \) with:

\[ a_r' = 2a/ q_0' = a_r F^{1/6}(T) \]

(11)

Force parameters \( \epsilon/k \) and \( q_0' \) can be obtained from the following equations:

\[ T_{c,r} = T_c / (\epsilon'/k) = f_T(a_r') \]

\[ P_{c,r} = P_c q_0'^3 / \epsilon' = f_P(a_r') \]

(12)

where \( f_T(a_r') \) and \( f_P(a_r') \) are the same expression of eqs. (4) and the pseudo-parameters \( \epsilon' \), \( q_0' \) and \( a_r' \) are given by eqs. (8) and (11) at the critical temperature. By solving simultaneously eqs. (12), with \( a_r \) calculated from R and the molecular shape, we get the unknowns \( \epsilon/k \) and \( q_0' \) from \( T_c \), \( P_c', \mu \), \( \alpha \), \( R \) and the molecular shape.

The values so obtained can be used to evaluate \( B_r \):
Calculations have been carried out for many fluids. Some results are shown in fig. 2.

\[ B = \frac{R P_c}{RT_c} = \frac{2}{3} \pi \frac{f_p}{f_T} \frac{F^{1/2}(T_c)}{F^{1/2}(T)} B_r \]  

(13)

Fig. 2 - Second virial coefficients for polar gases.
Conclusions

The proposed procedure allows to evaluate $B$ of polar fluids without using any adjustable parameter. The quality of the prediction for nonpolar fluids, is good except for large normal paraffins, where $B$ calculated from CST are too negative. For polar fluids the results are quite satisfactory if we exclude alcohols and other hydrogen bonding compounds.

Further refinements must be introduced in order to improve the correlations used to obtain the molecular parameters. Furthermore a procedure independent from the arbitrary assumption of any molecular shape should be advisable.

References

7. T.Kihara - Rev. Mod. Phys. 25, 831 (1953)
COMPARISON BETWEEN DIFFERENT MODELS FOR THE EXCESS FREE ENERGY

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(x) Instituttet for Kemiteknik, Danmarks Tekniske Hojskole, 2800 Lyngby, Denmark.

In the last years, for the description of the non-ideality in the liquid phase, several models were proposed. Even if there are formal differences in these models, some common features can be found.

In this work the correlation of vapor-liquid equilibrium data for binary systems with NRTL, UNIQUAC, Wilson, Effective UNIQUAC are compared with that obtained with new modifications of the UNIQUAC equation. The modification herein proposed consist in the introduction of an empirical parameter in the entropic part.

(+) The authors are grateful to CNR (Rome) for supporting the research.
Introduction

Fluid phase equilibrium data are essential in the design of separation processes. Obviously the use of computer methods in this type of calculation needs the data in analytical instead of tabular form. This utilization is not the only one, because otherwise, polynomial functions could be the right solution to the problem. From practical purposes it is hopeful to extrapolate data in temperature, pressure and composition ranges different from the experimental ones. As a consequence for this use of the correlation equations, the mathematical form has to be based on the hypothesis of the physical nature of the given phenomena. Moreover we must consider that an extrapolation seems less dangerous if it is realized through a "physical model" instead of the simple use of a polynomial interpolating. In this manner information on the nature of the interaction forces among the molecules in liquid state can be derived from the parameters of the model. No one of the models, until now proposed, is able to describe in a proper way all the thermodynamic properties of the mixture. For this reason in the literature various new modifications of the different models are proposed in order to increase the flexibility of the equations.

In this paper different possible modifications of the UNIQUAC equation are discussed. These UNIQUAC modified equations are used in the correlation of binary vapor-liquid equilibrium data.

Thermodynamic models

In the last years, for the description of the non-ideality in the liquid phase, several models were proposed. Even if there are formal differences in these models, some features can be found:
- they generally are based on the local composition concept;
- the behaviour of multicomponent mixtures is predicted on the basis of binary interactions;
- a clear and explicit dependence from the temperature of the excess free energy is not expressed, although, sometimes, an entropic and an enthalpic term are defined;
- the parameters of the models are generally interaction or enthalpic parameters.

From the last point of view the only equation different from the others is that proposed recently by Brandani (1). This equation, although not easily applicable for engineering purposes, from a theoretical point of view, allows the employment of an equation of state for the development of an equation from the excess free energy. From a practical point of view it uses two parameters, per binary mixture, which take into account also the molecular size and shape differences and not only the interactions between the different components, as normally made with the other models. As a consequence the first parameter is related to the excess entropy and the second one is an energetic or interaction parameter. In this way these parameters are less correlated and in principle should be able to adapt better the model to the different experimental conditions.

On the other hand, from empirical considerations, a certain influence of the combinatorial term of the UNIQUAC model on the fitting of binary data was recently observed (2). A modification of the model was made introducing a further parameter as exponent in the combinatorial term, similarly, in some instance, to that proposed by Donohue (3).

The equations relative to these two models, UNIQUAC3 and UNIDON3, with three parameters, are given in Table 1. From these models the corresponding ones with two parameters (UNIQUAC2 and UNIDON2) can be derived by calculating the interaction energies between equal molecules from the energy of vaporization of the pure components:

\[ u_{ii} = -\frac{\Delta u_{i,vap}}{q_i} \quad u_{ij} = u_{ji} = (1-k_{ij})/u_{ii}u_{jj} \]
Similarly to that proposed by Brandani, we have two parameters, the first parameter is of entropic type, the second one is of energetic type.

Table 1 considers a further modification of UNIQUAC equation, the Effective UNIQUAC proposed by Nagata\(^{(4)}\).

**Results and discussion**

In Table 2, the systems studied in this investigation are listed; for comparison purposes we have chosen some of the systems considered by Brandani\(^{(1)}\).

The parameter values of the models were obtained by a data reduction method based on the maximum likelihood principle\(^{(5)}\). We have used for the experimental uncertainties, the values: \(\sigma_p = 1.0\) torr, \(\sigma_T = 0.05^\circ K\), \(\sigma_x = 0.001\), \(\sigma_y = 0.003\), suggested by Anderson\(^{(6)}\).

Table 3 reports some typical results for the system Acetone-toluene. The variance of the fit is generally better with the modified UNIQUAC models respect to the original UNIQUAC. This is not surprising since in these cases we have three parameters derived from the fitting. Vice versa, the results obtained with UNIQUAC2 and UNIDON2 models are interesting since these models with two parameters seem to give excellent results and in any case comparable to those obtained with models containing three parameters. The effective UNIQUAC in these cases gives results comparable to those of the original UNIQUAC model.

In Table 4, we report the results obtained for the system Acetone-Acetonitrile. In this case we compare the UNIQUAC, UNIQUAC3, UNIDON3, NRTL and Effective UNIQUAC models. Also in this case, the two modifications seem very promising in the fitting vapor-liquid equilibrium data.

**Conclusion**

The results herein reported for the comparison of different thermo-
dynamic models justify the research of a more realistical entropic term for the excess Gibbs functions. It is our opinion that new models with more physical insight can be derived from the observations herein reported especially in regard of the need of a parameter which takes into account directly the entropy of the mixture.

References

(1) V.Brandani,J.M.Prausnitz,Fluid Phase Eq., in press
(4) I.Hagata,K.Katoh,Fluid Phase Eq., 5, 225, 1981
<table>
<thead>
<tr>
<th>MODEL</th>
<th>$E_{S_C}$</th>
<th>$E_{S_R}$</th>
<th>$\theta_i$</th>
<th>$\phi_i$</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNIQUAC</td>
<td>$\sum_i x_i \ln(\phi_i/x_i)$</td>
<td>$- \frac{1}{2} \sum_i q_i x_i \ln \theta_i$</td>
<td>$\tau_i^q$</td>
<td>$\tau_i^p$</td>
<td>$\tau_i^q$, $\tau_i^p$</td>
</tr>
<tr>
<td>EFF.UNIQUAC</td>
<td>&quot;</td>
<td>$-C \sum_i x_i \ln \theta_i \tau_i^q$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$C$, $\tau_i^q$, $\tau_i^p$</td>
</tr>
<tr>
<td>UNIQUAC3</td>
<td>&quot;</td>
<td>$- \frac{1}{2} \sum_i q_i x_i \ln \theta_i \tau_i^q$</td>
<td>&quot;</td>
<td>$\tau_i^q$</td>
<td>$\tau_i^q$, $\tau_i^p$</td>
</tr>
<tr>
<td>UNIQUAC2$(x)$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$p$, $k_{ij}$</td>
</tr>
<tr>
<td>UNIDON3</td>
<td>$\sum_i x_i \ln(\phi_i/x_i)$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$p$, $\tau_i^q$, $\tau_i^p$</td>
</tr>
<tr>
<td>UNIDON2$(x)$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$p$, $k_{ij}$</td>
</tr>
</tbody>
</table>

\[ \tau_{ij} = \exp(-\frac{u_{ij} - u_{ii}}{RT}) \]

\[ (x) \ u_{ij} = u_{ji} = (1-k_{ij})/u_{ii} \cdot u_{jj} \]

**TABLE 1**
### TABLE 2 - Systems investigated

<table>
<thead>
<tr>
<th>System</th>
<th>T (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitroethane-</td>
<td>25</td>
<td>&quot;</td>
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<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Nitropropane-</td>
<td>25</td>
<td>&quot;</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylacetate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3 - Root mean square deviations as obtained from data reduction using principle of max. likelihood for the system acetone-toluene.

<table>
<thead>
<tr>
<th>Model</th>
<th>$\sigma_p$, torr</th>
<th>$\sigma_T$, K</th>
<th>$10^3 \sigma_x$</th>
<th>$10^3 \sigma_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNIQUAC</td>
<td>1.09</td>
<td>0.04</td>
<td>0.8</td>
<td>2.5</td>
</tr>
<tr>
<td>WILSON</td>
<td>1.02</td>
<td>0.04</td>
<td>0.7</td>
<td>2.4</td>
</tr>
<tr>
<td>NRTL</td>
<td>0.98</td>
<td>0.04</td>
<td>0.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Eff.UNIQUAC</td>
<td>1.18</td>
<td>0.05</td>
<td>0.8</td>
<td>2.7</td>
</tr>
<tr>
<td>UNIQUAC3</td>
<td>0.76</td>
<td>0.03</td>
<td>0.5</td>
<td>1.8</td>
</tr>
<tr>
<td>UNIQUAC2</td>
<td>0.76</td>
<td>0.03</td>
<td>0.5</td>
<td>1.8</td>
</tr>
<tr>
<td>UNIDON3</td>
<td>0.78</td>
<td>0.03</td>
<td>0.6</td>
<td>1.9</td>
</tr>
<tr>
<td>UNIDON2</td>
<td>0.78</td>
<td>0.03</td>
<td>0.6</td>
<td>1.9</td>
</tr>
</tbody>
</table>

TABLE 4 - Root mean square deviations as obtained from data reduction using principle of max. likelihood for the system acetone-acetonitrile.

<table>
<thead>
<tr>
<th>Model</th>
<th>$\sigma_p$, torr</th>
<th>$\sigma_T$, K</th>
<th>$10^3 \sigma_x$</th>
<th>$10^3 \sigma_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNIQUAC</td>
<td>0.39</td>
<td>0.00</td>
<td>0.10</td>
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<tr>
<td>NRTL</td>
<td>0.80</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>Eff.UNIQUAC</td>
<td>0.34</td>
<td>0.01</td>
<td>0.20</td>
<td>1.9</td>
</tr>
<tr>
<td>UNIQUAC3</td>
<td>0.32</td>
<td>0.00</td>
<td>0.00</td>
<td>2.4</td>
</tr>
<tr>
<td>UNIDON3</td>
<td>0.32</td>
<td>0.00</td>
<td>0.00</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Phase equilibrium calculations using quasilattice models


*Technical University of Budapest, Department of Chemical Engineering, H-1521 Budapest, Hungary
**General Contracting and Designing Office for the Oil Industry, H-1519 Budapest, POB 270, Hungary

The authors recently proposed a new model for the configurational free energy of mixtures based on the quasilattice concept: "Modified Prigogine Model"/MPRG/. It gives a good approximation for the Gibbs free energy function from the state of complete disorder (ideal or athermal solutions) to extremely ordered states (complete phase separation or association of molecules). The model takes into account the geometry of molecules and has only one energy parameter per binary system to be determined from experimental data. In the representation of binary VLE data, the proposed model is inferior to the Wilson, NRTL and UNIQUAC Eqs but its predicting ability for multicomponent systems is comparable with them. It gives very good results for systems with limited miscibility.
The models based on local composition concept are very useful for representation of binary VLE data and they predict multicomponent equilibria better than any other model known before. They may fail however for highly ordered states / association and limited miscibility/. The aim of this contribution is to propose an almost exact model for the configuration free energy function, strictly on the basis of the lattice concept of rigid molecules.

**Lattice models for solutions**

Let us denote with $Z$ the partition function of a system with the following definition:

$$Z = \sum_r \exp \left(-\frac{E_r}{kT}\right)$$

(1)

where $r$ is the subscript of an energy state; $E_r$ the energy in the $r$-th energy state; $k$ the Boltzmann constant, $T$ the absolute temperature. The relation of the partition function to the Helmholtz free energy is:

$$f = -kT \ln Z$$

(2)

If it may be assumed, that the oscillation of molecules around their lattice point and the internal energies /vibration and rotation/ are not affected by mixing, the free energy of mixing can be expressed as follows:

$$f^M = -kT \ln \Omega_{\text{mixt}} \sum_i x_i \ln \Omega_i$$

(3)

where $\Omega$ stands for the configurational partition function for the mixture and that for the pure components, $x$ is the mole fraction. Neglecting the term $\Omega^F$ this is equal
to the Gibbs free energy of mixing.

Let us suppose a mixture of \( N_A \) molecules \( A \), \( N_B \) molecules \( B \) which are similar in size /regular mixture/. Introducing the definition of the interchange energy between an \( i-j \) pair of molecules as \( \varepsilon_{ij} = \varepsilon (u_{ij} - \frac{1}{2}u_{ii} - \frac{1}{2}u_{jj}) \), the change of configuration partition function on mixing is:

\[
\Omega^M = g(N_A, N_B, N_{AB}) \exp \left(-\frac{N_{AB}}{2kT} \varepsilon \right)
\]  \hspace{1cm} (4)

Here \( g(N_A, N_B, N_{AB}) \) is the so-called combinatorial factor, the number of possible arrangements of molecules with \( N_{AB} \). From this equation the activity coefficients would be obtained if the combinatorial factor \( g \) were known, but in the present state of the statistical mechanics it cannot be given exactly except in special cases. Assuming that the number of configurations may be calculated as if the various pairs did not interfere with one another, we would for a given value of \( N_{AB} \) have:

\[
g(N_A, N_B, N_{AB}) = \frac{[0.5 \varepsilon (N_A + N_B)]!}{[0.5 (zN_A - N_{AB})]^0.5 N_{AB}] !^2 [0.5 (zN_B - N_{AB})]!}
\]  \hspace{1cm} (5)

This equation gives too high values for the combinatorial factor \( g \). The essence of Guggenheim's quasichemical treatment [1] is to correct this error by multiplying Eqn (5) by a factor \( h(N_A, N_B) \) independent of \( N_{AB} \) in such a way that it gives the exact value at complete randomness. \( N_{AB} \) is determined by maximization of Eqn (4) with respect to \( N_{AB} \). Prigogine et al. [2] proposed a more refined correction, a linear function of \( g \):
The coefficients $\alpha$ and $\beta$ are determined from the following requirements:

a. in the case of complete disorder $N_{AB} = N^*$ one should get $g^{1/N} = 2$. For an equimolar mixture,

b. in the case of complete order $N_{AB} = 0$ one should get $g^{1/N} = 1$.

From Fig.1 it is seen that this correction gives good results in the vicinity of both complete order and complete disorder but in the intermediate domain there are serious deviations from the exact curves.

The new model

Extending the correction idea let us use the following more general form suggested by Fig.2:

$$\ln g^{1/N} = a + b \ln(g^{01/N}) + c f(\ln(g^{01/N}))$$  \hspace{1cm} (7)

The coefficients are to be determined from three conditions: a. and b. above and

c. in the vicinity of complete disorder it should fit close to Guggenheim's approximation, which is exact there: their slopes in this region should be equal.

Using polynomials exact curves can be calculated for equimolar mixtures for different numbers of nearest neighbours 4, 6, 8, and 12, an example is shown on Fig.3. It suggests the following choice for $f(\ln g^{01/N})$:

$$f(\ln g^{0}) = (\ln g^{0*} - \ln g^{0}) e^{-K(\ln g^{0*} - \ln g^{0})}$$  \hspace{1cm} (8)
The appropriate formulas for the excess Gibbs energy function and activity coefficients are derived also for molecules of different size and for multicomponent systems. As it is seen from Fig.1, this approximation gives remarkably well the values of $N_{AB}$.

Applying the model for practical calculations we found that it is inferior to the widely used two-parameter local composition models in representation of binary measured VLE data. This is not surprising because it has only one parameter to be fitted. For multicomponent mixtures the proposed model is not much inferior to the other ones in general but for the system shown with limited miscibility /Table I./ it is essentially better.

References
<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>UNIQUAC $s_y^2$</th>
<th>UNIQUAC $s_T^2$</th>
<th>MPRIG $s_y^2$</th>
<th>MPRIG $s_T^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene - cyclohexane - ethanol</td>
<td>1.88 $\cdot 10^{-4}$</td>
<td>1.49</td>
<td>1.51 $\cdot 10^{-3}$</td>
<td>8.72</td>
</tr>
<tr>
<td>benzene - CCl$_4$ - ethanol</td>
<td>4.2 $\cdot 10^{-4}$</td>
<td>0.22</td>
<td>1.31 $\cdot 10^{-3}$</td>
<td>2.45</td>
</tr>
<tr>
<td>acetone - CCl$_4$ - benzene</td>
<td>8.8 $\cdot 10^{-5}$</td>
<td>0.44</td>
<td>1.87 $\cdot 10^{-4}$</td>
<td>0.85</td>
</tr>
<tr>
<td>acetone - CCl$_4$ - chloroform</td>
<td>6.72 $\cdot 10^{-4}$</td>
<td>4.87</td>
<td>6.2 $\cdot 10^{-4}$</td>
<td>3.2</td>
</tr>
<tr>
<td>ethanol - ethyl acetate - water</td>
<td>1.16 $\cdot 10^{-3}$</td>
<td>3.25</td>
<td>1.14 $\cdot 10^{-4}$</td>
<td>0.63</td>
</tr>
</tbody>
</table>
\[
\frac{w}{z k T}
\]

\[
\frac{w}{z k T_c}
\]

\(z = 4\)

- Guggenheim
- Prigogine
- MPRIG \(\delta = 1.5\)
- \(K = 0\)
- Onsager (exact)

\[N_{AB} = z \chi \frac{N_A N_B}{N_A + N_B}\]

**FIG. 1**
In (g^1/N)

![Graph 1](#)

- Guggenheim
- Prigogine
- exact (polynomial)

**FIG. 2**

![Graph 2](#)

**FIG. 3**

\[ z = 6 \]

\[ z = 12 \]
GROUP CONTRIBUTION METHODS AND MOLECULES WITH TWO FUNCTIONAL GROUPS

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Istituto di Chimica Applicata e Industriale, Università di Trieste
Trieste, Italy

Group contribution methods allow an approximate representation of the physical reality and an useful prediction of the thermodynamic behaviour of a large number of mixtures on the basis of a limited number of experimental data. Normally, as postulate of the formulation of these theories, the different interactions derived by the different positions of the groups in the molecule are neglected. From an examination of the actually available interaction parameters it is possible to note that they were generally obtained from equilibrium data relative to molecules containing only a functional group different from the basis group $-\text{CH}_2$.

In this work the results obtained in a systematic study on the influence of two functional groups in the molecule on equilibrium data are reported. In particular molecules containing two functional groups of the same nature were considered such as molecules containing two $-\text{OH}, -\text{COOH}, -\text{CN}, -\text{NH}_2$ groups. The variation of the activity coefficients at infinite dilution of paraffinic hydrocarbons in stationary phases containing these functional groups are evaluated.

This work is supported by the Administration Council of the University of Trieste and by M.P.I.
Introduction

Fluid phase equilibrium data at low pressure are usually interpreted through excess functions so that the compositions of the phases at equilibrium can be calculated from excess quantities (activity coefficients) and vice versa. It is useful, in these conditions, to have a "model" which expresses the variation of the excess quantities with the different variables (normally temperature and composition). The majority of liquid solution models contain two arbitrary parameters per binary pair. This means that the amount of work required for the calculation of any equilibrium condition for a multicomponent system having n component will be enormous since n(n-1) interaction parameters are necessary. In order to overcome these difficulties methods based on group contribution concept come into use: in this case solution of groups replaces the concept of solution of molecular compounds. The prediction is made on the basis of certain number of parameters characteristic of the pure components and of certain number of parameters (usually two for each binary group mixture), previously determined through the reduction of data relative to systems containing the given functional groups. These theories are based on the oversimplified picture that the interactions in the liquid state are not influenced by the relative position of different functional groups in the molecular species and by the presence of other functional groups. In many cases, however, this hypothesis is not true and to overcome this difficulty, if two functional groups (different from the basic group -CH₂) are very close to each other, a new group containing both functional groups is normally defined. On the other hand organic compounds with different functional groups are quite commonly applied in fields other than petrochemistry. Thermodynamic data relative to these mixtures are not easily available and many times the data reported are not systematic as it is neces-
sary for establishing a tentative of correlation.

The present paper reports the results relative to the effect of two functional groups in the same molecule in the correlation and prediction of thermodynamic properties.

Experimental section

A thermal conductivity chromatograph Fractovap mod ATC/t (C.Erba) was used as GLC apparatus. The column temperature was controlled to within ±0.2°C and measured with an electronic thermometer. The carrier gas (hydrogen) flow rate was measured with a soap-film meter. The internal pressure gradient was measured to within ±1 mm Hg by a mercury manometer. The outlet pressure was atmospheric.

The operating conditions are summarized as follows: sample size injected 0.2 µl; stainless steel column (2 m long, 4 mm int. diameter); support 60-80 mesh Chromosorb W (C.Erba) acid washed and silanized; quantitative ratio of support to stationary phase =3/1 (by weight); internal pressure gradient 250-270 mm Hg.

The solutes and the stationary phases were reagent grade products (Fluka, C.Erba, Baker).

The activity coefficients at infinite dilution were calculated according to (1).

Results

Table 1 and 2 report infinite dilution activity coefficients of paraffins in a series of solvents containing one or two functional groups of the same type in the molecule.

In particular data relative to alcohols (2) and diols, nitriles and dinitriles, amine and diamine, acids (3) and diacids have been determined.

Some observations must be made. The introduction of a second functional group increases the non-ideality of paraffin-solvent mixtures.

As about the absolute values of activity coefficients at infinite
<table>
<thead>
<tr>
<th>Solvents</th>
<th>Temperature</th>
<th>Activity coefficients at inf. Dil.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>n.Pentane</td>
</tr>
<tr>
<td>Dodecanol</td>
<td>42.8</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>53.0</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>60.0</td>
<td>1.84</td>
</tr>
<tr>
<td>Tetradecanol</td>
<td>56.1</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>65.1</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>75.8</td>
<td>1.56</td>
</tr>
<tr>
<td>Hexandiol</td>
<td>60.7</td>
<td>13.19</td>
</tr>
<tr>
<td></td>
<td>70.2</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>81.0</td>
<td>12.80</td>
</tr>
<tr>
<td>Nonandiol</td>
<td>65.7</td>
<td>6.55</td>
</tr>
<tr>
<td></td>
<td>75.7</td>
<td>6.23</td>
</tr>
<tr>
<td></td>
<td>87.0</td>
<td>5.87</td>
</tr>
</tbody>
</table>

Table 1: Activity coefficients at infinite dilution of paraffins in alcohols and in diols.

In dilution it is possible to evaluate the influence of the paraffinic chain length on the non-ideality for alcohols and diols for which two solvents at different molecular weight were investigated.

In fact by passing from nonandiol to hexandiol and from tetradecanol to dodecanol, the activity coefficients of paraffins increases especially in diols for which the relative closeness of the two -OH groups influences in a remarkable way the activity coefficients (in hexandiol the activity coefficients at infinite dilution are twice as high as in nonandiol).
<table>
<thead>
<tr>
<th>Solvents</th>
<th>Temperature °C</th>
<th>Activity coefficients at inf.dil.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n.Pentane</td>
<td>n.Hexane</td>
</tr>
<tr>
<td>Cetylamine</td>
<td>61.5</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>76.8</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>88.0</td>
<td>1.07</td>
</tr>
<tr>
<td>Diamine</td>
<td>71.9</td>
<td>5.36</td>
</tr>
<tr>
<td>Dodecane</td>
<td>80.0</td>
<td>4.92</td>
</tr>
<tr>
<td></td>
<td>90.5</td>
<td>4.46</td>
</tr>
<tr>
<td>Heptadecane</td>
<td>70.0</td>
<td>1.51</td>
</tr>
<tr>
<td>Nitrile</td>
<td>82.0</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>91.5</td>
<td>1.13</td>
</tr>
<tr>
<td>Dodecane</td>
<td>70.9</td>
<td>3.63</td>
</tr>
<tr>
<td>Dinitrile</td>
<td>85.4</td>
<td>3.46</td>
</tr>
<tr>
<td></td>
<td>100.6</td>
<td>3.29</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>87.5</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>108.3</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>122.3</td>
<td>1.43</td>
</tr>
<tr>
<td>Sebacic acid</td>
<td>143.0</td>
<td>3.73</td>
</tr>
</tbody>
</table>

Table 2: Activity coefficients at infinite dilution of paraffins in amine, diamine, nitrile, dinitrile, acid and diacid.

Correlation and prediction

Activity coefficients in the extreme regions, such as those determined by GLC, can be used to estimate the group interaction parameters of a thermodynamic model as the UNIFAC. As shown previously, the parameters estimated from infinite dilution activity coefficients by using a modified version of UNIFAC are almost as reliable as parameters estimated from a vapor-liquid equi-
librium data base. Starting from this consideration, we can use the interaction parameters given in the literature and employ the modified equation (5) for predicting infinite dilution activity coefficients. Table 3 reports the standard deviations obtained in the calculation of activity coefficients of paraffins in the solvents investigated. It appears evident that the modification introduced is not sufficient for evaluating data relative to substances containing two functional groups in the molecule.

It is obvious that in this case the assumption that the interactions are not influenced by the relative position of the groups and by the presence of a second group is not more valid.

By trying empirical modifications we observed that the term which seems to be able to take into account the presence of a second group is the surface parameter of the group ($Q_k$).

Figure 1 reports as an example the effect of the surface parameter of the functional group on the standard deviation; the standard deviation (S.D.) is derived in the prediction of activity coefficients by using the already known vapor-liquid equilibrium parameters. Similar behaviour can be obtained in the standard deviation values by fitting the data.

In both cases the best value of surface parameter of the functional group of the solvent seems to be around $1.5Q_k$, only for diaminedodecane the minimum value is $2Q_k$ (see table 3).

This means that the surface parameter of $-\text{OH}$ in diols, of $-\text{CH}_2\text{NH}_2$ in amines seem to be higher than that relative to the surface parameter of the same group in molecules containing only one functional group.

A general conclusion cannot be derived at the moment since we need more data for the different situations. For example it seems interesting to evaluate the influence of the paraffinic chain; this can be derived from data relative to the same solutes in a class of solvents having different number of $n$ in the molecule $X-(\text{CH}_2)_n X$. 
<table>
<thead>
<tr>
<th>Solvents</th>
<th>S.D.(1 Qk)</th>
<th>S.D.(1.5 Qk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecanol</td>
<td>20.9</td>
<td>-</td>
</tr>
<tr>
<td>Tetradecanol</td>
<td>17.8</td>
<td>-</td>
</tr>
<tr>
<td>Hexandiol</td>
<td>48.9</td>
<td>14.5</td>
</tr>
<tr>
<td>Nonadiol</td>
<td>41.4</td>
<td>10.1</td>
</tr>
<tr>
<td>Cetylamine</td>
<td>8.8</td>
<td>-</td>
</tr>
<tr>
<td>Diaminedodecane</td>
<td>50.8</td>
<td>20.1(2 Qk)</td>
</tr>
<tr>
<td>Heptadecanenitrile</td>
<td>23.4</td>
<td>-</td>
</tr>
<tr>
<td>Dodecanedinitrile</td>
<td>26.5</td>
<td>15.8</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>15.4</td>
<td>-</td>
</tr>
<tr>
<td>Sebacic acid</td>
<td>28.3</td>
<td>18.1</td>
</tr>
</tbody>
</table>

Table 3: Standard Deviation in the prediction of activity coefficients at infinite dilution in mono-ë difunctional solvents

![Figure 1: Effect of Qk value on the standard deviation.](image)
Unfortunately, this involves experimental problems not easily resolvable, such as the availability of some substances. At the present more experimental work is needed especially in this direction in order to evaluate if the use of $1.5Q$ in the evaluation of activity coefficients at infinite dilution can be used in general or only when the functional groups are sufficiently far one from the other.

References

Vapour Pressure of Bourbonal and its Derivates
Measured by the Saturation Method.

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Department of Physical Chemistry,
Prague Institute of Chemical Technology

Using the saturation method vapour pressures of guaethol, 1,2-diethoxybenzene, 3,4-diethoxybenzaldehyde, 3-ethoxy-4-hydroxybenzaldehyde and 3-hydroxy-4-ethoxybenzaldehyde were determined at low pressures (~2000 Pa). As these substances are unstable at temperatures above their melting points all measurements were performed in short temperature interval (30 K). Gas chromatography was used as an analytical method in order to discriminate between main component and impurities, especially water.

The results obtained were correlated by the Antoine equation. For qualified extrapolation to higher temperatures the acentric factor \( \omega \) was calculated using the generalised Lee - Kessler equation and critical constants \( (T_c, P_c) \) estimated according to the Forman and Thodos method.

On the basis of measured data enthalpies of vaporation were calculated at the reduced temperature \( T_R = 0.5 \).
INTRODUCTION

There is enhanced interest in saturation vapour pressures of organic compounds, especially at low pressures. This interest is evoked by technological, ecological, economical as well as theoretical reasons. This investigation was undertaken in order to obtain data on vapour pressures and enthalpies of vaporation of bourbons and related compounds for which only few experimental data are available.

EXPERIMENTAL

Material.

All compounds of chromatographic purity were purchased from Research Institute of Fat Industry, Rakovnik.

\[
\begin{align*}
\text{2-ethoxyphenol} & \quad \text{1,2-diethoxybenzene} \\
(\text{Guethol}) & \\
\text{3-hydroxy-4-ethoxybenzaldehyde} & \quad \text{3-ethoxy-4-hydroxybenzaldehyde} \\
(\text{Bourbonal}) & \\
\text{3,4-diethoxybenzaldehyde} & 
\end{align*}
\]
Method.

The equipment for the vapour pressure measurement by the saturation method consists of flow regulator, saturator, collector and flowmeter (Fig. 1).

Nitrogen carrier gas is dried by passage over a trap (-70°C) (2) and a column packed with molecular sieve A4 (4). Dry nitrogen is run through the flow regulator (5) to the valve (6) which allows nitrogen to pass through the thermostated sample saturator (8) or to by-pass the saturator to the bubble flowmeter (17). Saturated nitrogen passed through heated line (10) to the sample collector (-70°C) filled with ethanol (14). Free nitrogen gas is then run through the thermostated line (25°C) (15) to the bubble flowmeter. Pressure measurements in the saturator are made with the mercury manometer (7). Flow rates varied between 0.25 and 0.3 cm³ s⁻¹. At least two different flow rates are used—this ensures sensitive indication of full saturation as well as complete trapping. The saturator (8) consists of 6 mm i.d. tube packed with support Rybosorb BLK coated with the sample material. The saturator has 7 turns with outer coil diameter 10 cm. All joints are made of stainless steel Swagelok type coupling with Teflon gaskets.

When gas flow through the saturator was finished the content of the sample collector (trap) was quantitatively transferred to 50 cm³ volume and analysed by gas chromatograph (Chrom 5). One of the measured compounds with
appropriate elution time was used as the inner standard. Chromatography conditions: Column length 1,2 - 3,5 m packed with Chezasorb AW + 15% Lukoil FD; nitrogen gas flow rate ∼1 cm³ s⁻¹. Resulting signal from flame ionisation detector was measured by the integrator IT2.

Saturation vapour pressure was calculated according to the relation 

\[ P^0 = \frac{m_2 RT_0 P}{m_2 RT_0 + M_2 P_a V_1^0} \]

where \( P_a \) is a barometric pressure (Pa), \( P \) pressure in the saturator (Pa), \( T_0 = 298.15 \) K, \( m_2 \) weight of the substance collected (g), \( V_1^0 \) volume of gas run through the saturator (m³), \( M_2 \) molecular weight of a substance (g mol⁻¹).

RESULTS

Vapour pressures are determined in a narrow temperature range of about 30 K to avoid condensation reaction (Fig.2). The measurement is started at temperature a few degrees above the melting point.

The measured vapour pressures are correlated by the Antoine equation

\[ \log P^0 (\text{Pa}) = A - B/(t + C) \]

with \( C = 230 \). Correlation constants are presented in Table 1. For extrapolation to higher temperatures the principle of corresponding state is applied. Critical pa-
Parameters ($T_c$, $P_c$) of measured substances were calculated by the Forman - Thodos method.\footnote{Non-available parameters of CH=O group were estimated using the critical data on benzaldehyde.}

The acentric factor is calculated by the reduction of experimental data using the Lee - Kesler generalised vapour pressure equation:\footnote{\textbf{The acentric factor is calculated by the reduction of experimental data using the Lee - Kesler generalised vapour pressure equation:\[\ln P^0 = P^{(0)}(T_c) + \omega P^{(1)}(T_c)\]}

The following objective function is used:

$$G(\omega) = \sum_i \left(\ln P^0_i - P_i^{(0)} - \omega P_i^{(1)}\right)^2$$

An attempt to calculate all three parameters ($T_c$, $P_c$, $\omega$) by the procedure of Armstrong\footnote{An attempt to calculate all three parameters ($T_c$, $P_c$, $\omega$) by the procedure of Armstrong was made. The results were not satisfactory as the temperature interval was too close. Values of $T_c$, $P_c$ and $\omega$ are given in Table 1.} was made. The results were not satisfactory as the temperature interval was too close. Values of $T_c$, $P_c$ and $\omega$ are given in Table 1.

Enthalpies of vaporization at $T = 0.5$ were calculated using Clausius - Clapeyron equation:

$$\Delta H_v = RT^2 \frac{d \ln P^0}{dT} = 2.303 RT^2 \frac{B}{(t+C)^2}$$

The derivative was determined using the Antoine equation. The results are given in Table 1.

\textbf{LITERATURE}

Figure 1: Layout of apparatus

1, N₂; 2, trap; 3, Dewar flask (-70°C); 4, drying column; 5, flow regulator; 6, valve; 7, gauge; 8, saturator; 9, oil thermostated bath (T<sub>exp.</sub>); 10, heated line; 11, regulator; 12, Cu-Ko thermocouple; 13, voltmeter MT100; 14, collector; 15, thermostated line; 16, thermostated bath (25°C); 17, bubble flowmeter
<table>
<thead>
<tr>
<th>Substance</th>
<th>Antoine constants(^+)</th>
<th>Temperature range</th>
<th>Estimated parameters</th>
<th>(\Delta H_v^{++})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ethoxyphenol</td>
<td>11.9716 2808.46</td>
<td>342 - 373</td>
<td>730 4 0.377 69.2</td>
<td></td>
</tr>
<tr>
<td>1,2-diethoxybenzene</td>
<td>12.0417 2902.38</td>
<td>353 - 378</td>
<td>703 2.77 0.484 72.9</td>
<td></td>
</tr>
<tr>
<td>3,4-diethoxybenzaldehyde</td>
<td>10.6022 2934.5</td>
<td>390 - 418</td>
<td>763 2.77 0.77 71.4</td>
<td></td>
</tr>
<tr>
<td>3-ethoxy-4-hydroxybenzaldehyde</td>
<td>10.5292 2927.96</td>
<td>393 - 418</td>
<td>823 3.78 0.571 70.0</td>
<td></td>
</tr>
<tr>
<td>3-hydroxy-4-ethoxybenzaldehyde</td>
<td>10.2716 2922.68</td>
<td>390 - 422</td>
<td>823 3.78 0.651 69.8</td>
<td></td>
</tr>
</tbody>
</table>

\(+ C = 230\)

\(++\Delta H_v\) at \(T_r = 0.5\)
Figure 2

1: 2-ethoxyphenol, 2: diethoxybenzene, 3: diethoxybenzaldehyde, 4: 3-ethoxy-4-hydroxybenzaldehyde, 5: 3-hydroxy-4-ethoxybenzaldehyde.
EXCESS VOLUMES AND EXCESS ENTHALPIES
OF TETRACHLOROMETHANE AND OF
CHLOROFORM WITH CYCLOALKANES:
COMPARISON WITH THEORY

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Institute of Chemical Technology
166 28 Prague 6, Czechoslovakia

Excess volumes and excess enthalpies of liquid mixtures of tetrachloromethane and of chloroform with cyclopentane, cyclohexane, cycloheptane, and cyclo-octane were calculated on the basis of the Snider-Herrington equation of state and the results were compared with experimental data. The good agreement was found when using the correction parameter for the geometric mean Berthelot rule. An attempt of prediction of this parameter from ionization potentials was made.
Introduction

The aim of the theories of liquid mixtures of non-electrolytes is the prediction of the properties of mixtures from the properties of pure liquids. The use of modern theories based on the distribution functions is numerically complicated and in the case of mixtures of complex molecules at least one adjustable parameter is usually necessary to obtain the agreement with experimental data. On the other hand the calculations based on the generalized van der Waals equation of state whose form is similar to the form of the equation of state of the first order perturbation theories yield comparable results.

In this paper the Snider–Herrington equation of state is used for calculations of excess volume and excess enthalpy of the mixtures of tetrachloromethane and of chloroform with cycloalkanes and the results are compared with experimental data.

Theory

The equation of state used can be written in a generalized form (at negligible pressure)

\[ z = \frac{PV}{RT} = 0 = z(y) - a/(VRT) \]  

where for pure component \( i \) is \( y = b_{11}/(4V_1) \), \( z(y) \) is the compressibility factor of the hard spheres (compressibility equation of the Percus–Yevick approximation)

\[ z(y) = (1 + y + y^2)(1 - y)^{-3} \]

and \( a = a_{11} \) and \( b_{11} \) are the parameters and \( V = V_1 \) molar
volume of pure component 1.

For the mixture Snider and Herrington used the expression for the mixture of additive hard spheres²:
\[ z(y) = (1+y)(1-y)^{-3} - 3y(\alpha_1 + \alpha_2 y)(1-y)^{-3} \]  (3)

where
\[ y = \frac{b_{11}x_1 + b_{22}x_2}{(4V)} \]  (4)
\[ \alpha_1 = \frac{(b_{11}^{1/3} - b_{22}^{1/3})^2(b_{11}^{1/3} + b_{22}^{1/3})(b_{11}x_1 + b_{22}x_2)^{2/3}}{x_1 x_2} \]  (5)
\[ \alpha_2 = \frac{(b_{11}^{1/3}b_{22}^{1/3})^{1/3}(b_{11}^{1/3} - b_{22}^{1/3})^2(b_{11}^{2/3}x_1 + b_{22}^{2/3}x_2)}{2(b_{11}x_1 + b_{22}x_2)^{2/3}} x_1 x_2. \]  (6)

Parameter \( a \) (equation (1)) is for the mixture
\[ a = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22} \]  (7)

where
\[ a_{12} = (1-k_{12})\left(\frac{a_{11}a_{22}}{b_{11}b_{22}}\right)^{1/2} \left(b_{11}^{1/3} + b_{22}^{1/3}\right)^3 \]  (8)

where \( k_{12} \) is the correction parameter expressing the deviation from the geometric mean Berthelot rule.

On the basis of the equations (1)–(8) the thermodynamic properties of the mixture can be predicted from the properties of pure components (assuming \( k_{12} = 0 \)) or it is possible to predict the thermodynamic properties of the mixture by adjusting of the \( k_{12} \) parameter to achieve the agreement between experimental and calculated values of selected thermodynamic property.

Results and discussion

The parameters \( a_{11}, b_{11} \) of pure components can be evaluated from gas-liquid critical constants, from heats of vaporization and molar volumes or from
thermal pressure coefficients $\beta = (\partial P/\partial T)_V$ and molar volumes of pure components. In this paper the last mentioned way was used. The values of molar volumes and thermal pressure coefficients at 298.15 K and calculated values of parameters are recorded in the table I.

Table I. Molar volumes $V$ at 298.15 K, thermal pressure coefficients $\beta$ at 298.15 K and calculated parameters of equation (1) for pure liquids

<table>
<thead>
<tr>
<th>Component</th>
<th>$V \times 10^6$</th>
<th>$\beta (\text{Ref.})$</th>
<th>$a \times 10^6$</th>
<th>$b \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclopentane</td>
<td>97.717</td>
<td>1.010(3)</td>
<td>2.7015</td>
<td>178.79</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>108.75</td>
<td>1.075(3)</td>
<td>3.7905</td>
<td>217.77</td>
</tr>
<tr>
<td>cycloheptane</td>
<td>121.70</td>
<td>1.154(4)</td>
<td>5.0959</td>
<td>255.92</td>
</tr>
<tr>
<td>cyclo-octane</td>
<td>134.86</td>
<td>1.222(3)</td>
<td>6.6263</td>
<td>294.94</td>
</tr>
<tr>
<td>tetrachloromethane</td>
<td>97.084</td>
<td>1.160(5,6)$^x$</td>
<td>3.2598</td>
<td>192.37</td>
</tr>
<tr>
<td>chloroform</td>
<td>80.677</td>
<td>1.274(6)$^x$</td>
<td>2.4723</td>
<td>155.65</td>
</tr>
</tbody>
</table>

$x \ldots$ calculated from thermal expansivities and isothermal compressibilities

Experimental dependences of excess volume $V^E$ and excess enthalpy $h^E$ of the mixtures investigated on mole fraction are nearly asymmetrical (except of $V^E$ for the mixture $\text{CCl}_4 + \text{c-C}_8\text{H}_{16}$) and hence it is possible to characterize each excess function by its value at equimolar composition $x=0.5$. A comparison of experimental and calculated values of excess volume and excess enthalpy at $x=0.5$ are presented in the table II. It is obvious from the table that the theory ($k_{12}=0$) yielded
the values of excess functions lower than experimental ones but the dependence of the excess volume on the size of cycloalkane molecule is expressed qualitatively well. When adjusting the $k_{12}$ value to achieve the agreement between experimental and calculated values of one excess function ($v^E$ or $h^E$) at $x=0.5$ the agreement of the calculated values of the other function ($h^E$ or $v^E$) with experiment was found to be good, even in the case of the mixtures containing polar molecules of chloroform. The obtained results indicate that excess volume and excess enthalpy of the mixtures investigated can be expressed by means of the only parameter the value of which is evaluated from experimental data of the mixture.

In the table II the values of excess functions calculated with the use of mean values of $k_{12}$ (i.e. arithmetic mean of the values of $k_{12}$ when fitting to $v_{\text{exp}}^E(0.5)$ and $k_{12}$ when fitting to $h_{\text{exp}}^E(0.5)$) are given.

It would be useful to determine the $k_{12}$ value from properties of pure components. Hiza and Duncan found that for the mixtures of simple molecules the deviations from the geometric mean rule depend on the difference between ionization potentials of the components and proposed the relation

$$k_{12} = 0.17 (I_1 - I_2)^{1/2} \ln(I_1/I_2), I_2/I_1. \quad (9)$$

The $k_{12}$ values calculated from equation (9) using the literature values of ionization potentials are recorded in the table II along with the calculated
Table II. A comparison of experimental and calculated values
of excess volume and excess enthalpy at x=0.5 and 298.15 K

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Experiment (Ref.)</th>
<th>Theory ( k_{12}=0 )</th>
<th>Theory Mean ( k_{12} ) (see text)</th>
<th>Theory ( k_{12} ) from eq. (9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CCl}_4 + \text{C}_2 \text{H}_10 )</td>
<td>-0.036(10) 79.7(12)</td>
<td>-0.093 3</td>
<td>0.00316 -0.030 73</td>
<td>0.0067 0.042 151</td>
</tr>
<tr>
<td>( \text{CCl}_4 + \text{C}<em>6 \text{H}</em>{12} )</td>
<td>0.166(10) 166.0(12)</td>
<td>-0.001 1</td>
<td>0.00799 0.153 182</td>
<td>0.0086 0.173 206</td>
</tr>
<tr>
<td>( \text{CCl}_4 + \text{C}<em>7 \text{H}</em>{14} )</td>
<td>0.098(11) 134.7(11)</td>
<td>-0.065 -86</td>
<td>0.00844 0.102 130</td>
<td>0.0100 0.134 169</td>
</tr>
<tr>
<td>( \text{CCl}_4 + \text{C}<em>9 \text{H}</em>{16} )</td>
<td>0.020(10) 109.2(11)</td>
<td>-0.228 -228</td>
<td>0.01261 0.017 114</td>
<td>0.0110 -0.015 71</td>
</tr>
<tr>
<td>( \text{CHCl}_3 + \text{C}_2 \text{H}_10 )</td>
<td>0.312(10) 551.1(13)</td>
<td>-0.069 64</td>
<td>0.02130 0.345 516</td>
<td>0.0059 0.044 190</td>
</tr>
<tr>
<td>( \text{CHCl}_3 + \text{C}<em>6 \text{H}</em>{12} )</td>
<td>0.546(10) 639.8(14)</td>
<td>-0.005 -19</td>
<td>0.02875 0.550 636</td>
<td>0.0077 0.142 156</td>
</tr>
<tr>
<td>( \text{CHCl}_3 + \text{C}<em>7 \text{H}</em>{14} )</td>
<td>0.455(11) 610.3(11)</td>
<td>-0.082 -139</td>
<td>0.03084 0.494 561</td>
<td>0.0090 0.084 30</td>
</tr>
<tr>
<td>( \text{CHCl}_3 + \text{C}<em>8 \text{H}</em>{16} )</td>
<td>0.359(10) 578.6(11)</td>
<td>-0.244 -409</td>
<td>0.03586 0.405 515</td>
<td>0.0100 -0.065 -151</td>
</tr>
</tbody>
</table>
values of the excess functions. In the case of the tetra-
chloromethane mixtures the agreement with the experiment
can be regarded as reasonably good. In the case of the
chloroform mixtures the equation (9) failed completely,
obviously because of the polarity of chloroform mole-
ules. Nevertheless, the $k_{12}$ values calculated from the
equation (9) are in both cases in qualitative agreement
with those evaluated from experimental values of excess
volume and excess enthalpy, i.e. the value of parameter
$k_{12}$ increases with the increasing number of carbon atoms
in cycloalkane molecule.

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LIQUID-LIQUID EQUILIBRIUM FOR TERNARY SYSTEMS WATER-ALCOHOL-
CHLOROCOMPOUNDS

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Istituto di Chimica Applicata e Industriale, Università di Trieste
Trieste, Italy

In the long-term program for the investigation of the behaviour of ternary systems containing water, the effect of the alcohols in the liquid-liquid equilibrium of ternary systems water-alcohol-
chlorocompounds is studied.

As alcohols 1-propanol and 1-butanol are considered.

In this paper ternary phase equilibrium data at 20°C for the systems chloroform-alcohol-water; tetrachloromethane-alcohol-
water; trichloroethane-alcohol-water; trichloroethylene-alcohol-
water are reported.

This work is supported by C.N.R. (Rome)
Introduction

In the literature one can find many liquid-liquid equilibrium data relative to systems containing water; nevertheless few and scanty data are known in regard to water-alcohol-chlorocompound ternary systems.

The aim of the present paper is to provide basic experimental liquid-liquid equilibrium data for evaluating the effect of the chlorocompounds in the separation of water-alcohol mixtures. In this connection, equilibrium data relative to water-1-propanol-chlorocompound and water-1-butanol-chlorocompound were experimentally determined at 20°C. The chlorocompounds considered were chloroform, methane tetrachloro, ethane trichloro and ethylene trichloro.

The effectiveness of these compounds in the separation of water-alcohol mixtures was compared with that given by other solvents for which the separation power was derived from literature data.

Experimental section

Water-alcohol-chlorocompound ternary systems were agitated for 2 hrs with a magnetic stirrer and left to settle at equilibrium for 24 hrs. The temperature of equilibration was 20°± 0.1°C.

The glass equilibrium cells employed were the same as reported by Kikic et al. Three samples were withdrawn for each phase by a syringe and analyzed by gas-chromatography. The GLC analyses were carried out with a thermal conductivity gas chromatograph C.Erba ATc/t equipped with a Shimadzu Chromatopac E-1A integrator.

The column for the analysis was a stainless steel column (4m. long, i.d. 4mm.) packed with 100-120 mesh Chromosorb W DMCD coated with heptadecane nitrile (25%).

The temperatures chosen for the analysis vary from 60° to 85°C depending on the system under investigation. A particular care was taken for the calculation of the correction factors considering
separately the aqueous and the organic phases.
The components of the systems were appropriately treated: alcohols (Fluka) were purified by the method suggested by Vogel (2), chlorocompounds (Fluka) by distillation.

Results and Discussion

Tables 1-3 present the experimental liquid-liquid equilibrium data obtained for water-1-propanol-chloroform, water-1-propanol-ethane-trichloro, water-1-propanol-ethylene trichloro systems. The complete liquid-liquid equilibrium data relative to all the systems investigated are reported in (3).

Figure 1 gives, as an example, the distribution isotherms for water-1-propanol-chloroform and water-1-butanol-chloroform systems. It must be outlined that the systems with propanol, ethanol and methanol are all of type 1 (one binary water-chloroform shows immiscibility and two binaries are completely miscible); the systems with butanol are all of type 2 (two binaries, water-butanol and water-chloroform exhibit immiscibility while one binary, chloroform-butanol is completely miscible).

Similar behaviour is given by the other chlorocompounds investigated. This general behaviour indicates that the alcohol has some effect on the miscibility gap: alcohols with lower molecular weight bring about a reduction in the miscibility gap, which means that the alcohol, going from butanol to methanol, gradually becomes the component that solubilizes better both water and chlorocompounds.

As about the effect of the chlorocompounds, the higher miscibility gap is given by methane tetrachloro (the liquid-liquid equilibrium data relative to the system water-1-propanol-methane tetrachloro are reported in (4)), then ethylene trichloro and finally chloroform and ethane trichloro.
<table>
<thead>
<tr>
<th>PHASE I</th>
<th>PHASE II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1$</td>
<td>$x_3$</td>
</tr>
<tr>
<td>0.9988</td>
<td>0.0012</td>
</tr>
<tr>
<td>0.9778</td>
<td>0.0013</td>
</tr>
<tr>
<td>0.9658</td>
<td>0.0015</td>
</tr>
<tr>
<td>0.9606</td>
<td>0.0015</td>
</tr>
<tr>
<td>0.9567</td>
<td>0.0016</td>
</tr>
<tr>
<td>0.9519</td>
<td>0.0017</td>
</tr>
<tr>
<td>0.9508</td>
<td>0.0019</td>
</tr>
<tr>
<td>0.9493</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

Table 1: Liquid-liquid equilibrium data (mole fraction) for water(l)-1-propanol (2)-chloroform (3) system at 20°C

<table>
<thead>
<tr>
<th>PHASE I</th>
<th>PHASE II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1$</td>
<td>$x_3$</td>
</tr>
<tr>
<td>0.9994</td>
<td>0.0006</td>
</tr>
<tr>
<td>0.9728</td>
<td>0.0006</td>
</tr>
<tr>
<td>0.9632</td>
<td>0.0007</td>
</tr>
<tr>
<td>0.9561</td>
<td>0.0008</td>
</tr>
<tr>
<td>0.9532</td>
<td>0.0009</td>
</tr>
<tr>
<td>0.9497</td>
<td>0.0009</td>
</tr>
<tr>
<td>0.9480</td>
<td>0.0010</td>
</tr>
<tr>
<td>0.9437</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

Table 2: Liquid-liquid equilibrium data (mole fraction) for water(l)-1-propanol(2)-ethylentrichloro(3) system at 20°C
PHASE I

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$x_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9998</td>
<td>0.0002</td>
</tr>
<tr>
<td>0.9608</td>
<td>0.0003</td>
</tr>
<tr>
<td>0.9589</td>
<td>0.0003</td>
</tr>
<tr>
<td>0.9541</td>
<td>0.0004</td>
</tr>
<tr>
<td>0.9464</td>
<td>0.0005</td>
</tr>
<tr>
<td>0.9452</td>
<td>0.0006</td>
</tr>
<tr>
<td>0.9423</td>
<td>0.0007</td>
</tr>
<tr>
<td>0.9412</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

PHASE II

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$x_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0021</td>
<td>0.9979</td>
</tr>
<tr>
<td>0.1498</td>
<td>0.5035</td>
</tr>
<tr>
<td>0.1933</td>
<td>0.4352</td>
</tr>
<tr>
<td>0.2208</td>
<td>0.3851</td>
</tr>
<tr>
<td>0.2941</td>
<td>0.2922</td>
</tr>
<tr>
<td>0.3843</td>
<td>0.2091</td>
</tr>
<tr>
<td>0.4769</td>
<td>0.1365</td>
</tr>
<tr>
<td>0.4984</td>
<td>0.1219</td>
</tr>
</tbody>
</table>

Table 3: Liquid-liquid equilibrium data (mole fraction) for water(l)-1-propanol(2)-trichloroethane(3) system at 20°C

Fig. 1: Distribution isotherms for water-1-propanol-chloroform and water-1-butanol-chloroform
Table 4: Selectivity values at zero content of alcohol in water for chlorocompounds and other solvents (+ ref. 5).

In order to compare the chlorocompounds with other solvents for the separation of water-alcohol mixtures, Table 4 reports data of $\ln \beta^*$ obtained by extrapolating to zero content of alcohol in water the selectivity of the solvents in respect to water-alcohol mixture expressed as

$$\beta = \frac{[\text{Alcohol}]_{\text{solv}}}{[\text{water}]_{\text{water}}} \cdot \frac{[\text{water}]_{\text{solv}}}{[\text{alcohol}]_{\text{water}}}$$

The data relative to the other solvents are derived from (5). It appears from the table that the selectivity of the chlorocompounds are higher than those given by the other solvents and that the chlorocompounds in general behave similarly.
References


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A NEW APPARATUS FOR MEASUREMENT OF LIQUID EQUILIBRIUM DATA

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Summary:
A new apparatus for measurement of liquid-liquid equilibrium (LLE) data is presented. It was designed for simultaneous measurements of 10 tie lines at the same temperature under pressure up to 6 bar. Thereby LLE-data can be measured above their atmospheric boiling point. To prove the efficiency of the new apparatus, results for LLE and density-data are presented for the system water-methanol-dichlormethane at 20 and 60°C.

Introduction:
Economizing energy, liquid liquid extraction is getting more attractive for industrial purposes. In spite of availability of data collections and data banks, new experimental information is still necessary due to limited number of known systems, especially at different temperature levels. The DECHEMA LLE Data Collection (Sørensen, Arlt, 1979), for example, which contains more than 1100 ternary systems, shows the interesting feature, that 75% of the data are within 10°C of room temperature, represented averagely by 4 - 6 tie lines.

Description of the apparatus
The main features of the apparatus are:
- possibility of simultaneous measurement of 10 tie lines under identical conditions
- using water for thermostating purposes, the temperature range is restricted from 20 up to 95°C
- pressures up to 6 bar
- sampling with the help of capillaries

The scheme of the apparatus is explained in fig. 1.

It consists of a series of ten magnetic stirred SCHOTT glass cells of about 80 ml. (commercially-available blind flanges). Fixed by SCHOTT's mounting system, the cells are leak tight to over 6 bar internal pressure. Every cell is supplied with nitrogen in this pressure range by a central line from a gas cylinder; there is the possibility to shut off
the cells hermetically by valves.

The principal idea, to shape a LLE equipment as pressure
tight cell originates from high pressure measurement
technique.

Application of pressure allows measurement at elevated
temperatures even above the atmospheric boiling point
of the mixture and installation of a capillary sampling
system, which is the most important factor for such intents.
From thermodynamic point of view, pressures up to 6 bar
can be neglected, since LLE are not sensitive in this
range. Bocko (1980) constructed an apparatus for special
purposes in a similar manner.

What is much more important, is the fact, that LLE show
strongly pronounced temperature dependence, especially in
the region of plate points. Therefore for any measurement
apparatus, where tie lines are measured successively, the
problem of temperature constancy respectively reproducibi-
li ty exists. To obviate the difficulties, the optimal
strategy is to perform simultaneous measurement by
installation of batteries of thermostated separating
funnels etc. It was one of the main intents in the design
of the apparatus, to find a comfortable and practicable
solution.

For this purpose, the ten cells, mounted on a rack, are
immersed in a thermostat bath of about 100 liter, filled
with water. The bath is a stainless steel - construction
and adequately isolated. On both sides there are thermo-
glass windows for observing the cells during operation.
The whole bath can be lifted hydraulically, till it is
closed by the upper part of the framework. There is also the
thermostating equipment, guaranteeing temperature constancy
of 0.01 - 0.03°C and a calibrated Pt-100 thermo sensor
with an accuracy of less than 0.01°C are installed.

As mentioned before, PTFE-covered magnetic bars are used
for agitation of the cells; therefore electrical driven
magnets are installed under the bottom of the bath, strong
enough to penetrate the steel, isolation and layer of
water. The single magnets are shielded, in order to reduce
interactions to a minimum. The speed of rotation is con-
trollable by external potentiometers to satisfactory extent.

The most important part of the apparatus is the sampling
system. Sampling is a special problem, if measurement tem-
perature is higher than ambient; in such cases the usual
technique of transferring samples by syringes is ineffi-
cient because of the tendency of phase separation prior
to analysis. That really may be a reason, why only few data
at elevated temperature can be found in literature. The
sampling system consists of two 1/16" steel capillaries
for each phase leading out of each cell as can be seen
from fig.2; all capillaries pass a heat exchanger and the
flow is controlled by valves. In front of the apparatus the samples can be collected. "Memory" effects are avoided by the minimal stagnant volume of about 0.04 ml per one capillary, valves included. Effects of phases split inside the lines (effected by cooling) will not distort the results due to high flow rates and predominating plug flow.

Additionally there is the possibility to measure the densities of the phases in state of equilibrium. Density measurement is based on oscillation principle (Leopold et al., 1977); the oscillation cell is thermostated by a circulating stream of water and can be directly connected with any sample capillary. So the measurements are performed under identical temperature conditions as inside the equilibrium cells and especially at the same pressure, in order to avoid degasing of nitrogen and boiling. At present the connection lines and the inlet of the density cell are not thermostated, which causes errors of systematical nature due to phase split effects prior to measurement at elevated temperatures.

Experimental Procedure

For the purpose of testing the apparatus, especially at elevated temperatures, the system water-methanol-dichloromethane had been measured at 20 and 60°C. The system had been chosen because of the volatility of dichloromethane (b.p. 40 - 41°C). Literature data, at least for 20°C are available (Khanina et al., 1978) for comparison. The organic compounds were supplied by MERCK as absolute p.a. reagents. The content of water permanently was controlled by Fischer analysis and was found to be 0.02 % averagely. Water, comming to use, was demineralized and distilled.

Having a weight of about 200 g, the glass cells offer the possibility of weighting in the components directly; ten mixtures of about 70 ml were prepared allowing measurement till up to the plate point and splitting into two phases of about identical volume. Since the over all composition is known exactly, the accuracy of the measurement can be checked easily: the two equilibrium compositions and the over all composition should lie on a line as best as possible.

The mixtures were equilibrated over night at 19.45 ± 0.05°C (resp. 59.70 ± 0.03°C) at about a pressure of 2 bar (resp. 3.5 bar). The pressures were chosen to be about half a bar greater than the mixture's vapor pressure at corresponding temperature. Prior to analysis, the phases were allowed to settle for 2 - 3 hours.

Analysis

Samples of about 1 - 1.5 ml, cooled down to temperature of tap water, were filled into ampullas; after adding of
minimal amounts of 0.1 - 0.25 ml n-propanol, just enough to remove appearing phase split and after capping, the samples were ready for gas chromatography analysis. Using a thermal conductivity detector, also water could be analyzed. The content of water in the organic phases additionally was analyzed by conventional Fischer titration. Samples for Fischer titration in the range of 0.5 - 5 g were taken with the help of a weight buret, which a minimal amount of desiccated methanol was weighted in as dissolving intermediary. Water, imported in the samples by n-propanol, had been corrected numerically, but has no significance on the results, what concerns two or three positions after the comma. Performing density measurement, at 60°C the mean deviation went up to 4% due to phase separation effects in the connection lines as mentioned before. Measurements at 20°C, however, have no more deviation than 0.05 %.

Discussion of Results

In fig. 3 and 4 the results for the system water-methanol-dichlormethane are presented for 19.45 ± 0.05°C and 59.70 ± 0.03°C. Experimental error can be estimated as usual in gas chromatography.

In fig. 3 the data from Khanina (1978) (taken from Sørensen, Arlt, 1979) additionally are drawn in; conformity is satisfactory. Better valuation can be made by comparison of computed binodal curves by NRTL- or UNIQUAC-model: great deviations can be observed of the NRTL - shape in fig. 3 in the regions of increasing methanol concentration; one reason for this behaviour is, that the literature data, measured only in the lower part of the two phase region, are not suitable for extrapolation the upper part satisfactorily. This can be confirmed by performing NRTL-fittings of our results without the three upper tie lines: the two phase region is getting wider and a plate point is estimated, which according experimental evidence lies outside the two phase region.

Fig. 5 shows the experimental concentration ratios of the solvent and the good fitting results from NRTL- estimation. All calculations have been made by an UNIVAC 1100 calculator.

In fig. 6 the results of density measurement are presented. As can be seen, the results for 60°C are affected with greater systematic errors due to separation of phases in the connection lines prior to measurement.

Conclusions

The main intent in the design of the apparatus was compactness and the possibility of quick and comfortable measurement of reliable LLE data. This was achieved by simultaneous measurement of ten tie lines at the same temperature. Pressurizing the cells allows measurement above
atmospherical boiling point and a capillary sampling system. The experimental procedure, being a good compromise between maximal accuracy and instrumental expense, guarantees reliable results. The measurements of the system water-methanol-dichlormethane prove the adequacy of these intents.

Acknowledgements

The authors thank to Fonds zur Förderung der wissenschaftlichen Forschung for the research grant No.4046, which has made this work possible; furthermore to Mr.Aage Fredenslund for kindly placing the fitting programs at our disposal and to Mr.Wastian (workshop) for manufacture of the equipment.

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Fluid Phase Equilibria 3 (1979) 47 - 82
Bocko P; Fluid Phase Equilibria 4 (1980) 137-150
fig. 1 general scheme of the apparatus

a... temperature bath, b...stirring equipment, c...thermostat
d... equilibrium cell, e...sample capillaries, f...sample valves,
g... heat exchanger, h...gas cylinder, i...heating and expansion vessel, j...valve for N₂, k...central lines for N₂,
l...ventilation valve, m...magnetic stirrer

fig. 2 constructive detail of equilibrium cell
fig. 3 System water-methanol-dichlormethane at 20°C
NRTL fit; NRTL fit without three upper tie lines; NRTL fit lit.data

fig. 4 System water-methanol-dichlormethane at 60°C
NRTL fit
fig. 5  concentration ratios of CH₃OH

fig. 6  densities of phases in equilibrium
Possibilities of the description of liquid-liquid equilibria

Introduction

The liquid phase splitting is an old technique for the separation of liquids. It started with Berthelot in 1872 and Nernst in 1891. This technique, first used in chemical laboratories, has become a technical process. It was therefore necessary to describe the phase splitting quantitatively. Starting with the interpolation of measured values in former times it is now possible to predict the concentrations to a certain extent, through the use of theories which describe the concentration dependence of the excess Gibbs free energy. It is the aim of our paper to present modern methods of the prediction of phase splitting and the problems involved.

Thermodynamic Principles

Under equilibrium conditions in a heterogeneous closed system, the intensive state variables, temperature T, pressure P and chemical potential \( \mu \), have the same values in all phases. It can be derived that this is also true for the auxiliary functions fugacity f and activity a.
The chemical potential $\mu_i$ of component $i$ is defined as the partial molar quantity of the free molar enthalpy of mixing, i.e. for a two component system,

$$\mu_i = g - x_2 \frac{\partial g}{\partial x_2}$$

Under the condition of the equality of chemical potentials this equation can be transformed to

$$\left( \frac{\partial g}{\partial x_1} \right)_{P,T}^{' \, \prime} = \left( \frac{\partial g}{\partial x_1} \right)_{P,T}^{'' \, ''} = \text{phases}$$

This means that there should be a common tangent for two points of the free molar enthalpy of mixing if phase splitting occurs. The above equation is a necessary but not sufficient criterion. It is necessary that the total Gibbs free energy reaches a minimum. In order to check this the higher differentials of $g$ must be computed. Especially the second differential $\frac{\partial^2 g}{\partial x^2}$ should be positive at this point. It is illustrated in figure 1.

From the left edge to point "a" there is the miscible region. The shape of the curve inside the miscibility gap is controlled by the thermodynamic stability.

Note that the equilibrium point is not the same as the mi-
minimum. The following ascent of the g-curve and the \( \frac{dg}{dx} \)-
curve is positive; we are in a metastable region and the
equilibrium point found previously was a stable one.

The next minimum between lines c and d is unstable, because
there are unstable regions in the neighborhood, and the
point found is not a general minimum.

It is evident that for liquid-liquid-equilibrium (LLE) cal-
culations only the shape of the curve is essential but not
its absolute value.

This is not true in the case of vapor-liquid equilibria. If
we consider that g is a function of an ideal and a non-ide-
al term, we have

\[
g = \sum x_i \ln x_i + \sum x_i \ln \gamma_i
\]

The first term is called \( g^{id} \) and the second \( g^E \). The activi-
ty coefficient \( \gamma \) is given for vapor-liquid-equilibrium by

\[
\gamma_i = \frac{P_i}{x_i p_i^s}
\]

\( P_i = \) Partial pressure
\( p_i^s = \) saturation pressure

The absolute value of \( g^E \) and consequently of \( g \) is important
for vapor-liquid-equilibria (VLE). If we want to fit mis-
cibility data by a model representing \( g^E \) as a function of
composition, the model is forced to describe a curvature
as mentioned in figure 1. Because there is no hint to its absolute value, the curve is fitted such that the extreme values are represented correctly. Its ordinate value is chosen randomly. If we want to calculate VLE data with the same model, the $g^E$-value becomes important and determines the phase equilibrium. There is no doubt that the representation of the VLE data is bad, generally speaking.

It should be impossible to calculate VLE-data from LLE correctly. Let us summarize all difficulties in describing phase equilibria:

1) The thermodynamic stability is dependent on the curvature of the $g$-curve

2) Inside the one-liquid phase region, the phase equilibrium is determined by the coexistence equations. Inside the immiscible region the thermodynamic functions follow the thermodynamic stability criterion. It is true that the variables of the coexistence equations remain constant inside the two-liquid phase region.

3) The temperature dependence of LLE is much more stronger than those of VLE. A temperature extrapolation of LLE data using VLE data becomes imprecise and leads to errors. This is because the activity coefficient is a correction to VLE, where the temperature
dependence is mainly given by the vapor pressure. Unfortunately, the common models for the description of the activity coefficient give a poor representation of the temperature shift of the activity coefficient.

4) Sometimes both data, VLE and LLE, are needed inside an apparatus, e.g. for an extractive distillation. Here both data have to be represented by different models in order to avoid large errors. The prediction of LLE from VLE is much more complicated here, because the VLE data itself is quite erroneous. The reason is that the extractant solvent is normally a high boiling one, and the determination of its partial pressure is subject to analytical errors.

We want to demonstrate the above-mentioned problems with some binary systems, where VLE and LLE data are available (Figures 2-3). The shape of the Gibbs energy in a ternary system is difficult to imagine. An ideal system should form a symmetrical tent. An example is given in figure 5 with the system water-succinic-acid-butanol-1. Components 1 and 3 show the well known phase splitting. In fact, the influence on the whole shape is remarkably small. It disappears with the eighth line corresponding to an experimental critical point of 10 mole % of succinic acid.

If two immiscible binaries are present in a system the shape of figure 7 is usual. The miscibility gap is formed by the systems heptane-aniline and methylcyclohexane-aniline. The
non-miscible area is spanned from one side to the other, clearly indicated by a ridge at the top of the plot. Even in this case the phase splitting plays a minor role compared to the binary Gibbs energy of the model equation used, as figure 8 shows.

A very unusual case is given in figure 10. The shape of the figure is determined by a large positive energy of a dioxalane derivative and pentadecane. The miscibility gap is very broad and cannot be taken from the picture. Even from a binary plot, given in figure 11, no hint can be derived.

Calculation of liquid-liquid-equilibria

Up to the publication of Wilson’s local composition concept, calculation of LLE was based mainly on empirical equations. Examples are the methods of Hand, Varteressian and Fenske, Ewell, Rod, Alders and other authors. These are methods which are derived for the interpolation of tie lines. An outstanding exception is the regular solution theory, developed by Hildebrand and Scatchard.

1.) Regular Solution Model

Strictly speaking the theory is valid only for solutions with zero excess volume and with zero excess entropy. There—
fore the method should not be applicable to aqueous mix-
tures. This assumption is true for mixtures of non-polar
liquids. The activity coefficient is given as a function
of the volume fraction of components, the molar volume and
a solubility parameter. Following the theory, solubility
parameters can be calculated from the heat of vaporization
and the molar volume. There are tables in many textbooks
(e.g. in the Handbook of Chemistry and Physics) where cal-
culated parameters are tabulated. Further, if no experimen-
tal data are available, molar attraction constants can be
calculated by the method of Small. Bittrich\textsuperscript{1)} used the Hil-
debrand-Scatchard equation for the determination of the up-
per critical dissolution temperature of systems with di-
methylformamide and N-methylcaprolactame combined with ali-
phatic hydrocarbons. He found that the prediction of tempe-
rate is only fair. The use of the Flory-Huggins equation
did not improve the result. Bittrich concludes that the Hil-
debrand-Scatchard equation should be used only for the shor-
ter hydrocarbons.

2. The Leo/Hansch Approach\textsuperscript{2)}

A second predictive method for liquid-liquid equilibria
(LLE) was born in a part of natural science which normally
is not involved in phase equilibria.

In 1899 the German scientists Meyer and Overton examined
the relative narcotic activities of drugs. They revealed
that the activity is often parallel to the oil/water partition coefficient. Collander showed in 1951 that the partition coefficient of a mixture in one solvent can easily be recalculated for another one. In order to reduce the experimental work, the system octanol-water was taken as a reference system. They derived an incremental method to determine the influence of derivatives on the partition coefficient in the octanol/water-system. The additivity of groups was established in a study of a substituent constant in an analogous fashion to the Hammett constant $\sigma$. The Hammett equation is well known to chemists in order to predict the influence of substituents on reaction rates. If the partition coefficient is known for the reference system, it can be recalculated for another solvent system. The method is useful only for room temperature and ternary systems. Its advantage is the large data base for measured and calculated partition coefficients (more than 5800 solutes) and the possibility of incrementation of unknown substances following the method of Hammett.

3. Activity coefficient and VLE data

Since the development of the local composition concept by Wilson several equations have been established to describe the composition dependence of the Gibbs molar excess enthalpy. The most common equations are called NRTL and UNIQUAC. The theory of these models includes the fact that
for the representation of multicomponent equilibria only binary data have to be used. This fact avoids the need for multicomponent data points. For multicomponent liquid-liquid equilibria the problem occurs that the miscible binary systems can naturally not be determined by LLE data. A way out is the use of vapor-liquid equilibria (VLE) or the use of common parameters which will be explained later.

The use of VLE data is doubtful, because this data is usually not available at the LLE system temperature, which is near room temperature. On the other hand it is well known in the literature that the temperature extrapolation of the activity coefficient is erroneous. A second disadvantage is the fact that because of model inefficiencies the correlation of VLE and LLE data leads to different minima of the objective function. We have investigated this problem in former times\(^3\). Figures 12 and 13 show that there is no coincidence between ebulliometric data and UNIQUAC calculated LLE data. The vapor liquid equilibrium has been investigated in a special ebulliometric device outside the miscibility gap.

Several authors tried to circumvent the problem by a modification of the existing models. The latest ones are those of Nagata\(^4\) with NRTL equation and of Malanowski\(^5\)
with UNIQUAC equation. We cannot hope to solve the problem by merely empirical corrections to semi-empirical equations.

4.) Activity coefficient and common parameters

A more promising way has been proposed by Sorensen and Arlt. They tabulate more than 1000 UNIQUAC parameter pairs for miscible and immiscible binaries. For an immiscible binary mixture the common parameters are calculated from the miscibility gap near 20°C. This ensures that the separating boundary system is correctly reproduced during later predictions. The second step is the determination of parameters for the binary miscible systems from LLE data.

Figure 14 illustrates the procedure. The ternary system ABC has an open miscibility gap. In total, six parameters are required for the description of the system using the UNIQUAC equation. The two parameter pairs A-B and A-C are determined from the miscibility gap. This leaves the parameters for the pair A-C. The open literature was scanned for ternary systems XAC, where X is an arbitrary extra component whose parameter X-A and X-C are known. In the example given in figure 14 this system A-D-C was found. If we suppose that the parameters C-D are known from previous calculations, parameter pair A-C remains to be de-
terminated. These parameters A–C are now calculated by optimizing all the data sets simultaneously in which the component pair A–C occurs. This makes the binary UNIQUAC parameters of A–C generally valid, "common".

The advantage of these parameters is that they are taken from LLE data. In this case the model inefficiency is not revealed.

5.) Activity coefficient and UNIFAC

An important step towards the calculation of phase equilibria was the development of the incremental method UNIFAC. It comes out of the same theoretical background as the UNIFAC equation. The objective of the incremental methods is to convert the substance combinations, too numerous for consideration, into combinations of functional groups, the number of which can be handled. It may be assumed that 80 groups represent the majority of industrially important substances. The liquid is considered as a mixture of structural groups. One disadvantage is that it is not always possible to differentiate between isomers. Because of the problems mentioned above, parameter tables have been established for VLE and LLE calculations separately. The VLE table is much broader in application, because the database used (Dortmund Data Bank) contains a number of measured data. The LLE database is much smaller and therefore
the table for LLE calculations is small. From our experience, the use of VLE UNIFAC is equivalent to experimental VLE data. The accuracy is often not sufficient for industrial applications, i.e. the slope of the binodal curve and the limits of miscibility. The first term influences the amount of solvent used and is not so critical. The second term determines the solubility of the solvent in the mixture to be treated. This counter-solubility is important if waste water problems occur. It is recommended to determine the mutual solubility of all components.

The accuracy of LLE-UNIFAC is similar to that of common UNIQUAC parameters. The parameter table contains 32 main groups and is not very dense. The reason is that the same base (Dortmund Lyngby databank) was used as for the common parameters. Even with its limited applicability the method is a valuable tool for the scientist and the engineer (figure 15).

6.) Fugacity

As mentioned before, the equilibrium is attained if the fugacities of each component in each phase are equal. For liquid-liquid-equilibria fugacities are not commonly used. The normal procedure is to replace them through the activities. The reason is that the models for the description.
of the activity coefficient are based on theories of solids or high molecular liquids. They are "extrapolated" to short length molecules.

Most of the models for the description of fugacities are derived from theories of the gaseous state and must be extrapolated to the denser medium "liquid". The last mentioned way is accompanied by greater uncertainties. To the best of our knowledge equations of state are not practically used for the description of solvent extraction.

7.) Empirical methods

A good review about these methods is given by Horvath\textsuperscript{9).} As it can be derived from Clausius-Clapeyron equation these methods use a linear relationship between the logarithm of the solubility (preferably in water) and a molecular quantity. All these methods are often limited in applicability and limited to binary systems. Therefore they play a minor role in the calculation of multicomponent liquid-liquid equilibria.

What is to do?

The main problem for the calculation of liquid-liquid equilibria (LLE) is the temperature dependence of the phase
equilibrium. Even if information is available at several temperatures the models (e.g. NRTL and UNIQUAC) for the activity coefficient are not able to represent it in their original form. One way-out is to describe the parameters through a temperature dependent polynomial. Based on our experience the UNIQUAC constants are often linear functions of the temperature. If the user dares of extrapolate the existing data, UNIQUAC is recommended. The problem cannot be solved by cosmetic and empirical corrections to the existing equations.

The second problem is to find a model which is so accurate that VLE data can be used for the description of the miscible binaries. The use of the common UNIQUAC parameters should be an interim solution.

And last, a practical method should be developed to describe the influence of salts on the activity coefficient. Especially the liquid extraction is a process where "salting out" occurs frequently.

We gratefully acknowledge the help of Miss C. Günther who wrote the computer programs to prepare the plots.
Literature

1.) H.-J. Bittrich, I. Hammer, D. Lempe, A. Sarius

2.) A. Leo, C. Hansch, D. Elkins

3.) W. Arlt, U. Onken

4.) I. Nagata, Y. Nakamiya, K. Katoh, J. Koyabu
   Thermochimica Acta 36, 153 (1981)

5.) A. Malanowski, S. Skjold-Jorgensen, P. Rasmussen,
    Aa. Fredenslund

6.) W. Arlt, P. Grenzheuser, J. M. Sorensen

7.) J. M. Sorensen, W. Arlt
    DECHHEMA Chemistry Data Series, Vol. V, Parts 1-3,
    Frankfurt 1979, 1980

8.) T. Magnussen, P. Rasmussen, Aa. Fredenslund

9.) A. L. Horvath: "Halogenated Hydrocarbons"
    Marcel Dekker, New York 1982
Figure 1: Free-enthalpy of mixing, plotted as a function of mole fraction, as calculated by a model equation.
Figure 2: Free enthalpy of mixing (cal/mole) of the system nitromethane-hexanol-1 as a function of the mole fraction
(blue line: VLE data at 21 and 40°C
black line: LLE data at 20, 25, 30 and 34°C)

Figure 3: Free enthalpy of mixing (cal/mole) of the system butanol-1 - water as a function of the mole fraction
(blue line: VLE data at 25 and 60°C
black line: LLE data at 0, 20, 25, 40, 60, 80, 100 and 120°C)
BERGER R.
EUR. FED. CHEM. ENG., RECOMM. Syst. LIQ. EXTR. STUD., EDITOR: T. MIŠEK
(1978)

TEMPERATURE = 10.0 DEG C  TYPE OF SYSTEM = 1

EXPERIMENTAL TIE LINES IN MOLE PCT (GRAPH. INTERPOL.)

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SPECIFIC MODEL PARAMETERS IN KELVIN

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MEAN DEV. BETWEEN CALC. AND EXP. CONC. IN MOLE PCT

UNIQUAC (SPECIFIC PARAMETERS) 0.04
NRTL (SPECIFIC PARAMETERS) 0.06
Figure 5: Free enthalpy mixing (cal/mole) of the ternary system water-succinic-acid-butanol-1 as a function of the mole fraction (UNIQUAC equation)
TEMPERATURE = 25.0 DEG C  TYPE OF SYSTEM = 3

EXPERIMENTAL TIE LINES IN MOLE PCT

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MEAN DEV. BETWEEN CALC. AND EXP. CONC. IN MOLE PCT

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| NRTL (SPECIFIC PARAMETERS) | 0.14 |
| UNIQUAC (COMMON PARAMETERS) | 0.19 |
Figure 7: Free enthalpy of mixing (cal/mole) of the ternary system heptane-methylcyclohexane-aniline (NRTL equation)

Figure 8: Free enthalpy of mixing (cal/mole) of the ternary system heptane-methylcyclohexane-aniline (UNIQUAC equation)
(1) C15H32 PENTADECANE
(2) C15H33 1,3-DIOXOLAN-2-ONE, 4-METHYL

GUSHCHENKO N.F., ROGZEKIN V.A., PETRUNKHOVA A.I.
KHIM.TEKNOL.TOPL.MASEL (197) 15, 16

TEMPERATURE = 20.0 DEG C  TYPE OF SYSTEM = 1

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MEAN DEV. BETWEEN CALC. AND EXP. CONC. IN MOLE PCT

| UNIQUAC (SPECIFIC PARAMETERS) | 0.90 |
| NRTL (SPECIFIC PARAMETERS) | 0.97 |
| UNIQUAC (COMMON PARAMETERS) | 1.07 |

EXP. TIE LINE
CALC. GIBBS
NRTL(SP) ----- NRTL(SP) ----- UNIQC(S) ----- UNIQC(S) ----

EXP. DISTR. RATIO
CALC. DISTR. RATIO
NRTL(SP) ----- NRTL(SP) ----- UNIQC(S) ----- UNIQC(S) ----
Figure 10: Free enthalpy of mixing (cal/mole) of the ternary system 1,3 dioxalan 2 one 4 methyl-toluene-pentadecane (common UNIQUAC parameter)

Figure 11: Free enthalpy of mixing (cal/mole) of the binary system 1,3 dioxalane 2 one 4 methyl-pentadecane (common UNIQUAC parameter)
Figure 12: Activity coefficients at infinite dilution in the system aniline-methylcyclohexane.

- from ebulliometric data
- from LLE data (authors' measurements, correlated with UNIQUAC)
- VLE data by Röck (extrapolated with UNIQUAC)
Figure 13: Activity coefficient at infinite dilution in the system aniline - n-octane
parameters for 
A - B
B - C
A - C
are taken from 
binary miscibility gap
" " "
to determine

parameters for 
A - D
D - C
A - C
are taken from 
binary miscibility gap
previously determined
to determine
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**VLE**: Vapour - Liquid Equilibrium
A new algorithm is proposed for determining the equilibrium composition on the basis of the knowledge of Gibbs energy of N-component system. The method is modified for chemical-engineering applications, that is for the case when the composition of coexisting phases to a given overall composition is sought (flash calculations). As initial approximation the composition of coexisting phases of binary system can be used.
The difficulties of calculating the composition of coexisting phases have been one of the main hindrances of application of the thermodynamic description to the liquid-liquid phase equilibrium. The most rapid calculation is achieved by solving the non-linear equations

\[ \ln a_i(\tilde{x}) = \ln a_i(\tilde{x}) \quad i=1,2,...,N \quad (1) \]

by the Newton method, where \( a_i = x_i f_i \) is the activity of \( i \)-th component. The efficiency of the Newton method excels especially at a suitable initial estimate of composition of coexisting phases. This method is used by Joy, Renon and coworkers, Novák and coworkers, Magnussen and coworkers. The calculation is rather complicated as it requires the calculation of the activity coefficients \( f_i \) and also their derivatives with respect to composition. These derivatives can be determined either numerically or analytically. The numerical way of calculating extends considerably the calculation especially in case of multicomponent systems.

In application we meet different types of problems. A new method is proposed in this work for determining the equilibrium liquid-liquid composition of \( N \)-component system. The method is modified for chemical-engineering application, that is for the case when the composition of coexisting phases to a given overall composition is sought.

Let the overall composition of heterogeneous mixture \( w = (w_1, w_2, ..., w_{N-1}) \) be given. The equations of material
balance have the vectorial record

\[(1 - \phi)\bar{x} + \phi \bar{\bar{x}} = w\]  \hspace{1cm} (2)

where \(\bar{x} = (\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_{N-1})\) or \(\bar{\bar{x}} = (\bar{\bar{x}}_1, \bar{\bar{x}}_2, \ldots, \bar{\bar{x}}_{N-1})\) is vector of molar fractions of first or second phase and \(\phi\) is relative amount of the second phase, \(\phi \in (0,1)\). Therefore we seek the composition of such a pair of coexisting phases whose tie-line goes through the point \(w\). The equilibrium conditions and the equations of material balance take then the form

\[
\begin{align*}
\ln a_i(\bar{x}) &= \ln a_i(\bar{\bar{x}}) && i=1,2,\ldots,N \\
(1 - \phi)\bar{x}_j + \phi \bar{\bar{x}}_j &= w_j && j=1,2,\ldots,N-1
\end{align*}
\]  \hspace{1cm} (3)

The system of non-linear equations (3) is a system of \(2N-1\) equations for \(2N-1\) unknowns \(\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_{N-1}\), and for the parameter \(\phi\). The equations of material balance can be rearranged into the form

\[
(\bar{x}_i - \bar{x}_1)(w_1 - \bar{x}_1) = (w_i - \bar{x}_1)(\bar{x}_1 - \bar{x}_i)
\]  \hspace{1cm} (4)

which has arisen so that the parameter \(\phi\) has been expressed from the first equation of system (2) and its value has been inserted into the remaining equations of material balance. Let us assume that we know the vectors of initial approximation of composition of coexisting phases \(\bar{x}_i^0, \bar{\bar{x}}_i^0\). The choice of initial approximation will be discussed later. From the relations

\[
\bar{x}_i = \bar{x}_i^0 + \Delta \bar{x}_i \hspace{1cm} \bar{\bar{x}}_i = \bar{\bar{x}}_i^0 + \Delta \bar{\bar{x}}_i \hspace{1cm} i=1,2,\ldots,N-1
\]  \hspace{1cm} (5)
follows that the equations of material balance (4) can be expressed in the form

\[(\alpha_1 + \Delta\bar{x}_1 - \Delta\bar{x}_1)(\beta_1 - \Delta\bar{x}_1) = (\beta_1 - \Delta\bar{x}_1)(\alpha_1 + \Delta\bar{x}_1 - \Delta\bar{x}_1) = 0 \quad i=2,3,...,N-1 \tag{6}\]

where we have designed

\[\alpha_1 = \bar{x}_1^0 - \bar{x}_1^0, \quad \beta_1 = w_1 - \bar{x}_1^0 \quad i=1,2,...,N-1 \tag{7}\]

By multiplying the parentheses in eq. (6) and neglecting the increments of the second order we obtain

\[\beta_1 \Delta\bar{x}_1 + (\alpha_1 - \beta_1) \Delta\bar{x}_1 = \beta_1 \Delta\bar{x}_1 - (\alpha_1 - \beta_1) \Delta\bar{x}_1 = \beta_1 \alpha_1 - \beta_1 \beta_1 \quad i=2,3,...,N-1 \tag{8}\]

By replacing the equilibrium conditions (1) by the Taylor series at the points \(\bar{x}^0, \bar{x}^0\) and neglecting the second and higher powers of increments \(\Delta\bar{x}_1, \Delta\bar{x}_1\) we get the system of linear equations

\[\sum_{j=1}^{N-1} \left( \frac{\partial \ln a_i(\bar{x}^0)}{\partial x_j} \Delta\bar{x}_j - \frac{\partial \ln a_i(\bar{x}^0)}{\partial x_j} \alpha\bar{x}_j \right) = \ln \frac{a_i(\bar{x}^0)}{a_i(\bar{x}^0)} \quad i=1,2,...,N \tag{9}\]

By combining systems of equations (8) and (9) we obtain a linear system of \(2N-2\) equations for \(2N-2\) unknown increments \(\Delta\bar{x}_1, \Delta\bar{x}_1\).

Since the vectors of initial approximation \(\bar{x}^0\) and \(\bar{x}^0\) can differ significantly from the solution of system of equations (3), it is necessary, at least in several initial iteration steps of the Newton method, to use the reducing
(relaxation) parameter \( \eta \in (0, 1) \)

\[
\bar{x}_i = \bar{x}_i^0 + \eta \Delta x_i , \quad \bar{x}_i = \bar{x}_i^0 + \eta \Delta \bar{x}_i \quad i=1,2,\ldots,N-1 \tag{10}
\]

When determining \( \eta \) we can proceed e.g. in the following way: Let us denote

\[
S_1 = \sqrt{\sum_{i=1}^{N-1} (\Delta x_i)^2} , \quad S_2 = \sqrt{\sum_{i=1}^{N-1} (\Delta \bar{x}_i)^2} , \quad S = \max(S_1, S_2). \tag{11}
\]

If \( S > \delta \), where \( \delta \) represents the allowed "step" which was usually chosen equal to 0.05, then we have for the reducing parameter

\[
\eta = \delta / S. \tag{12}
\]

In the opposite case \( \eta = 1 \).

Convergence of the Newton method is always subject to a factor of uncertainty and therefore as the most sure we recommend the following variant. This variant can be especially advantageous in the case when the vector \( w \) is "very" far from conode \( \bar{x}^0, \bar{x}^0 \). The convergence can be ensured if we proceed in the following way:

1) We construct the line segment \( w, w^0 \) whose one end point is the point \( w \) and the second one a hitherto undetermined point \( w^0 \) on the line segment \( \bar{x}^0, \bar{x}^0 \) — see Fig. 1. The construction of the point \( w^0 \) will be explained later.

2) On the line segment \( w, w^0 \) we choose \( M \) equidistant points \( w_1, w_2, \ldots, w_M \). It holds \( w_j = (1 - \gamma_j)w^0 + \gamma_j w \), where \( \gamma_j = j/(M + 1) \), \( j=1,2,\ldots,M \). If e.g. \( M=9 \) is chosen (and consequently the parameter \( \gamma \) takes gradually the values...
Pigel The course of line segments $x^i, x^o$ and $w^o, w$ in a ternary system.

We have

$w^1 = 0.9 w^o + 0.1 w$

$w^2 = 0.8 w^o + 0.2 w$

$\ldots$

$w^9 = 0.1 w^o + 0.9 w$

3) Let us solve first the system of non-linear equations (3) where, however, the point $w$ will be replaced by $w^1$. The solution obtained will be then used as the initial approximation for solving the system of non-linear equations (3), where the point $w$ is substituted by the point $w^2$, etc. It is evident that sufficiently large value of $M$ guarantees the convergence of numerical process. During practical calculations we proceed so that we choose such $M$ that the distance of adjoining points should
not be larger than e.g. 0.05. Since the initial approximation in the given procedure is very close to the true solution, it is possible to use the modified Newton method.

The coordinates of the point \( w^0 \) are best chosen so that the line segment \( w, w^0 \) should be normal to the line segment \( \bar{x}, \bar{x}^0 \), i.e., the point \( w^0 \) should exhibit the shortest distance from point \( w \) of all the points of line segment \( \bar{x}, \bar{x}^0 \). For the point \( w^0 \) holds \( w^0 = (1 - \phi_0) \bar{x}^0 + \phi_0 \bar{x}^0 \), where \( \phi_0 \) is a number from the interval \( (0,1) \). Let us construct the function

\[
 f(\phi_0) = \sum_{i=1}^{N-1} (w_i - w_i^0)^2 = \sum_{i=1}^{N-1} [w_i - (1 - \phi_0)\bar{x}_i^0 - \phi_0\bar{x}_i^0]^2
\]

which gives square of the distance of point \( w \) from point \( w^0 \). From the condition \( df/d\phi_0 = 0 \) follows

\[
 \phi_0 = \frac{\sum_{i=1}^{N-1} (\bar{x}_i^0 - w_i)(\bar{x}_i^0 - \bar{x}_i^0)}{\sum_{i=1}^{N-1} (\bar{x}_i^0 - \bar{x}_i^0)^2}
\]

As far as we get \( \phi_0 < 0 \) or \( \phi_0 > 1 \), then we choose \( w^0 = \bar{x}^0 \) or \( w^0 = \bar{x}^0 \), respectively.

System of equations (8), (9) can be solved only in the case that the points \( \bar{x}^0, \bar{x}^0 \) are the inside points of \( N \)-component system, i.e., \( \bar{x}_1^0, \bar{x}_1^0 \neq 0 \) holds for all \( i=1,2, \ldots,N \). This condition is not satisfied if e.g. we use the composition of coexisting phases of binary system as the initial approximation. Let us assume that \( \bar{x}_k^0 = \bar{x}_k^0 = 0 \) holds for a component \( k, k \neq N \). Then the value \( \partial \ln a_k / \partial x_k \) in system of equations (9) is not finite, for \( \ln a_k = \ln x_k + \ln f'_k \) holds. Instead of condition \( \ln a_k(\bar{x}) = \ln a_k(\bar{x}) \)
we consider the equivalent condition \( a_k(\bar{x}) = a_k(\bar{x}) \). It
follows from the relations \( a_k = x_k f_k \) and \( \bar{x}_k = \bar{x}_k = 0 \)
\[ \frac{\partial a_k(\bar{x})}{\partial x_j} = \frac{\partial a_k(\bar{x})}{\partial x_j} = 0 \quad j \neq k \]
\[ \frac{\partial a_k(\bar{x})}{\partial x_k} = f'_k(\bar{x}) \quad \frac{\partial a_k(\bar{x})}{\partial x_k} = f'_k(\bar{x}) \] (16)
where \( f'_k(\bar{x}) \) or \( f'_k(\bar{x}) \) is the limiting activity coefficient of the \( k \)-th component. It follows from the analogous application of the Taylor series that the \( k \)-th equation of system (9) is considered in this case in the form
\[ f'_k(\bar{x}) \Delta \bar{x}_k = f'_k(\bar{x}) \Delta \bar{x}_k = 0 \] (17)
It would be possible to derive easily an analogous equation for \( k = N \). However, the condition \( k \neq N \) can be always satisfied by exchanging the order of compounds.

\section*{Literature}

LIQUID-LIQUID DATA CORRELATION WITH MAXIMUM LIKELIHOOD.
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Abstract:
Liquid-liquid equilibrium data of ternary systems can be treated in many different ways in order to obtain the parameters of a correlation equation. Two main methods have been developed in the technical literature: the former is based on the "isoactivity" objective function, namely on the property for which the activity of each component is the same in each phase at equilibrium; the latter is based on objective function built up with the residuals between experimental and calculated compositions of each phase.

When data reduction is performed using least-square estimate, two foregoing methods afford very different results; the parameters estimated from the former don't reproduce correctly the experimental tie lines. Parameters estimation with Maximum Likelihood principle overcomes this difficulty. It affords statistically equivalent parameters irrespective of the objective function used, provided the same set of experimental data is treated. Therefore, the objective function more convenient from the computational point of view can be used.

Some ternary data of isothermal systems have been reduced using a computer program based on the M.L. principle in the general form developed by Box [6]; the results show that the isoactivity function is fully equivalent to that based on concentrations, and the same values of parameters are obtained from accurate enough experimental data.
Introduction

In recent years a major interest has been devoted to Maximum Likelihood estimate of the parameters of thermodynamic functions which are useful for phase equilibrium data correlation [3,2,12]. Vapor-liquid equilibrium has been mainly considered, while few papers deal with other data sources, as liquid-liquid equilibria or neat of mixing; where these data were concerned, the aim of the studies was the contemporary reduction of different type of data[4,10]. Recently, a review (to which we will often refer) on liquid-liquid equilibrium data retrieval, correlation and prediction has been published[15]; several methods of data reduction are described, but they are all based on least-square principle. An analysis of Maximum Likelihood application to this subject is still missing.

Computer programs until now published are based on L.S.[13,14,16]: they have to overcome several difficulties connected with L-L data reduction, which is more troublesome than vapor-liquid equilibrium. Two main reasons are at the heart of this matter: the former is concerned with the thermodynamic model, which does not allow the computation of experimental values of excess free energy (or, which is the same, of the individual values of activity coefficients); the latter is of a statistical kind, and results from the mismatch between the hypothesis for least-square reduction, which considers that the independent variables are errors free, and the actual characteristics of experimental data. These topics make the choice of data reduction procedure very critical in order to obtain good parameters.

Ternary liquid-liquid data reduction.

As the pressure is not significant, five variables describe the liquid-liquid equilibrium of a ternary system. Besides P the system has 2 degrees of freedom: temperature and concentration of one component in one of two phases are sufficient to fully determine the equilibrium. The other concentrations are computed from the system

\[ f(x_1, x_2, \theta) = x_1^T \psi_1(x_1, \theta) - x_2^T \psi_2(x_2, \theta) = 0 \]
Two main methods have been used in order to estimate the vector of model parameters: the former minimizes the residuals between calculated and experimental mole fractions; the latter minimizes the "isoactivity" criterion. Some topics of these methods will be shortly discussed. For the computational problems the reader is referred to cited literature.

**Concentration objective function.**

The objective function to be minimized is

\[ O_F = \sum_{i=1}^{N} \sum_{j=1}^{2} \sum_{k=1}^{2} (x_{ijk}^{calc} - x_{ijk}^{exp})^2 w_{ijk} \]  

where \( w \) is a weight factor. The \( x_{ijk}^{calc} \) are computed by solving equations 1 and 2 at the current \( \theta \)’s value. This system contains 5 equations and 6 unknowns. One concentration is chosen as independent variable and its value is set equal to the experimental one. This choice is not correct: as we have already said all concentrations are experimentally measured quantities: none of them is error free and matches the requisites for L.S. application. The estimated parameters are heavy dependent on the concentration chosen as independent variable.

In order to avoid previous difficulties a new constraint is added to system 2, namely that the distance between experimental and calculated tie lines is minimal

\[ \sum_{i=1}^{2} \sum_{j=1}^{2} (x_{ijk}^{calc} - x_{ijk}^{exp})^2 \equiv \text{min} \]  

This method, proposed by Varhegyi [16], requires several computational efforts: an excellent computer program has been recently published[14]. Convergence requires good initial guess of parameters. They can be obtained from isoactivity criterion.

**Isoactivity objective function.**

This is a more common criterion for liquid-liquid data reduction. The experimental values are substituted for \( x_i \) and \( x_2 \) in equation 1, and the sum of \( f_k \) vectors norms is minimized as a function of
parameters:
\[ \sum \sum f_i^2 = \sum \sum (a_{i1k} - a_{i2k})^2 \geq \min \]  [15]

This method does not afford computational troubles, but it generally gives "bad" parameters. Residuals do not have to be null when \( \theta \) is equal to its true value, due to the experimental errors on \( \mathbf{x} \) and \( T \). Equation 1 actually holds only for the "true" values of concentrations.

Equation 5 is an O.F. of a multiresponse model, so that suitable weights have to be assigned in order to take into account even the minor components activities; actually, relative O.F. are preferred

\[ \text{O.F.} = \sum \sum \left( \frac{a_{i1k} - a_{i2k}}{a_{i1k} + a_{i2k}} \right)^2 \]  [16]

or

\[ \text{O.F.} = \sum \sum \left( \ln a_{i1k} - \ln a_{i2k} \right)^2 \]  [17]

The Maximum Likelihood Principle.

Difficulties which occur with the isoactivity O.F. are due to the following items:

i - all the variables are affected by experimental errors;

ii - the model responses (isoactivities) are not actually measured, but they are computed from other quantities;

iii - the model is a set of relationships between quantities which cannot be classified as independent and dependent variables.

Box [6] proposed for similar models the use of M.L. principle.

The criterion to be minimized is the quadratic form

\[ \Phi = \mathbf{g}^T \mathbf{V}^{-1} \mathbf{g} \]  [18]

where \( \mathbf{g} \) is defined as a generic vector of residuals

\[ \mathbf{g}(x, \theta) = \mathbf{0} \]  [19]

Vector length is \( Z \) (model responses) x \( N \) (number of experiments). \( \mathbf{V} \) is the \( Z \times Z \) variance-covariance matrix of residuals \( \mathbf{g} \), defined as
\[ V = J^T V J \]

The \( V \) matrix is the variance-covariance matrix or the measured variables (a diagonal matrix when they are uncorrelated), while \( J \) is the Jacobian \( J \) with respect to measured variables:

\[ \{ \mathbf{u} \} = \left\{ \frac{\partial g_k}{\partial r} \right\} \]

If different experiments are uncorrelated, the term \( J \) can be reduced to

\[ \Phi = \sum_{k=1}^{N} g_k^T V_k^{-1} g_k \]

where \( g_k \) and \( V_k \) are relative to experiment \( k \).

For the lack of activity criterion residuals \( g \) are the same as \( (\text{eq. } 4.1) \), the terms of the Jacobian are calculated as

\[ \frac{\partial g_{i1}}{\partial r_1} = \frac{\partial a_{i1}}{\partial r_1} - \frac{\partial a_{i2}}{\partial r_1} \]

\[ r^T = (x_{11}, x_{21}, x_{12}, x_{22}, T) \]

The search for minimum...

Minimization of eq. 12 for liquid-liquid ternary data is a very expensive task if a least search method is not available. A computer program we had developed made use of a Rosenbrock type algorithm\( \text{[91]} \) which required a very high number of iterations (about 1000) to reach convergence. As the Jacobian \( J_k \) was evaluated numerically, residuals \( J \) had to be computed 7 times for each step, and the \( y \) calculation routine had to be called 14000 times for a typical system with 10 tie lines. CPU time on UNIVAC 1100/30 was 13.15 minutes.

Computer time is greatly reduced when Marquardt search method as modified by Fletcher\( \text{[9]} \), is used. A quite low number of iterations, about 50, are typically required to reach the minimum, with minor problems on the start guess of parameters. This method requires computation of gradient and Hessian of O.F.

When the former is evaluated analytically and the latter numerically, the minimum is reached in 2.3 minutes. Computation
Application to literature data.

We have chosen 4 systems from the literature. Two of them are "open type" (cyclohexane-isoctane-furfural [9] and isobutanol-ethyl acetate-water [5]), while the remaining two are "closed type" (cyclohexane-benzene-sulfolane [17] and toluene-isopropyl alcohol-water [18]). UNIJUAC model [1] of excess free energy has been used. The standard deviations have been set equal for all systems: we have chosen 0.005 for mole fractions and 0.5 for temperature.

Data of each system have been reduced with an unweighted isoactivity criterion, with mole fraction O.F. and with M.L. isoactivity. All six parameters of the model were always estimated. Two quantities measure the fit between calculated and experimental data [15]:

i- the root mean square deviation between calculated and experimental mole fractions

\[ \text{rms} = \left( \frac{1}{N} \sum \left( x_{i,k}^{\text{cal}} - x_{i,k}^{\text{exp}} \right)^2 \right)^{1/2} \tag{15} \]

ii- the RMS deviation between the distribution ratios

\[ \beta_{i,k} = \frac{x_{i,k}}{x_{12,k}} \tag{16} \]

for the component \( i \)

\[ \Delta \beta_i = \left( \frac{1}{N} \sum \left( \hat{\beta}_{i,k}^{\text{cal}} - \beta_{i,k}^{\text{exp}} \right)^2 \right)^{1/2} \tag{17} \]

For closed systems \( \Delta \beta \) is calculated for the component miscible with the other two; for open systems it is computed for the components of miscible couple.

As table 1 shows, unweighted isoactivity criterion gives worse RMS deviations on mole fractions and higher \( \Delta \beta \) on an average. The isoactivity criterion weighted following M.L. gives as good results as mole fractions O.F. on RMS, and slightly better values of \( \Delta \beta \). It must be realized that the concentration O.F. minimizes directly the RMS we take as test of fit goodness, while M.L. isoactivity minimizes a very different quantity.

Table 1 shows the estimated parameter values. Those obtained from M.L. are coupled with their 96% fiducial limits obtained
from diagonal terms of variance covariance matrix of parameters

\[ W = (J_p^T W^{-1} J_p)^{-1} \sigma_m^2 \]  \[ \text{[18]} \]

where \( J_p \) is the jacobian of residuals \( g \) with respect to model parameters. The model variance \( \sigma_m^2 \) is calculated from the ratio between the O.F. value of the minimum and its expected value \( \lambda = \mu - 6 \) \[ \text{[3]} \]. Individuals \( \Delta \theta_i \) are obtained from the diagonal terms of \( W \) and from the \( t \) of Student for the \( \alpha/2 \) fiducial level with \( v \) degrees of freedom

\[ \Delta \theta_i = t(\alpha/2, v) \sqrt{w_i} \]  \[ \text{[19]} \]

For the system cyclohexane-isooctane-furfural the mole fraction O.F. and A.L. give the same values of parameters. The other systems give parameters equivalent only in a statistical sense, because estimated values lie in the same fiducial range.

For the mole fraction O.F. the minimum is obtained with the constraint that the distance between experimental and calculated tie lines is minimal; the calculated values of mole fractions are an estimation of the "true" values of measured variables. Anderson [3] developed a M.L. method which contemporary estimates both parameters and true values of variables. In the case of 1-1 equilibrium data, errors on temperature are negligible compared to those on mole fractions, and the variances can be taken equal for all concentrations. In these hypothesis, the concentration O.F. correspond to the Anderson's method of M.L. [3]. Recently Beau [17] proved that the method of Anderson (the estimated deviation method) and that of Box (observed deviation method) estimate the same values of parameters with the same variance covariance matrix, provided:

a) the model is error free;
b) the model can be linearized as a function of experimental errors on variables, i.e. the errors are small.

Among the systems considered in this work, equivalence of the two methods is satisfied only by Henty's data. The question arises if the differences obtained for the other data are due to model inadequacy or to too high experimental errors. It is very difficult to answer to first question, while we were able to
further investigate for the second one.

with a set of six parameters (those of the system cyclohexane-benzene-sulfolane estimated from concentration O.F.),
we computed the equilibrium mole fractions of 9 tie lines. Then
we generated 3 sets of random numbers with 3 mean
and, respectively .0001 , .0005 , .005 standard deviations. By
applying these numbers to calculated concentrations, which
represent the "true" values of variables, we obtained 3 sets of
"experimental" data, different in accuracy. Temperature has been
taken as error free. These fictitious experimental data surely
agree with the regressional model.

Previous 3 data sets have been reduced both with Box's and
Anderson's methods. The former (Table 2) gives parameters very
near to true values, even at the highest error level. Instead, the
latter estimates parameters very different from the true ones at
the .0005 error level. This is a limit in order to match the
hypothesis for which the parameters given by the two methods are
equal. The observed deviation method looks more stable. RMS
deviations between experimental and calculated mole fractions
obviously grow with imposed standard deviations. If systematic
errors are lacking, RMS is the measure of random experimental
errors. The Henry's data show a RMS smaller than the other
systems: they match the hypothesis for the methods equivalence.

The other systems investigated show RMS similar to that obtained
from fictitious data affected by the highest error, and different
procedures afford different results.

Conclusions.

As for vapor liquid equilibrium, liquid-liquid data have to be
reduced following a powerful statistical criterion. Maximum
likelihood principle, in the two implementations developed by
Anderson and Box, allows good parameters estimate. Box method is
simpler from the computational point of view, and it can be
treated with standard minimization routines. However, economy
requirements recommend the use of a fast search algorithm, like
Naguard's, and the analytical computation of first derivatives.

Experimental errors play a conclusive role in numerical values
of parameters obtained from 1-1 data. Often current literature data are not so accurate to make equivalent all O.F., weighted with w. In our experience the parameters estimation with isoactivity O.F. is less sensitive to the experimental errors than that performed by other functions.

**Literature cited**

Appendix
The determinant criterion to be minimized is
\[ \Phi = g^T V^{-1} g \]  
A 1

The Marquardt algorithm of minimum search computes the increments of parameters at each iteration by solving the equation
\[ \Delta \theta_{n+1} = -A_n^{-1} \text{grad} \Phi_n \]  
A 2

where
\[ A_n = (H_n + \lambda D_n^2) \]  
A 3

The gradient of \( \Phi \) is obtained from
\[ \text{grad} \Phi = 2 (J_p V^{-1} + g^T r) g \]  
A 4

\( r \) is the derivative of \( V \) with respect to parameters. As \( V = J_p V \) results
\[ \text{grad} \Phi = 2 (J_p V^{-1} + g^T r) g \]  
A 5

\( J_{\theta \theta} \) is the mixed second derivative of \( g \) with respect to independent variables and parameters. The hessian matrix is given by
\[ \frac{1}{2} H = J_{\theta \theta} V^{-1} g + 2 ((J_p g)^T + (J_p g)^T) + g^T r g + J_p V^{-1} J_p \]  
A 7

In equation A3, \( \lambda \) is the Marquardt's parameter, while \( D \) is a diagonal matrix whose terms are equal to the square root of absolute values of the corresponding diagonal elements of \( H \). When the model can be linearized with respect to the parameters increments near the minimum, it is customary to disregard the second derivatives of the model[2]. The approximated hessian should result
\[ \frac{1}{2} H = J_{\theta \theta} V^{-1} J_p + 2 ((J_p g) + (J_p g)^T) \]  
A 8

This approximation is not suitable for our problem. In order to
obtain fast convergence, the hessian must be exactly computed. As the computation of second derivatives is time consuming, we calculated the hessian numerically.

**TABLE 2.** Comparison between the estimations of UNIQUAC parameters with Anderson's-like and Box's Maximum Likelihood methods for the fictitious system at three error levels. True values of parameters are those obtained from the third system of Table 1 with the concentration O.F.

<table>
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<th>Error level</th>
<th>Concentr. O.F.</th>
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<td>22: 409.59</td>
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<tr>
<td></td>
<td>23: 72.49</td>
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</tr>
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<td>24: -43.65</td>
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</tr>
<tr>
<td></td>
<td>Δβ2</td>
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</tr>
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<td></td>
<td>11: -2975.90</td>
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<tr>
<td></td>
<td>21: 384.83</td>
<td>20: 413.63</td>
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<tr>
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<td>22: 439.84</td>
<td>20: 420.57</td>
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<tr>
<td></td>
<td>23: 66.29</td>
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<td></td>
<td>Δβ2</td>
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<tr>
<td></td>
<td>rms</td>
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TABLE 1. Comparison between the estimations of UNICUAC parameters with the three criteria discussed in this paper for 4 isothermal systems. Parameters are given in Kelvin.

<table>
<thead>
<tr>
<th>System</th>
<th>System type</th>
<th>Unweighted isoactivity</th>
<th>Concentr. O.F.</th>
<th>M. Likelihood isoactivity</th>
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<tbody>
<tr>
<td>Cyclohexane(2)</td>
<td>Open</td>
<td>1st -195.04</td>
<td>-71.67</td>
<td>-71.11 ± 106</td>
</tr>
<tr>
<td>isoctane(1)</td>
<td></td>
<td>2nd 303.64</td>
<td>77.14</td>
<td>76.58 ± 136</td>
</tr>
<tr>
<td>furfural(3)</td>
<td></td>
<td>3rd 429.54</td>
<td>419.50</td>
<td>419.61 ± 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4th -15.88</td>
<td>-15.19</td>
<td>-15.29 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5th 416.74</td>
<td>377.34</td>
<td>377.30 ± 17</td>
</tr>
<tr>
<td>Δβ1</td>
<td></td>
<td>5.0</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>Δβ2</td>
<td></td>
<td>4.9</td>
<td>16.6</td>
<td>16.5</td>
</tr>
<tr>
<td>rms</td>
<td></td>
<td>0.32</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Isobutanol(2)</td>
<td>Open</td>
<td>1st 20.47</td>
<td>30.30</td>
<td>-0.24 ± 160</td>
</tr>
<tr>
<td>Ethyl acetate(1)</td>
<td></td>
<td>2nd 20.78</td>
<td>70.79</td>
<td>96.34 ± 151</td>
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<tr>
<td>Water(3)</td>
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<td>3rd 289.84</td>
<td>449.07</td>
<td>439.90 ± 17</td>
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<tr>
<td></td>
<td></td>
<td>4th 97.02</td>
<td>49.91</td>
<td>51.44 ± 22</td>
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<tr>
<td></td>
<td></td>
<td>5th 78.94</td>
<td>-0.26</td>
<td>9.69 ± 36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6th 175.04</td>
<td>271.12</td>
<td>255.31 ± 49</td>
</tr>
<tr>
<td>Δβ1</td>
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<td>7.3</td>
<td>20.0</td>
<td>15.5</td>
</tr>
<tr>
<td>Δβ2</td>
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<td>14.0</td>
<td>20.0</td>
<td>19.8</td>
</tr>
<tr>
<td>rms</td>
<td></td>
<td>2.98</td>
<td>0.20</td>
<td>0.23</td>
</tr>
<tr>
<td>Cyclohexane(1)</td>
<td>Closed</td>
<td>1st -12.72</td>
<td>-1330.90</td>
<td>-320.76 ± 139</td>
</tr>
<tr>
<td>Benzene(2)</td>
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<td>399.81</td>
<td>145.50 ± 297</td>
</tr>
<tr>
<td>Sulfolane(3)</td>
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<td>3rd 387.64</td>
<td>407.11</td>
<td>450.50 ± 96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4th 68.01</td>
<td>73.18</td>
<td>59.14 ± 32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5th -15.10</td>
<td>-41.45</td>
<td>-93.18 ± 75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6th 50.20</td>
<td>-1000.90</td>
<td>-26.80 ± 67</td>
</tr>
<tr>
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<td>5.4</td>
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<td>5.6</td>
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<tr>
<td>Δβ2</td>
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<td>1.58</td>
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<td>0.37</td>
</tr>
<tr>
<td>rms</td>
<td></td>
<td>8.00</td>
<td>0.44</td>
<td>0.50</td>
</tr>
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<td>Toluene(1)</td>
<td>Closed</td>
<td>1st 386.78</td>
<td>415.37</td>
<td>427.70 ± 37</td>
</tr>
<tr>
<td>Isopropanol(2)</td>
<td></td>
<td>2nd -128.58</td>
<td>-155.69</td>
<td>-159.82 ± 17</td>
</tr>
<tr>
<td>Water(3)</td>
<td></td>
<td>3rd 630.15</td>
<td>4100.80</td>
<td>1535.10 ± 1100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4th 314.76</td>
<td>95.02</td>
<td>84.31 ± 19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5th 42.09</td>
<td>-43.64</td>
<td>-13.44 ± 36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6th 49.34</td>
<td>153.74</td>
<td>115.97 ± 46</td>
</tr>
<tr>
<td>Δβ1</td>
<td></td>
<td>50.2</td>
<td>31.1</td>
<td>27.2</td>
</tr>
<tr>
<td>Δβ2</td>
<td></td>
<td>8.00</td>
<td>0.44</td>
<td>0.50</td>
</tr>
</tbody>
</table>
The double application of the Newton method (DAN method) for calculating composition of coexisting phases using an equation of state

Novák J.P., Malijevský A., Růžička V., Matouš J.
Department of Physical Chemistry
Institute of Chemical Technology
166 28 Praha 6, Czechoslovakia

A new computational technique for calculating vapor-liquid equilibria using an equation of state is proposed. The procedure consists in the double application of the Newton method to the set of equilibrium conditions. The algorithm is very effective as it provides both values of equilibrium variables and a very qualified first estimate of the next equilibrium point. This enables to proceed along an equilibrium curve rather quickly and to achieve the convergence within 2 - 4 iterations.
Calculation of vapor-liquid equilibria by an equation of state consists in solving the following set of equilibrium conditions:

\[
\begin{align*}
  p &= p^V = p(T, d^V, \bar{y}) , \quad (1a) \\
  p &= p^L = p(T, d^L, \bar{x}) , \quad (1b) \\
  f_i &= f_i^V = f_i(T, d^V, \bar{y}) = \\
  &= f_i^L = f_i(T, d^L, \bar{x}) , \quad i = 1, 2, \ldots, N \quad (1c)
\end{align*}
\]

where \( p \) denotes pressure, \( T \) temperature, \( f_i \) fugacity of \( i \)-th component and \( d \) saturated density. Superscripts \( L \) and \( V \) indicate vapor and liquid phase, respectively. \( \bar{x} \) and \( \bar{y} \) are vectors of \( N - 1 \) independent mole fractions in liquid and vapor phases, respectively \( \bar{x} = (x_1, x_2, \ldots, x_{N-1}) ; \bar{y} = (y_1, y_2, \ldots, y_{N-1}) \). In the \( N \)-component system this set of nonlinear equations gives \( N + 2 \) conditions for \( 2(N + 1) \) variables \( T, p, d^V, d^L, \bar{x}, \bar{y} \). Therefore, \( N \) variables must be specified in advance before the remaining \( N + 2 \) unknown ones are calculated by solving the equations (1).

The procedure suggested in this work is based on the double application of the Newton method to the set of Eqs. (1). The algorithm is very effective as it provides not only a solution of the particular set of equations but also gives a very qualified estimate of the next equilibrium point. An example is presented below on the application of the suggested procedure to calculation of the bubble-point pressure.
Calculation of bubble-point pressure for specified $T$ and $x$

Expanding pressures and fugacities in Taylor series and canceling all but linear terms the set of equations (1) can be modified into the form

$$
\begin{align*}
(p/\partial d)^V \Delta d^V + \sum_{j=1}^{N-1} (p/\partial y_j)^V \Delta y_j - (p/\partial d)^L \Delta d^L &= p_o^L - p_o^V + \\
+ \left[ (p/\partial T)^L - (p/\partial T)^V \right] \Delta T + \sum_{j=1}^{N-1} (p/\partial x_j)^L \Delta x_j, \\
(p/\partial d)^V \Delta d^V + \sum_{j=1}^{N-1} (p/\partial y_j)^V \Delta y_j - (p/\partial d)^L \Delta d^L &= \\
= (x_1)_o^L - (x_1)_o^V + \left[ (p/\partial T)^L - (p/\partial T)^V \right] \Delta T + \\
+ \sum_{j=1}^{N-1} (p/\partial x_j)^L \Delta x_j, \quad i=1,2,\ldots,N. \quad (2)
\end{align*}
$$

Here subscript $o$ denotes quantity which corresponds to values of variables $T, d^V, d^L, x, y$ calculated in the preceding iteration. As the system pressure is not specified in this case, equations (1a) and (1u) are joined into one equation.

The calculation procedure includes the following steps:

1. At the beginning a first estimate of vapor and liquid densities $d^V$ and $d^L$ and the vapor phase composition $\tilde{y}$ must be supplied. This can be done by using, for example, the Raoult and the Amagat laws.

2. Coefficients of the set of equations (2) are evaluated using values of $d^V, d^L$ and $\tilde{y}$ determined in the preceding step. The increments $\Delta T$ and $\Delta x$ are equal to zero. By
solving the set of equations (2) the increments are obtained. Then the quantity can be calculated
\[ S = (\Delta_d V / d_c V)^2 + (\Delta_d L / d_c L)^2 + \sum_{j=1}^{N-1} (\Delta y_j)^2 \] (3)
where \( d_c V \) and \( d_c L \) are the pseudocritical densities of the phases.

3. According to the size of \( S \) three different cases can occur:

3.1. If \( S \) is less than \( \varepsilon_0 \), a computation of the bubble-point pressure is finished. Here \( \varepsilon_0 \) is the chosen accuracy which was set to \( 10^{-7} \).

3.2. If \( S \) exceeds a maximum step \( \varepsilon_1 \approx 0.1 \) permitted in one iteration, values of calculated increments are reduced
\[
(\Delta \psi)_{\text{red}} = (\Delta \psi) \varepsilon_1 / S
\] (4)
where \( \psi \) stands for \( d_V, d_L \) and \( y \). This step-limiting often avoids a divergence of iterations. A value of \( \varepsilon_1 \) of 0.1 is recommended. After the reduction the calculation proceeds to step 3.3.

3.3 If the relation \( \varepsilon_0 < S < \varepsilon_1 \) is obeyed new values of variables are calculated
\[
\psi_{i+1} = \psi_i + \Delta \psi
\] (5)
where \( \psi \) is \( d_V, d_L \) and \( y \). The calculation then continues to the step 2.

4. If it is desired to proceed along an equilibrium curve the solution for given \( T, x \), i.e. the values of \( d_V, d_L \) and \( y \) are utilized as a first estimate of the next point characterized by \( T_{II} \) and \( x_{II} \). Differences
between temperatures and compositions yield increments 
\[ \Delta T = T_{II} - T \] and 
\[ \Delta \bar{x} = \bar{x}_{II} - \bar{x}. \] Using these increments 
right-hand sides of the set of equations (2) are evaluated. The coefficients on the left-hand sides are known 
from the last iteration step.

5. The solution of Eqs. (2) with the coefficients of the 
matrix obtained in the step 4 gives new values of incre-
ments \( \Delta d^V, \Delta d^L \) and \( \Delta \bar{y} \). Thus, a new value of \( S \) is determi-
ned. According to its size two cases are considered:

5.1. If \( S \) is less or equal to a maximum allowed step 
along an equilibrium curve \( \varepsilon_2 < 0.1 \), values of \( \psi_{II} \) gi-
gen by

\[ \psi_{II} = \psi + \Delta \psi \quad (6) \]

( \( \psi = d^V, d^L, \bar{y} \) ) are used for the calculation of the 
equilibrium point specified by \( T_{II} \) and \( \bar{x}_{II} \). The calcu-
lation now returns to the step 2.

5.2. If \( S \) is greater than \( \varepsilon_2 \) the next equilibrium point 
is too far from the preceding one. Then it is desirable 
to insert an intermediate step thus ensuring the calcu-
lation not to fail. In this case the intermediate point 
is calculated with parameters

\[ \psi' = \psi + \Delta \psi \left( \frac{\varepsilon_2}{S} \right) \quad (7) \]

where \( \psi' \) stands for \( T, d^V, d^L, \bar{x}, \bar{y} \). Here the cal-
culation is also returned to the step 2.
Conclusions

Procedures for the calculation of the bubble- and dew-point pressures and temperatures and for flash calculation were developed. These computational techniques were applied to both binary and multicomponent mixtures using the Soave equation of state. Convergence was obtained also for wide-boiling mixtures such as whole crude oils. In applications of the suggested procedure the problems arising from poor initial estimates were avoided. At conditions where an initial estimate obtained by the Raoult and the Amagat laws did not guarantee convergent iteration even with step-limiting, the calculation was started at more favourable conditions. Once a solution of an equilibrium point was obtained it was possible to construct an equilibrium curve rather quickly.

For binary mixtures it was possible to reach a close vicinity of the critical point, where the corresponding mole fractions in equilibrium phases differed by no more than 0.01.

Appendix

The equation of state used throughout this work takes the form

\[ z = \frac{pV}{nRT} = \frac{p}{RTd} = z(T,d,x) \]

where \( z \) is compressibility factor. To calculate thermodynamic quantities the following dimensionless quantities are defined:

\[ \]
Fugacities of components, pressure and their derivatives with respect to temperature, density and composition are given by

\[
Q_d = z + d \left( \frac{\partial z}{\partial d} \right)_{T,x}
\]

\[
Q_T = z + T \left( \frac{\partial z}{\partial T} \right)_{d,x}
\]

\[
\tilde{z}_i = z + (\partial z/\partial x_i)_{T,d} x_{k\neq i} - \sum_{j=1}^{N-1} x_j (\partial z/\partial x_j)_{T,d} x_{k\neq j}
\]

\[
Q_{F,i} = \int_0^d (\tilde{z}_i - 1) \, d \ln d
\]

\[
Q_{U,i} = T \left( \frac{\partial Q_{F,i}}{\partial T} \right)_{d,x}
\]

The list of dimensionless quantities evaluated from the Redlich-Kwong, the Redlich-Kwong-Soave and the Peng-Robinson equations of state is available from one of the authors (J.P. Novák) on request.
References

Thermodynamic consistency test for binary vapor-liquid equilibrium data

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* Department of Mathematics
** Department of Chemical Engineering

Van Ness et al in 1973 proposed a consistency test for isothermic binary VLE data, it has been being widely used also for isobaric data sets. In this work a modified spline regression algorithm is proposed both for isothermic and isobaric data. The admissibility of the neglection of $H^E$ in the case of isobaric experiments is discussed and checked during proceeding the test. The existence of systematic errors is investigated by means of exact statistical test procedures: Abbe's and Student test for residuals. A consistency test algorithm for VLE data with limited miscibility is also proposed.
\[
\frac{\partial g}{\partial x_1} = \frac{dg}{dx_1} - \frac{V^E}{RT} \frac{dP}{dx_1} + \frac{H^E}{RT^2} \frac{dT}{dx_1}
\]  

(5)

and the last term usually cannot be neglected. In these cases even a crude approximation of the \( H^E \) function improves the situation. The proposed method was extended also to systems showing limited miscibility in the liquid phase. The main difficulty in this case is caused by the lack of experimental VLE data in the region of immiscibility. An example is shown on Fig. 2.

Statistical tests for systematic errors

Fredenslund et al. [41] proposed a useful criterion of consistency: the average of absolute deviations in \( y \) should be smaller than 0.01 / mole fraction / . This criterion, however, does not allow to separate random and systematic errors and the prescribed limit is somewhat arbitrary. This criterion was accepted also for the DDB volumes by Gmehling et al. [51]. A severe and in mathematical statistical sense strict test to check if there is a trend in residuals was proposed by Abbe [61]. Its null hypothesis: 

\[ M[y] = a \]

where \( M \) stands for the expected value and \( a \) is a non-specified constant. The expression of the test statistics is the following:
The null hypothesis is accepted if \( R > R_{\text{crit}(n)} \), \( R_{\text{crit}} \) is taken from a table. For data without systematic errors the constant \( a \) above should be equal to zero. A Student test is appropriate to check this null hypothesis.

These statistical tests give an algorithm for a well established decision concerning the thermodynamic consistency of measured VLE data.

References
1. H.C. Van Ness, S.M. Byer, R.E. Gibbs:
   AIChe Journal 19 238(1973)
2. F.O. Mixon, B. Gumowski, B.H. Carpenter:
   Ind. Eng. Chem. Fundam. 4 455 (1965)
   CHISA'78, Prague, Czechoslovakia, 1978.
5. J. Gmehling, U. Onken: Vapor-liquid equilibrium data collections. Dechema Chemistry Data Series
6. J.W. Linnik: Die Methode der kleinsten Quadrate in moderner Darstellung,
The prediction of multicomponent equilibria basing on binary measurement data requires appropriate models and data of good quality. The "good quality" means small random errors and lack of systematic errors. The aim of this work is after some refinement of the methods applied earlier, to algorithmize and establish the decision on the consistency of data. The proposed method is also applicable for systems with limited miscibility.

The well known area tests are not very sensitive and the measured total pressure data do not appear in them. The method by Van Ness et al. [1] for isothermal vapor-liquid measurement data utilizes the fact that three of the usually measured four variables \(x, y, t, P\) are sufficient to estimate the parameters of a model. They apply the highly reliable and flexible spline polynomials as model. The plot of deviations between the measured and computed values of the unused fourth variable may be used to check the thermodynamic consistency of the measured data. The main expressions used in the Van Ness' method are:

\[
\frac{g}{RT} = x_1 \ln \delta_1 + x_2 \ln \delta_2 \tag{1}
\]

\[
\ln \delta_1 = g + x_2 \frac{\partial g}{\partial x_1} \quad ; \quad \ln \delta_2 = g - x_1 \frac{\partial g}{\partial x_1} \tag{2}
\]

\[
P = x_1 p_1^0 \delta_1 + x_2 p_2^0 \delta_2 = x_1 p_1^0 \exp \left( g + x_2 \frac{\partial g}{\partial x_1} \right) + x_2 p_2^0 \exp \left( g - x_1 \frac{\partial g}{\partial x_1} \right) \tag{3}
\]
One first obtains a least square spline fit to the $P$ vs $x$ data, then a $g$ vs $x$ relation has to be found numerically integrating the differential Eqn (3) [2]. In the course of the integration the following assumptions are made for isothermic data:

$$\frac{\partial g}{\partial x_1} \approx \frac{dg}{dx_1} \approx \frac{Ag}{Ax_1} \quad (4)$$

From the $g(x)$ function $y$ values are calculated through the computation of activity coefficients /Eqn (2)/.

Some refinements were applied to the spline regression: we rejected the arbitrary condition of the second power of the spline function in the first and last interval. This improved the approximation as illustrated by Fig 1., where the originally proposed spline fit is compared with the modified one through the plot of $\Delta y$ residuals. In optimal case the spline intervals are of different length and contain approximately equal number of data points /3-5 data points were found appropriate/.

In the case of isobaric VLE measurement data a similar method was proposed [3]. First a least squares spline fit is made to the $t$ vs $x$ data, then Eqn (3) is solved numerically, then $y$ values are calculated and compared with the measured $y$ values.

The assumptions expressed by Eqn (4) are more awkward in isobaric cases because of the Gibbs-Duhem equation:
Van Ness' spline

proposed spline

FIG. 1
PREDICTION OF BUBBLE- AND DEW-POINTS
OF PETROLEUM FRACTIONS

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166 28 Prague 6, Czechoslovakia

Summary

Two calculation methods for predicting vapor-liquid equilibria (VLE) of undefined mixtures are presented. Complex petroleum fractions are described in terms of model compounds. The first method is based on the UNIFAC group-contribution model for predicting activity coefficients and pure-component vapor pressures. The second method based on the Soave equation of state consists in the double application of the Newton method to the set of equilibrium conditions. Examples are given on the application of both procedures on light and medium petroleum fractions. The results show that for nearly ideal hydrocarbon mixtures the procedure based on the Soave equation of state is slightly superior to the UNIFAC method.
In petroleum and gas industry and chemical processing of coal a chemical or a process engineer has to deal with the so-called undefined mixtures such as petroleum fractions, gas condensates, coal-derived liquids, etc. These complex mixtures consist of a high number of components.

In contrary to mixtures of defined components, the composition of undefined mixtures is not known. Hence, prior to the application of methods developed for defined mixtures the composition of an undefined mixture has to be represented in terms of model compounds usually called pseudo-compounds.

Computational Techniques

Two different methods for predicting VLE of complex hydrocarbon mixtures are presented and compared here. The first method is based on the UNIFAC group-contribution model for predicting activity coefficients\(^1\) and pure-component vapor pressures\(^2\). The second method uses as a basis an equation of state.

The input data required in both methods include the true boiling point (TBP) distillation curve and density. In addition, the UNIFAC method requires also a PNA analysis giving the amount of paraffins, naphthenes and aromatics.
The first step in both procedures entails the division of the TBP-curve into a number of subfractions. Each subfraction is characterized by the mid-volume boiling point, density and volume fraction. The UNIFAC method assumes that each subfraction is represented by a mixture of three components, viz. a paraffinic, a naphthenic and an aromatic. In the procedure based on an equation of state each subfraction is represented by a single pseudo-compound.

The second step of the UNIFAC method consists in the definition of model components for each subfraction in terms of UNIFAC groups. The adjustment of the number of groups in each model molecule is done so as to match the mid-volume boiling point for each subfraction. In order to use the procedure based on an equation of state, the properties of pseudo-compounds must be calculated using generalized correlations. Molecular weight, critical temperature, critical pressure and acentric factor are estimated from the known boiling point and density.

Thus, the first result of both procedures is a set of well-defined model compounds which represent a complex petroleum mixture.
Calculation of bubble- and dew-points by the UNIFAC method is straightforward and does not need further explanation. Calculation of VLE by an equation of state is based on solution of the equilibrium conditions set. The algorithm adopted in this work was suggested by Novák et al.\textsuperscript{5}

Results

Reported values for light and medium petroleum fractions\textsuperscript{6} were chosen to evaluate both methods. The Soave equation of state with vapor pressure function suggested by Graboski and Daubert\textsuperscript{7} was employed in the procedure based on an equation of state. The results of calculation of bubble- and dew-points are shown in Table 1. For some of the petroleum fractions given in Tab. 1 flash calculations were also performed. An agreement between experimental and predicted results was tested indirectly by comparing enthalpies in a two-phase region. The results are shown in Table 2. The number of experimental and predicted points lying in a two-phase region is also given.

Bubble- and dew-points predicted by the Soave equation of state are slightly better than those calculated by UNIFAC. This is also true for two-phase enthalpies.
Note however that the number of subfractions into which each petroleum fraction was divided, was approximately two times higher for the procedure based on the Soave equation of state than for the UNIFAC method. It is reasonable to expect that a complex mixture is properly represented by model compounds if the boiling range of the subfraction is sufficiently low. Furthermore as the pressure increases bubble- and dew-points predicted by UNIFAC deviate from experimental data due to extrapolation problems mainly in pure-component vapor pressures.

Due to the lack of experimental data on the whole crude oils it was not possible to compare both methods applied to these extremely wide-boiling mixtures. It can only be stated that for such mixtures convergence was achieved for the procedure based on an equation of state even with poor initial estimates.

Conclusions

The procedure based on an equation of state is preferable for predicting VLE of nearly ideal systems such as hydrocarbon mixtures. Especially the first part of this procedure, i.e. the estimation of properties of pseudo-compounds is much easier in comparison with the
The UNIFAC method should be applied to calculation of phase-equilibria of non-ideal systems such as encountered, for example, in liquid extraction. Such work which must first provide experimental data is in preparation.

Literature cited

Table 1. Comparison of experimental and predicted bubble- and dew-points

<table>
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<tr>
<th>petroleum fraction</th>
<th>average % deviation&lt;sup&gt;a&lt;/sup&gt;</th>
<th>no. points bubble(dew)</th>
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<tr>
<td></td>
<td>bubble-point</td>
<td>dew-point</td>
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<tr>
<td></td>
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<td>Soave</td>
</tr>
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<td>1.1</td>
</tr>
<tr>
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<td>1.0</td>
</tr>
<tr>
<td>highly aromatic naphtha</td>
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<tr>
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<sup>a</sup> average % deviation = \[100\frac{(\text{exp-pred})}{\text{exp}}\]
Table 2. Comparison of experimental and predicted enthalpies in a two-phase region

<table>
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<th>average error, kJ/kg</th>
<th>number of points</th>
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<tr>
<td>kerosine</td>
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<tr>
<td>fuel oil</td>
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<td>-</td>
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</table>

\(^a\) average error = exper - pred
UNIFAC MODEL AND THE GAS-SOLUBILITY

P.Alessi, E.Cressi, I.Kikic
Istituto di Chimica Applicata e Industriale, Università di Trieste
Trieste, Italy

Group-contribution methods for the prediction of fluid phase equilibria have gained an increasing interest because they constitute a basis for a rough evaluation of properties of industrial interest. The aim of this communication is to report the results obtained in the utilization of the UNIFAC model for the description of the gas-liquid equilibria. We utilized, when it is possible, the same interaction parameter table of the vapor-liquid equilibrium and we have introduced a modification on the combinatorial part. This modification is justified from the difference in size of the molecules involved in the gas-liquid equilibrium. The results obtained by correlating the data with the modified equation are in the opinion of the authors the best compromise obtainable with the actual model.

This work is supported by the Administration Council of the University of Trieste
Introduction

Gas-liquid solubility data are quite important in the chemical industry for the design of absorption and stripping units. Nevertheless, a noticeable lack of these data exists in the literature; for this reason the experimental determination of gas solubility in liquids appears necessary and, in the same time, it becomes urgent the development of predictive models which allow an adequate evaluation of these quantities.

In the present work experimental solubility data of CO, CO₂, COS in high boiling liquids, determined by gas-liquid chromatographic technique, are reported. A group contribution method is used for the correlation of these data.

Experimental section

The operative conditions and the relationship between chromatographic retention quantities and Henry constants are reported in detail in (2).

The liquids used as stationary phases were: paraffins, alcohols, ketones, chloroparaffins, nitriles, thiols, and glycols (Fluka A.G.). The gas investigated were CO₂, CO, COS, N₂, O₂, Ar, H₂S, NH₃ (the data relative to the last gases are reported in (3)) and light paraffins and olefins (data reported in (2)).

Results

Tables 1 and 2 report Henry constants of CO₂, CO, and COS in various stationary phases. For a complete view of the results of this research the reader can refer to (2, 3).

Particular attention must be taken when GLC data of gases are considered. An experimental difficulty encountered in this research was the definition of the dead time, that is, the retention time of a non-retained solute. The retention time of paraffins, olefins
and CO₂ is quite high in comparison to the dead time: the accuracy of the Henry constant values was estimated to be 3-5%; the retention times of the other gases are close to the retention time of the inert and in these cases the accuracy was estimated to be 7-12%.

Correlation

From the Henry constant it is possible to calculate the activity coefficient at infinite dilution by evaluating the fugacity in the reference state through Peng-Robinson equation(4) and by extrapolating the value at the column temperature.

The activity coefficients at infinite dilution were correlated by using UNIFAC methods. Since the original UNIFAC(5) and the modified UNIFAC(6) give activity coefficients too high, a modification of the UNIFAC equation was proposed. In particular a new parameter p was proposed in substitution of the fixed numerical value 2/3 suggested in (6) so that the combinatorial term assumes different values depending on the size of the molecules present.

The p parameter, for the different systems investigated, has an optimal value for which the standard deviation between calculated and experimental value is minimum. However the parameter value ranges between 0.2 and 0.66.

The residual term was not modified and this means that we assumed that the interactions between the molecules (and the groups) in the vapor-liquid equilibrium are the same as in the gas-liquid equilibrium. This assumption allowed us to use the same interaction parameters derived by correlating vapor-liquid equilibrium data and reported in the literature(7).

In the cases of mixtures containing paraffins and olefins as gases the best results in the correlation were obtained with p=0.35.

This value is a good compromise and allows a flexibility and generality in the application of the model.
For utilizing the UNIFAC model it was necessary to calculate $R_k$ and $Q_k$ parameters; for CO $R_k = 1.3224$ and $Q_k = 1.360$, for CO$_2$ $R_k = 0.7713$ and $Q_k = 0.640$, for COS $R_k = 1.6898$ and $Q_k = 1.465$.

In conclusion of this investigation we report in Table 3 the interaction parameters obtained in the fitting of the data relative to the gases considered by using a fixed value of the parameter $p (=0.35)$. The standard deviations were generally lower than 12%.

References

<table>
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<th>Henry constant</th>
<th>Solvent</th>
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**TABLE 1** - Henry constant values (atm.) of CO₂ in different solvents.
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**TABLE 2 - Henry constant values (atm.) of CO and COS in different solvents.**
### TABLE 3 - Interaction parameters

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The description of the non ideality of the liquid mixtures is a stimulating subject of research, especially in the industry as a consequence of the practical problems involved. The largest deviations from ideality for each component of the mixture are given in the infinite diluted regions. Equilibrium data in diluted regions are needed for the design of industrial separation processes interested to the removal of traces. In this connection we started with the research program having the following objectives:

- to develop a series of computer programs for the calculation of $y^*$ from experimental quantities on the basis of maximum likelihood principle;
- to organize a data bank of experimental determined $y^*$;
- to develop a series of computer programs for the prediction of fluid phase eq. data at finite concentration starting from the data contained in the data bank.

(+): The authors are grateful to NATO and to CNR (Rome) for supporting the project.
Introduction
A common request from industry is mathematical models and computer programs which allow the prediction of non-ideality of liquid mixtures. The largest deviations from ideality are obtained in the infinite diluted regions and this justifies the theoretical interest for the determination and calculation of infinite dilution activity coefficients. Moreover, industry requires infinite dilution data and models for the design of industrial processes interested in the removal of traces.

This paper describes a computer program package which can be used in the design of separation processes and in many practical calculations where the prediction of vapor-liquid (VLE) or liquid-liquid (LLE) equilibria is needed. This package is also a useful tool in the treatment of the directly measured quantities from experimental work to obtain the thermodynamic data used as input for the data reduction program. The computer program package presented in this paper consists of the following programs (fig.1):
- experimental data treatment;
- data reduction for the attainment of model parameters;
- prediction of thermodynamic properties in the whole concentration range with the parameters obtained in the previous step.

Thermodynamic remarks
The useful condition for fluid phase equilibria between two phases A and B is:

\[ f_i^A = f_i^B \] (1)

where \( f_i^A \) and \( f_i^B \) are the fugacity of the component \( i \) in the phase A and B respectively. The phases A and B can be liquid or vapor, then it is necessary to calculate the fugacity of liquid and vapor phases.

\[ f_i^V = y_i P \phi_i \] (2)
\[ f_i^1 = x_i P \phi_i^1 \]  \hspace{1cm} (3)

or

\[ f_i^1 = x_i \gamma_i \phi_i = x_i \gamma_i \gamma_i^P \phi_i^s \]  \hspace{1cm} (4)

where \( \phi_i \) and \( \phi_i^1 \) are the fugacity coefficients of the component \( i \) in the vapor and in the liquid phase respectively, \( f_i^0 \) is the standard state fugacity of component \( i \), \( P_i^s \) is the pure component vapor pressure, \( P \) is the total pressure, \( \phi_i^s \) is the fugacity coefficient of the pure liquid at the temperature of the system and at the \( P_i^s \).

**Thermodynamic models**

Several different models are used to describe the thermodynamic properties of the components in the mixture.

1. **Equations of state for the fugacity coefficient in the vapor phase.**

   The virial equation of state, truncated after the second coefficient, may be used for relatively low pressure, to estimate \( \phi_i^v \). The form of the equation is:

   \[ \frac{P_v}{RT} = 1 + B \rho \]  \hspace{1cm} (5)

   Hayden and O'Connell\(^2\) correlation for the second virial coefficient is used; when organic acid are present the chemical theory by Marek\(^3\) is used to describe associations in the vapor phase.

2. **Equations of state for the fugacity in the vapor and in the liquid phases.**

   The Redlich-Kwong or the Redlich-Kwong-Soave\(^4\) equations of state may be used to calculate both the fugacity coefficient in the liquid and in the vapour phase. In this case:

   \[ \ln \gamma_i = \ln \phi_i^1 - \ln \phi_i^s \]  \hspace{1cm} (6)

   where \( \phi_i^s \) is the fugacity coefficient of the pure component at temperature and pressure of the system.

   For calculating the parameters of the equation of state it is
possible to use both the random mixing rule or the local composition concept. In any case the binary interaction parameter can be calculated from infinite dilution activity coefficients.

c - Excess Gibbs energy models.
The NRTL, UNIQUAC (6) and Effective UNIQUAC (7) equations may be used to calculate the activity coefficient in the equation (4) as a function of composition, temperature and pressure. For VLE and LLE, parameters of the model are often available in the literature. The general expression for the parameter of these models is:

\[ P_{ij} = \frac{U_{ij} - U_{jj}}{R} \]  

Then we have two parameters per binary mixture. If we identify \( U_{jj} \) with the heat of vaporization of the pure component \( j \) it is possible to calculate \( U_{ij} \) through:

\[ U_{ij} = U_{ji} = (1 - K_{ij}) \sqrt{U_{ii} U_{jj}} \]  

and we reduce the number of parameters of the model from two to one.

In most cases the infinite dilution activity coefficient can be determined at one side only for a binary mixture. For this reason it is possible to use these data in connection with one parameter models such as Wilson or Uniquac as seen before. Another possibility is to use the activity coefficient at infinite dilution and some other experimental data (for example liquid-liquid solubilities) in order to obtain two interaction parameters of a molecular model. It is possible also to use activity coefficient at infinite dilution in connection with group contribution models (UNIFAC) (8) if the functional group of interest appears in both the solute and the solvent molecule.

**Experimental techniques for \( \gamma \) determination**

Experimental techniques normally applied for the determination of activity coefficients at infinite dilution are gas liquid chromato-
graphic technique, the saturation method with the dilutor and the ebulliometric technique. A detailed discussion of these techniques has been presented in (9).

The activity coefficient at infinite dilution can be, in a simple way expressed as:

$$\ln \gamma_i^\infty = f(\rho)$$  \hspace{1cm} (9)

where $\rho$ is the vector of the experimental determined quantities.

The total differential of the natural logarithm of the activity coefficient at constant temperature is:

$$\left( d \ln \gamma_i^\infty \right) = \sum_{j} \frac{\partial \ln \gamma_i^\infty}{\partial \rho_j} dp_j$$  \hspace{1cm} (10)

So it is possible to calculate the propagation errors of the measured quantities in the activity coefficient at infinite dilution; in this way the natural logarithm of the activity coefficient at infinite dilution at the given temperature and the errors $\Delta \ln \gamma_i^\infty$ and $\Delta T$ can be evaluated.

The vector $\rho$ will be different according to the methodology employed in the determination of the activity coefficient at infinite dilution.

In GLC technique the activity coefficient is a function of:

$$\ln \gamma_i^\infty = f(\, F, w, p_i, \rho, t, t_a)$$  \hspace{1cm} (11)

where $t_r$ is the retention time of the solute, $t_a$ is the dead time, $F$ is the flow rate of the carrier gas, $p_i$ and $p_o$ are the inlet and outlet pressure, $w$ is the weight of the stationary phase.

In the saturation method (10) with the dilutor we have:

$$\ln \gamma_i^\infty = f(\, P, D, S, S_o, N)$$  \hspace{1cm} (12)

where $P$ is the total pressure at equilibrium, $D$ is the carrier gas flow rate, $N$ is the total amount of the solvent in the still, $S$ is the solute peak area at time $t$, $S_o$ is the solute peak area of reference.

In the ebulliometric method we have:
In \( \gamma_i^w = f \left( P, T, w_{\text{sol}}, w_{\text{solv}} \right) \) (13)

where \( w_{\text{sol}} \) and \( w_{\text{solv}} \) are the amount of the solute and the solvent in the still, \( P \) is the pressure and \( T \) the temperature.

Programs and subroutines included in the package

In the first session of the program package we include the following programs:

- **GLC** for the treatment of gas-liquid chromatographic data.
- **DILU** for the treatment of data obtained from the saturation method with the dilutor. If the solvent presents at the temperature examined a high vapor pressure, a correction factor must be introduced according to Duhem and Vidal (12).
- **EBUL** for the treatment of ebulliometric data.

The data resulting from the programs GLC, DILU, EBUL are infinite dilution activity coefficients and temperatures with the uncertainties of their measurement. The second part of the package concerns the treatment of the data obtained in the first part in order to obtain the parameters of the thermodynamic models.

The following programs are, at the moment, included:

- **PAIN** This program calculates the parameters of the excess Gibbs energy model from one, or two activity coefficients at infinite dilution. In the case of one single data, a one-parameter model is used. The program is organized in such a way that the first step is the calculation of one parameter model which is the initial point for the calculation of two parameter values. Newton-Raphson technique is used for the solution of the system of equations and the analytical derivatives of the models are provided.
- **PAINUN** This program estimate the UNIFAC parameters describing the interactions between the A group and the B group from limiting activity coefficient of xxxx-A in xxxxxxxxxxxx-B and of xxx-B in xxxxxxxxxxxx-A, where the length of the x blocks indicates the diffe-
ferences in the molecular weights of the components.

The input of the program is a set of activity coefficients at infinite dilution and temperatures data of different molecules containing the functional group A in one or more solvents containing the functional group B and, when it is possible, vice versa.

The parameters obtained from the data reduction can be different from those reported in the literature but they represent in a quite good way the behaviour of the mixture in the diluted region. From these parameters one calculate directly, or through molecular models the equilibrium and all the thermodynamic properties necessary for the design of separation processes.

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    Dev.,21,118,1982
Figure 1 - Program package
VAPOUR-LIQUID EQUILIBRIUM OF TERNARY ASSOCIATED SYSTEMS WITH ASSOCIATION OF ONE COMPONENT IN BOTH PHASES

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A thermodynamic model is proposed for the analysis of association effects in multicomponent systems. The algorithm for the reduction of vapour-liquid equilibrium (VLE) data have been developed for ternary systems with association of one component in both phases, taking into account a composition-dependent liquid phase association constant. This algorithm has been verified with experimental VLE data of the following systems: acetic acid-acetone-water and acetic acid-xylene-water. The calculated activity coefficients of ternary associated systems were compared with those predicted on the basis of corresponding binaries.
INTRODUCTION

Phase equilibria for systems in which association occurs in one or more phases have been studied over a long period of time. The classical works of Prigogine and Defay (1,2) give the model of ideal associated solutions. Francesconi, Trevissoi and Cojutti (3,4) and works of Tamir and Wisniak (5-7) considered the association reaction only in the vapour phase. Marek and Standart (8,9) developed in their papers the phase and chemical equilibrium for association reaction occurring in the vapour and liquid phases for binary systems. Jenkins and Gibson-Robinson (10,11) have modified the model of Marek and Standart assuming that the liquid phase association constant is a function of the temperature and associates composition of the mixture. For the vapour phase association constants of the mixture it was assumed that they equal to that for the pure associating component. Jenkins and Gibson-Robinson were studied only binary associated systems. Savković-Stevanović, Tasić and Djordjević (12) were considered reduction of VLE isobaric and isothermal data for binary systems.

The purpose of the present article was to investigate the association effects on the reduction of the vapour-Liquid multicomponent systems, with association of one component in both phases.

DEVELOPMENT OF ASSOCIATION EFFECTS IN TERNARY SYSTEMS

For association reaction \( 2A_1 + B + C \rightleftharpoons A_2 + B + C \), the phase equilibrium for associating component \( A \) is given by equation

\[
P_A Z_A g_A = p_{A_0} x_A S_A y_A
\]

(1)

For the non-associating components \( B \) and \( C \) equations are as follows
The model taking into account a composition dependent liquid phase association constant states that

\[ K = K_A = f(T) \text{ and } k = f(T, x_A), \text{ i.e. } k = k_A \beta_A \]  

where \( \beta \) is a ratio of correction factors given by

\[ \beta = \frac{Z_A \sigma_A \sqrt{1/2 \sigma_A \sigma_A}}{\sigma_A} \]  

where

\[ Z_A = \frac{2K_A P_A (4KP + 1/y_A - 2KP y_A)}{2(K_P A^2 + 4KP - 4KP y_A)(2K_A P_A + 1 - \sqrt{4K_A P_A + 1})} \]  

and

\[ \sigma_A = \frac{2k_A (4k + 1/x_A - 2k x_A)}{2(k x_A^2 + 4k - 4k x_A)(2k_A + 1 - \sqrt{4k_A + 1})} \]  

The block diagram of the computer program for the calculation procedure of VLE data according to the equations (1)-(7) is shown on Figure 1. In this work only part of the deviation is assumed to be due to the dimerization.

**DATA - SETS Examined**

The sets of data for acetic acid-acetone-water, acetic acid-water, acetone-water and acetic acid-acetone mixtures were examined by York and Holmes (13) at 101325 Pa. The data for acetic acid-xylene-water system were examined by Murogova et al. (14) at 101325 Pa. The set of data for
acetic acid-xylene system were determined by Othmer (15) also at 101325 Pa. The data for water-xylene were examined by Gebelin (16) and Carlson and Colburn (17) approximate-ly at 101325 Pa.

The saturated vapour pressure was obtained for acetic acid from the Antoine equation reported by Ambrose et al (18) and Marek (9). For acetone, water and xylene the Antoine constants were reported by Prausnitz et al. (19).

Vapour phase non-idealities were handled by the method of Prausnitz et al. (19), except for acetic acid, where the correction factor of Marek and Standart and Marek (9) was used. The pure component association constants were obtained from the work of Ritter and Simons (20) for the vapour phases and from Freedman (21) as correlated by Barton and Hsu (22), for the liquid phase. The K used is that obtained by Ritter and Simons assuming dimer formation only; they also present a K for dimerisation to be used together with one for tetramer formation.

DISCUSSION

Reduction VLE data of investigated system was per-formed by means of the NRTL model (23). Barker fits (24) are only strictly valid for isothermal data unless the activity coefficients are corrected to isothermal conditions through the enthalpy of mixing.

Comparison of the activity coefficients predicted by the NRTL model with those calculated from the experimen-tal VLE data on the bases of the block diagram (see Fig.1) is shown in Figure 2. for acetic acid-acetone-water system at 101325 Pa. The results for isobaric data of acetic acid-xylene-water system are shown in Figure 3. In both cases obtained results are satisfactory.

CONCLUSIONS

The obtained results for modeling of acetic acid-
acetone-water and acetic acid-xylene-water ternary systems indicate that the model using a concentration-dependent liquid phase association constant is adequate. Proposed thermodynamic model which takes into account the association effects in multicomponent systems successfully represents the experimental data.

Acknowledgement. The authors wish to express their gratitude to the Scientific Research Fund of SR Srbija for a grant which have made this research possible.

NOTATION

\( A \) - associating component
\( B, C \) - non-associating component
\( A_1, A_2 \) - monomer, dimer
\( P \) - total pressure of system, Pa
\( T \) - temperature, K
\( K \) - vapour phase association constant at total pressure of mixture
\( K_A \) - vapour phase association constant at saturated vapour pressure of pure associating component \( p_{Ao} \)
\( k \) - liquid phase association constant for the mixture
\( k_A \) - liquid phase association constant for the pure associating component
\( p_{Ao} \) - saturated vapour pressure of the pure associating component, Pa
\( p_{Bo}, p_{Co} \) - saturated vapour pressure of pure non-associating B and C, respectively
\( x_A \) - nominal liquid phase mole fraction of the associating component
\( x_B, x_C \) - nominal liquid phase mole fraction of non-associating components B and C, respectively
\( y_A \) - nominal vapour phase mole fraction of the associating component
\( y_B, y_C \) - nominal vapour phase mole fraction of the non-associating components B and C, respectively
\( Z_A \) - vapour phase correction factor for the monomer
Greek symbols

$\phi_A$ - vapour phase fugacity coefficient of the associating component, ratio of fugacity coefficient of monomer in mixture to that of monomer in pure associating component

$\phi_A^*$ - fugacity coefficient ratio for the dimer

$\phi_B, \phi_C$ - overall vapour phase fugacity coefficient of non-associating component

$\delta_A$ - liquid phase correction factor of the associating component for monomer

$\delta_A^*$ - liquid phase correction factor for the associating component for dimer

$\delta_B, \delta_C$ - liquid phase correction factor for non-associating components B and C, respectively

$\gamma_A, \gamma_B, \gamma_C$ - nominal liquid phase activity coefficients of the associating and non-associating components, respectively.

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Fig. 1. Flow chart of the algorithm for the reduction of VLE data for ternary associated systems.
Fig. 2. Comparison of the activity coefficients predicted by NRTL model with those calculated from the experimental VLE data for acetic acid-acetone-water system.

Fig. 3. Composition dependence of association constant for acetic acid-xylene-water system at 101325 Pa.
THE CALCULATION OF COMPLEX ABSORPTION EQUILIBRIA OF IONOGEN SUBSTANCES IN AQUEOUS SOLVENTS WITH REACTION MODELS

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ABSTRACT:

The solubility of ionogen gases in water and aqueous ionogene solutions is very important for computation of absorption processes. Resulting systems with complex reaction equilibria behave themselves extremely nonideal. The concepts of nonideal thermodynamics only enable to determine properties of real systems in simple cases.

The model used in this work is based on ideal calculation of reaction equilibria and gas solubility.

The mathematical formalism leads to nonlinear systems of equations considering reaction equilibria. Equilibrium reactions are selected according to Brinkley's method.

In an inner loop the solutions of the nonlinear systems of equations are performed for every data point. Using the Maximum-Likelihood-Principle, the model parameters are optimized in an outer regressions loop. The used model is able to fit experimental data (partial pressure, total concentration of gas) satisfactory and the resulting model parameters from simultaneous data regression for different temperatures ensure a simple correlation of van't Hoff.

Introduction

Absorption arises as a problem of chemical phase equilibrium and is integrated in many chemical production plants. Mostly, this equilibrium problem becomes very complex, because many chemical components have to be taken into consideration to get a representative calculation of phase equilibrium. (Ref. 1, 2)

In cases of ionogen gases, additionally chemical reaction equilibrium in the liquid phase must be taken into account.

Nevertheless, the solution of absorption equilibrium gives the basis for calculating mass balance and mass transfer and is necessary for the planning and optimization of absorption equipment.
Generally, concepts of non ideal thermodynamics are to be used to calculate phase equilibrium. Therein the concept of fugacities renders the correlation of the gaseous phase and according to the unperfect behavior of the system, the phase equilibrium is expressed by the Henry correlation. The liquid phase is correlated with activity concepts.

Existing models for the calculation of non ideal reaction and phase equilibria mostly neglect decisive phenomena as dissociation equilibria or gas mixtures. Hence it follows a not admissable simplification of a complex system, so that these models are not usable for the determination of complex absorption equilibria. The only possibility left to compute complex absorption equilibria is to apply ideal concepts of thermodynamics.

The Ideal Reaction Model

A complex absorption problem is specified by one or more gaseous components and a solvent, which consists of a mixture of substances like water and MEA or water and salt. Using ideal correlation concepts of thermodynamics, the gaseous phase is defined by Dalton's law and the correlation of phase equilibrium is performed with Henry's law too.

\[ P_{\text{ges}} = P_i \times Y_i \]  \hspace{1cm} (Gl. 1)

\[ P_i = H_i \times x_i \]  \hspace{1cm} (Gl. 2)

The experimental information for an absorption problem is often referred to the partial pressure of the gas \( i \) to be solved and the concentration of the component \( i \) in the liquid phase, where this concentration includes the total amount of \( i \), physically solved and chemically bound. Using different expressions for the concentration of \( i \), the Henry correlation must be rewritten:

\[ P_i = H_i^{\text{K}} \times x_i = H_i^{\text{M}} \times m_i = H_i^{\text{C}} \times c_i \]  \hspace{1cm} (Gl. 3)

The possibility to use the total amount of \( i \) in the liquid phase to correlate phase equilibrium with Henry's law for ionogene gases leads to an extremely nonideal consideration of the system. This is caused by chemical phenomena, because ionic substances are correlated with dissociation equilibrium. Therefore the total concentration of \( i \) is to split in physically solved and chemi-
cally bound parts to get a true correlation of phase equilibrium with Henry's low for such systems.

\[ P_1 = H_i \cdot x_{1,ph} \]  

( Gl. 4)

Under this circumstance, a mass balance for the liquid phase must be performed.

**Mass Balance of the Liquid Phase**

The determination of the mass balance of the liquid phase leads to the formulation of a non linear system of equations with \( n \) equations and \( n \) unknowns. From these equations \( r \) ones regard to reaction equilibrium, \( s \) equations express the mass balances of the chemical elements and one equation stands for the balance of the total number of particles in the liquid phase, expressed in mole fractions, so that \( n \) becomes

\[ n = r + s + 1 \]  

( Gl. 5)

According to Brinkley's method for every reacting system a number of independent equilibrium reactions is resulting, which will be shown by the system \( \text{H}_2\text{O} - \text{CO}_2 - \text{MEA} \). From the chemical constitution of this system \( p \) species are selected. These species are \( \text{CO}_2 \), \( \text{H}_2\text{O} \), \( \text{H}_2\text{CO}_3 \), \( \text{HCO}_3^- \), \( \text{CO}_3^- \), \( \text{RNCOO}^- \), \( \text{RNH} \), \( \text{RNH}_2^+ \), \( \text{OH}^- \), \( \text{H}^+ \). Considering the \( s \) chemical elements \( \text{H} \), \( \text{O} \), \( \text{C} \) and \( \text{RN} \), it is possibile to construct \( p \) formul vectors where the assumption of these vectors yield a matrix \( U \) from the type \( (s \times p) \). The rank \( a \) of this matrix has the meaning of the number of necessary, independent equilibrium reactions for determining the simultaneous reacting system. In this example \( a \) has the value of 5, so that (Ref.3,4)

- \( R1: \text{H}_2\text{CO}_3 \leftarrow \text{K}_1 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \)
- \( R2: \text{H}_2\text{CO}_3 \leftarrow \text{K}_2 \rightarrow \text{H}^+ + \text{HCO}_3^- \)
- \( R3: \text{HCO}_3^- \leftarrow \text{K}_3 \rightarrow \text{H}^+ + \text{CO}_3^- \)
- \( R4: \text{H}^+ + \text{RR'NH} \leftarrow \text{K}_4 \rightarrow \text{RR'NH}_2^+ \)
- \( R5: \text{RR'NCOO}^- + \text{H}_2\text{O} \leftarrow \text{K}_5 \rightarrow \text{RR'NH} + \text{HCO}_3^- \)

are selected.
It is possible to formulate other equilibrium reactions for this system, but they are linearly dependent from the reactions R1-R5 listed before. The performance of the nonlinear system of equations gives the following result.

From the equilibrium reactions R1-R5 r equations are resulting, using the law of mass action.

\[
\begin{align*}
F_1 &= x_{H_2CO_3} - x_{H_2O} - x_{CO_2} - K_1 = 0 \\
F_2 &= x_{H_2CO_3} - (K_w - x_{H_2O}/x_{OH^-}) - x_{HCO_3^-} = 0 \\
F_3 &= x_{HCO_3^-} - (K_w - x_{H_2O}/x_{OH^-}) - x_{CO_3^{2-}} = 0 \\
F_4 &= (K_w - x_{H_2O}/x_{OH^-}) \cdot x_{RR'NH} - x_{RR'NH^+} - K_4 = 0 \\
F_5 &= x_{RR'NCOO^-} - x_{H_2O} - x_{RR'NH} - x_{HCO_3^-} - K_5 = 0
\end{align*}
\]

Further four equations result from the balance of the chemical elements.

\[
\begin{align*}
F_6 &= C_0^\circ / N_{ges} = (x_{H_2O} + x_{OH^-} + 3x_{H_2CO_3} + 3x_{HCO_3^-} + 3x_{CO_3^{2-}} + 2x_{CO_2} + 2x_{RR'NCOO^-}) = 0 \\
F_7 &= C_H^\circ / N_{ges} = (2x_{H_2O} + x_{OH^-} + (K_w - x_{H_2O}/x_{OH^-})) + 2x_{H_2CO_3} + x_{HCO_3^-} + 2x_{CO_3^{2-}} + 2x_{RR'NH_2} + x_{RR'NH}) = 0 \\
F_8 &= C_C^\circ / N_{ges} = (x_{H_2CO_3} + x_{HCO_3^-} + x_{CO_3^{2-}} + x_{CO_2} + x_{RR'NCOO^-}) = 0 \\
F_9 &= C_{RR'N} / N_{ges} = (x_{RR'NH} + x_{RR'NH^+} + x_{RR'NCOO^-}) = 0
\end{align*}
\]

Where N_{ges} is the total number of particles in the liquid phase and C represents the total concentration of the chemical elements. Another possibility to create conditions for the mass balance is to take in the physically solved CO₂ using the Henry equation instead of equation F8.

\[
F_8 = p_{CO_2}^{gem} / x_{CO_2} - x_{CO_2,ph} = 0
\]
The n-th equation for the system determines the balance of the total number of particles in the liquid phase.

\[ F_{10} = 1 - (X_{H_2O} + X_{OH^-} + (K_{H^+}X_{H_2O}/X_{OH^-}) + X_{H_2CO_3} \]
\[ + X_{HCO_3^-} + X_{CO_3^2-} + X_{RR'NH} + X_{RR'NH_2^+} \]
\[ + X_{RR'NCOO^-} + X_{CO_2} = 0 \]

Regarding to the acidity of the solution the reaction of water dissociation is expressed by

\[ X_{OH^-} = K_w \cdot \frac{X_{H^+}}{X_{H_2O}} \text{ bzw. } X_{H^+} = K_w \cdot X_{OH^-} \]

If the values for the reaction equilibrium constants \( K_i \) and the Henry constant \( H \) and \( K_w \) are known, the non linear systems of equations \( F1-F10 \) and \( F1=F7, F8, F9 \) and \( F10 \) are easily to solve by well established numerical methods (Ref.5). Otherwise the values for these parameters must be calculated from data regression.

**Performance of Data Regression**

Most experimental examinations of absorption equilibria yield experimental data for the partial pressure of the gas and the total concentration of the dissolved gas. Usually the data regression is performed considering one variable, pressure or concentration in this case, erroneous, while the other one is supposed to be without error.

According to the nonlinear systems of equations stated in the chapter before, the following conditions for data regression are possible. Using the equations \( F1-F10 \) to compute the mass balance of the liquid phase, the partial pressure \( p_i \) of the dissolved gas in the system is a free variable and can be cited to perform a condition for data regression like

\[ Z_p = p_{CO_2}^{gem} - p_{CO_2}^{cal} \neq 0 \] (Gl. 6)

with

\[ p_{CO_2}^{cal} = X_{CO_2, ph} \cdot H_{CO_2}^x \]

On the other hand, from the shape of equations, \( F1-F7,F8, F9 \) and \( F10 \) the total concentration of \( CO_2 \) in the solution, physically solved and chemically bound, is the free variable and can be used to formulate a condition for the data regression as

\[ Z_C = C_{CO_2}^{gem} - C_{CO_2}^{cal} \neq 0 \] (Gl. 7)
with

\[ C_{\text{cal}}^n = N_{\text{ges}} \cdot \left( x_{H_2CO_3} + x_{HCO^-} + x_{CO_2^-} + x_{CO_2^+} + x_{RR'NCOO^-} \right) \]

But according to a chosen method of measurement both variables are faulty and the only possibility to accommodate to this circumstance is to use the Maximum Likelihood Principle implementing the data regression (Ref: 6). For the data regression itself several numerical methods are available (Ref: 7), in this work a method of Marquart (Ref: 8) was performed. The sum of least squares is expressed like

\[ s = \frac{1}{\sigma^2_p} \cdot \sum_{i=1}^{mp} \frac{(z_i^2)}{\sigma^2_c} + \frac{1}{\sigma^2_c} \cdot \sum_{i=1}^{mp} (z_i^2) \leq \min \quad (Gl.8) \]

\( \sigma^2_p \) and \( \sigma^2_c \) are the variances to pressure and concentration, which have to be estimated if they are not listed with the experimental data.

The physical significance of the ideal reaction model can be checked by the van't Hoff equation. In this correlation, the parameters \( K_i (H) \) are correlated with the temperature.

\[ \ln(K^v) = \frac{A}{T} + B \quad (Gl.9) \]

The parameters \( A \) and \( B \) can be determined by simultaneous data regression over a temperature interval. If the model parameters \( K_i \) and \( H \) from the individual data regressions at a temperature \( T \) do not follow van't Hoff's law, the simultaneous data fit represents a better numerical method for the selected model.

**Results**

The chemical system MEA-\( \text{CO}_2^- - \text{H}_2\text{O} \) has great importance in chemical technology. As shown before the mathematical formulation for this system includes 10 unknowns for the non linear system of equations and 7 model parameters. The results for the single data regressions at the temperatures 313.15, 333.15, 353.15 and 373.15 K are listed in table 1 and are presented in the figures 1a - 1d graphically.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \ln(K_1) )</th>
<th>( \ln(K_2) )</th>
<th>( \ln(K_3) )</th>
<th>( \ln(K_4) )</th>
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### Table

<table>
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<th>$T(\text{°K})$</th>
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<th>$\ln K_w$</th>
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<tr>
<td>373.15</td>
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- $\circ$ measured data point
- + calculated data point
- — smoothed curve

### Figures 1a - 1d

- MEA-C02 (T=40 C)
- MEA-C02 (T=60 C)
- MEA-C02 (T=80 C)
- MEA-C02 (T=100 C)
The calculation of the temperature dependence of the model parameters by simultaneous data regression at the temperature interval from $T_1=313.15$ to $T_2=373.15$ K using van't Hoff's law, yielded results for the parameters $A$ and $B$, which are shown in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$A$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>1.977894±004</td>
<td>-9821873</td>
</tr>
<tr>
<td>$K_2$</td>
<td>-2.498530±003</td>
<td>-2.362449±001</td>
</tr>
<tr>
<td>$K_3$</td>
<td>4.549974±004</td>
<td>-3.094549±002</td>
</tr>
<tr>
<td>$K_4$</td>
<td>3.489828±003</td>
<td>-2.203520±002</td>
</tr>
<tr>
<td>$K_5$</td>
<td>-3.686830±003</td>
<td>-1.752203±002</td>
</tr>
<tr>
<td>$K_w$</td>
<td>0.000000</td>
<td>-3.634309±002</td>
</tr>
<tr>
<td>$H$</td>
<td>-7.055119±004</td>
<td>4.456797±002</td>
</tr>
</tbody>
</table>

Table 3 presents the results of single and simultaneous data regression comparatively.

### Table 3

<table>
<thead>
<tr>
<th>$T(K)$</th>
<th>$\sigma_p$</th>
<th>$\sigma_p^\mu$</th>
<th>$\sigma_C$</th>
<th>$\sigma_C^\mu$</th>
<th>MP</th>
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<tbody>
<tr>
<td>313.15</td>
<td>1.33</td>
<td>3.94</td>
<td>0.04</td>
<td>0.12</td>
<td>8</td>
</tr>
<tr>
<td>333.15</td>
<td>2.98</td>
<td>4.83</td>
<td>0.09</td>
<td>0.16</td>
<td>8</td>
</tr>
<tr>
<td>353.15</td>
<td>1.01</td>
<td>3.83</td>
<td>0.04</td>
<td>0.15</td>
<td>8</td>
</tr>
<tr>
<td>373.15</td>
<td>1.53</td>
<td>2.27</td>
<td>0.10</td>
<td>0.12</td>
<td>8</td>
</tr>
</tbody>
</table>

Experimental data for the system MEA-$CO_2$-$H_2O$ are taken from Ref. 9.
Discussion

Using the ideal reaction model for the determination of complex absorption equilibria, a set of model parameters can be calculated for every chemical system. Regarding to the van't Hoff correlation these parameters, $K_i$ and $H$, should be reproduced by a straight line, which is defined by $\ln (k_i)$ versus $1/T$.

As a result of this work it is shown, that the parameters, which can be computed by several data regressions at a given temperature $T$, do not fit to the van't Hoff correlation. The reasons for these effects are found in the numerical instability of the system. First of all, there exists more than one set of model parameters, which guarantee the same solution for the nonlinear system of equations and additionally, not all concentrations of the chemical species are really needed for the data regression.

Therefore the data regressions at several temperatures are to be interpreted as simple data fittings and yield fitting parameters, which guarantee satisfactory results.

The determination of the parameters $A$ and $B$ represents in any case a better physical method, because the model parameters $K_i$ and $H$ calculated from the van't Hoff equation are valid in a temperature interval and also supply a representation of experimental data with technical accuracy.

Because for same chemical reactions in different reaction systems the values for the concerning parameters are different, the model parameters $K_i$ and $H$ are no universal equilibrium constants. For the calculation of universal equilibrium constants it is necessary to consider the imperfect behavior of the chemical system.
References:

1.) J.M. Prausnitz, J. Gmehling: Thermodynamik der Phasengleichgewichte, Krauskopfverlag, Mainz (1980)
5.) NAG - Library, Rechenzentrum Graz (1978)

Nomenclature:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>pressure</td>
</tr>
<tr>
<td>y,x</td>
<td>mole fractions</td>
</tr>
<tr>
<td>m</td>
<td>molality</td>
</tr>
<tr>
<td>c,C</td>
<td>concentration</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>K</td>
<td>model parameter</td>
</tr>
<tr>
<td>H</td>
<td>Henry's constant</td>
</tr>
<tr>
<td>MP</td>
<td>number of data points</td>
</tr>
<tr>
<td>A,B</td>
<td>van't Hoff parameters</td>
</tr>
<tr>
<td>Z</td>
<td>standard deviation</td>
</tr>
<tr>
<td>S</td>
<td>variance</td>
</tr>
<tr>
<td>i</td>
<td>condition for data regression</td>
</tr>
<tr>
<td>F</td>
<td>residuum</td>
</tr>
<tr>
<td>S</td>
<td>sum of least squares</td>
</tr>
</tbody>
</table>

Indices:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
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<td>i</td>
<td>component</td>
</tr>
<tr>
<td>ph</td>
<td>physically solved</td>
</tr>
<tr>
<td>m</td>
<td>measured</td>
</tr>
<tr>
<td>cal</td>
<td>calculated</td>
</tr>
<tr>
<td>o</td>
<td>total</td>
</tr>
<tr>
<td>c</td>
<td>according to concentration</td>
</tr>
<tr>
<td>m</td>
<td>according to molality</td>
</tr>
<tr>
<td>x</td>
<td>according to mole fraction</td>
</tr>
<tr>
<td>v</td>
<td>according to van't Hoff</td>
</tr>
</tbody>
</table>
THE COMPARISON OF METHODS FOR THE PREDICTION OF THE THERMAL CONDUCTIVITY OF LIQUIDS

Pavel Chuchvalec and Libuše Hudcová
Department of Physical Chemistry, Institute of Chemical Technology, 166 28 Prague 6, Czechoslovakia

Summary
The thermal conductivities of liquids are important as fundamental data in the engineering calculations of heat transfer. A method for the prediction of the thermal conductivity is therefore of a great practical interest. Chosen methods for calculation of the thermal conductivity of liquids were tested on the set of organic and inorganic compounds. A special attention was devoted to methods based on the corresponding states theory. The reliability of the estimation procedures presented is discussed with respect to their practical use.
A knowledge of physico-chemical properties is a fundamental requirement of all design activities in the chemical industry. Ideally, the designer would prefer to use correlations based on accurate experimental measurements of the property concerned but even for pure substances these are not always available. Methods of predicting thermodynamic and transport properties are, therefore, of great importance and their use has become routine, particularly in computer design procedures. The aim of this work was to test some methods for estimation of the thermal conductivity of liquids and the best ones include in the predictive computational system. The process leading to the selection of procedures predicting the thermal conductivity of liquids is illustrated below.

The thermal conductivities of many substances have been measured by various workers and compiled e.g. by Jamieson et al.\textsuperscript{1} and ESDU\textsuperscript{2}. As shown in the literature there are few data for liquid mixtures although a number of thermal conductivity data have been reported for pure liquids. It is impossible to measure this property for all liquids and liquid mixtures of interest, especially since values over a wide range of temperature and pressure may be needed in process calculati-
Reliable methods of prediction are therefore of great practical interest.

Methods tested

A number of methods has been published in recent years to predict thermal conductivity of liquids. The survey of methods appearing in the literature up to 1976 is performed by Latini and Pacetti. The critical review of various estimation procedures for thermal conductivity of liquids and their mixtures presents Reid et al. On the basis of these works and literature sources up to 1981, the selection of methods for the test of their practical use was performed. Chosen methods are simple and involve easy-to-find physical properties. The evaluation of results was done with respect to the comparison of experimental and predicted data as well as to the general purpose of formulas. The only chosen method which enables the continuity of calculation in the gas phase, needs pressure as the input value. All the others the effect of pressure neglect. To use the selected methods in the wide temperature range were some formulas (originally developed for specific temperature levels) extended to include the effect of temperature on the thermal conductivity. The temperature dependency of thermal con-
ductivity is satisfactorily described by Riedel equation:

$$\lambda = A[1 + \frac{20}{3}(1 - T_x)^{0.666}]$$

(1)

Following elder methods: Missenard\textsuperscript{10}-Riedel, Vargaftik\textsuperscript{11}-Riedel, Sato\textsuperscript{4}-Riedel and Sakiadis-Coates\textsuperscript{4} were included to the first group of formulas and tested on the set of 113 compounds. From recently published methods were chosen that based on the GCST. The method of Christensen\textsuperscript{5}, which starts from Tham and Gubbins\textsuperscript{7} model, is assigned to the prediction of the thermal conductivity of nonpolar compounds in both the liquid and gas states. The region of use is restricted to substances with known factors of hindered rotation. The second one of methods based on the GCST chosen for the test was the correlation due to Teja and Rice\textsuperscript{8}. These authors developed an extension of the three parameter corresponding states principle based on the properties of two non-spherical reference fluids for the thermal conductivity of liquids and liquid mixtures. The method uses Pitzer's acentric factor for a linear interpolation/extrapolation of the reference fluid properties and the van der Waals one-fluid model to extend the pure liquid predictions to mixtures. The last two methods were included into the second group of methods selected for the verification.
Results and discussion

The comparison of experimental and predicted data was developed using the experimental data collected by Jamieson\(^1\), Landolt-Börnstein tables\(^9\) and ESDU\(^2\). Since at a fixed temperature experimental values of various authors differ within ±5% and more, the average of the reliable available data was assumed. Most of input data for investigated methods were taken from the standard compilation by Reid et al.\(^4\). The set of compounds for the test was grouped on the basis of their chemical structure.

The Sato-Riedel method is recommended for simplicity. It is giving the best results for n-alkanes and aromatic hydrocarbons (the average error 4.1%) as well as for halogenderivatives of hydrocarbons (6.0%). The Sakiadis-Coates formula seems to be the most suitable method for branched alkanes (3.7%) and for oxygenderivatives of hydrocarbons (5.8%). However this method is applicable only to limited amount of organic liquids. All methods of the first group failed in the case of organic acids. The best results for the group of amines and sulphides were achieved by Vargaftik-Riedel formula (7.1%).

The method of Christensen from the second group of selected formulas was tested by the author originally on the set of six pure substances and two mixtures,
with methane as the reference fluid. The test was in the present case extended to 17 compounds representing more than 600 experimental points. The possibility of modifying of the method by using the Redlich-Kwong equation for the state behaviour description was examined. The satisfactory results were obtained for the gas phase only, in the case of liquid state the deviations were 2-3 times higher than those for the gas phase. The similar deviations as for the pure substances were found for binary mixtures. It is apparent that the quality of the prediction responds in this case to the accuracy of the state behaviour description. Nevertheless this modified form of the method can be used with good results for the calculation of thermal conductivity of nonpolar gases at low pressure.

The last method investigated (Teja and Rice) achieved good results especially for binary mixtures. The advantage of this procedure is the need easy-to-find input data only if the temperature dependency of the thermal conductivity of two reference substances is known. With a suitable choice of reference fluids and of the reference fluid equation, good agreement between calculated and experimental thermal conductivities may be obtained. The authors tested the method for a large group of binary mixtures and for the pure n-alcohols. We have extended the test on the subset of organic acids...
(where all methods of the first group failed) and amines. The results have shown the possibility of a practical use of the method for pure substances in homologic series. The average deviation for seven acids tested was 6.7% and for amines 8.6%. However the main field of the effective use of this method is for mixtures. The maximal deviation for the set of binary mixtures tested did not exceed 4%, the average deviation was 1.2%. With the help of this method better results were achieved than with the Li-equation, commonly used for prediction of thermal conductivity of multicomponent liquid systems.

The comparison of predictive methods for pure liquids indicate that the present correlations based on a simplified theory are less accurate than the merely empirical ones. The extension of the three parameter CST using the van der Waals one-fluid model seems to be the most suitable correlation for the prediction of the thermal conductivity in the case of liquid mixtures consisting of nonspherical fluids.

Literature cited
2. Eng.Sci.Data 75 003, 75 009 and 75 024, Institution of Chemical Engineers, U.K., 1975
5. Christensen P.L., Measurement and Prediction of the Thermal Conductivity of Natural Gases, Instituttefor Kemiteknik, Denmark Tekniske Højskole, 2800 Lyngby, Denmark 1979
SESSION B:
SEPARATION PROCESSES
Wärme- und Energietechnik
Stahlbau und Maschinenbau
Anlagenbau
Montage

WAAGNER-BIRÓ

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Is there any Scope for Research Left?

Martin Molzahn and Dieter Wolf *)

Mass transfer separation processes have been the subject of scientific investigations for more than half a century. Knowledge and mastery of process fundamentals and their engineering techniques have reached a stage which few other unit operations have attained. Nevertheless, the engineer working on the separation of fluid mixtures may still today come across obstacles and untrodden paths, be it in phase equilibria, fluid dynamics, or mass transfer.

1. Introduction

Ever since process technology has found a place in teaching and research, mass transfer separation processes have been the subject of scientific investigation. This important position in research corresponds to the wide use and great importance of such processes in the petrochemical and chemical industries. Even though, under the pressure of commercial activity, industrial implementation tends to be somewhat ahead of research, the scientific understanding in this field has nevertheless reached a depth which few other unit operations can show. Looking back on more than half a century of intensive research, and taking into account the amount of more recent work, which has been carried out rather with the incentive of scientific activity and publication than with the object of filling gaps in knowledge, the authors seek to answer the question: "Is there any scope for research left in this field?"

It is indeed true that the field of "Mass transfer separation of mixtures" looks more like a well-cultivated landscape than an untouched, almost impenetrable jungle. Nevertheless, anyone concerned with chemical engineering problems in this field will, again and again, encounter obstacles and almost untrodden paths. It is proposed to indicate some of these problems and in doing so, to make suggestions about research activities which might contribute to mastering the problems with which an engineer in a chemical company has to cope.

Looking at it from this point of view, such research work as intended solely for scientific confirmation of empirical knowledge will be included only to the extent that the lack of such confirmation constitutes a handicap in industrial practice.

In considering this topic, it is proposed to follow the pattern of development of a separation process.

This can, very roughly, be resolved into:

- Process ideas
- Process selection and optimization
- Selection and design of equipment.

2. Physical Properties: Phase Equilibria

Amongst the physical properties required to carry out the design and calculations of a separation process, the most important are the vapour/liquid and liquid/liquid phase equilibria (VLE and LLE respectively).

The design and optimization of a distillation process, based on calculation, is nowadays, to a large extent, possible, with a considerable accuracy. This is primarily due to physically well-founded relationships, available for setting up models and making predictions of VLE in multicomponent mixtures, as well as to the development of electronic data processing.

The chemical industry predominantly processes mixtures of polar, chemically very different materials, in which the equilibrium is determined by the real behaviour of the liquid phases. For such mixtures, the Wilson equation of 1964 /1/ and the NRTL equation of 1968 /2/ have, for a number of years, proved very suitable; for any particular type of mixture, either one or the other equation may be more advantageous. More recently, the UNIQUAC model has been put forward in 1975 /3/. It serves as the basis for a method of predicting activity coefficients (UNIFAC) both for VLE and LLE /4/.

The usefulness of the NRTL and UNIQUAC relations is found to be limited in the case of application to mixtures with a miscibility gap. Whilst the prediction of multicomponent VLE from binary data is, even in such a case, still sufficiently reliable, the models of the corresponding LLE are, as a rule, very unsatisfactory. This problem is generally appreciated and work on improving the method is currently being carried out in various institutes.

A large number of measured VLE data, varying in quality, have been published. Critical assessment of these measurements, their processing with expert understanding and their availability as a data collection, such as the Dortmund Data Bank /5/, are important achievements. Where measured data are not yet available, and this is often the case at the beginning of a process development, the UNIFAC method /4/ indicates a way of predicting the activity coefficients from the contribution of functional groups in the molecules. Further development of this method is also to be welcomed.
With the available means, the majority of distillation problems can be treated without great difficulty. However, some special processes pose unanswered questions even today. Most of these are well-known and have already been frequently discussed /6/:

- Phase equilibria of electrolyte solutions and of mixtures of electrolytes and non-electrolytes
- Behaviour of mixtures in the vicinity of the critical point
- Standard fugacity in the supercritical temperature range.

Some other questions will be discussed later.

Much less satisfactory is the position in the case of liquid/liquid equilibria, which are of importance in extraction problems. This type of problem is much more difficult; in vapour/liquid equilibria it is, above all, the vapour pressure which determines the equilibrium, and the activity coefficient merely represents a correction for non-ideal behaviour. In contrast, LLE exhibit exclusively non-ideal behaviour, i.e., existence of strong interactions determines phase separation and equilibrium. In practice, in most cases, it proves possible to reduce an extraction problem, at least step by step, to a 3-component system on which measurements can be carried out and which can be described by empirical equations /7/. Where such a simplification is not permissible, there is an urgent need for a method which allows a prediction of the LLE in a multicomponent mixture from measured ternary and binary data. The basic assumptions of NRTL and UNIQUAC are suitable for this problem, but the difficulties which arise in determining the correct parameters, i.e., meaningless parameter combinations and numerical convergence problems, still stand very much in the way of a routine application. Consideration should also be given to whether the currently applied model assumptions can, in fact, lead to a satisfactory solution.

A successful chemical engineer must not only be well acquainted with the methods of process and equipment design in his particular field, but he also needs ideas. Optimum heat utilization, sophisticated networks, or correct choice of equipment are, of course, very important. But it is far more the ideas, e.g., how, using an additive, might the equilibria be advantageously shifted, which determine the economic success of the process as a whole. This finding of a suitable additive for use in extraction or extractive distillation still largely remains a matter of intuition. A systematic approach, coupled with a data bank, would be eagerly adopted by industry. In addition to the conventional solvents such as hydrocarbons, esters, ketones etc., particular interest is attached nowadays to substances whose action is based on strong reversible chemical bonding, i.e., materials in the transition region between polar solvents and liquid ion exchangers. Thus, in a BASF process for producing anhydrous formic acid, it proved possible, by adding a suitable component, to reduce the energy consumption from 5.0 to 2.5 kg steam/kg formic acid /8/. 
The prediction of distribution coefficients by the UNIFAC method may provide a rough indication for the selection and assessment of solvents. Unfortunately, this method fails just in the case of the most interesting solvents, since it does not consider chemical reactions. Table 1 shows as an example the distribution coefficients of acetic acid between water and some conventional solvents as well as between water and two chemically active solvents. But also in the case of conventional solvents, the distribution coefficients extrapolated from experimental data differ widely from those estimated by the UNIFAC method. One reason for these differences is the uncertainty of extrapolation, but they can also be attributed to VLE and LLE representation.

One of the most widely used separation processes, employing chemically reactive additives, is gas scrubbing in petrochemical processes in order to remove CO₂ and H₂S. As a result of numerous scientific investigations of absorption with superimposed chemical reaction, models with a sound physical foundation are available. The practical application lags far behind the development of the models, in some important cases. This happens for various reasons, including that of simple lack of fundamental physical data. A recent publication by Cornelissen /11/ on the selective absorption of CO₂ and H₂S by aqueous solutions of amines indicates that several question marks apply even to the mechanism of the reaction of CO₂ with amines:

Model 1:
\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{HCO}_3^- & \text{slow} \\
\text{R}_3\text{N} + \text{H}^+ & \rightarrow \text{R}_3\text{NH}^+ & \text{infinitely fast} \\
\text{CO}_2 + \text{H}_2\text{O} + \text{R}_3\text{N} & \rightarrow \text{R}_3\text{NH}^+ + \text{HCO}_3^- \\
\end{align*}
\]

Model 2:
\[
\begin{align*}
-\text{COH} + \text{OH}^- & \rightarrow -\text{CO}^- + \text{H}_2\text{O} & \text{fast} \\
-\text{CO}^- + \text{CO}_2 & \rightarrow -\text{CO}_2\text{CO}_3 & \text{slow} \\
-\text{COH} + \text{OH}^- + \text{CO}_2 & \rightarrow -\text{CO}_2\text{CO}_3 + \text{H}_2\text{O} \\
\end{align*}
\]

Model 3:
\[
\begin{align*}
\text{R}_3\text{N} + \text{H}_2\text{O} & \rightarrow \text{R}_3\text{NH}^+ + \text{OH}^- & \text{infinitely fast} \\
\text{CO} + \text{OH}^- & \rightarrow \text{HCO}_3^- & \text{moderately fast} \\
\text{CO}_2 + \text{H}_2\text{O} + \text{R}_3\text{N} & \rightarrow \text{R}_3\text{NH}^+ + \text{HCO}_3^- \\
\end{align*}
\]

This is also true in the case of such a well-known system as formaldehyde/water (Fig. 1). Formaldehyde reacts with water to form a large number of oxymethylene oligomers. The literature contains various indications of possible reaction mechanisms /12 - 15/. However, information on reaction equilibria and kinetics and, e.g., the effect of pH on the above, is sparse and not without contradictions. If additional components, such as alcohols, are present in the same system, one is still groping completely in the dark.
In this context, attention should also be drawn to a requirement, which the description of phase equilibria should meet but which, unfortunately, is frequently overlooked. For mass transfer calculations, the distribution of resistances to mass transfer between the gas and liquid phases must be known. This depends not only on the fluid-dynamic properties of the equipment, as expressed by the mass transfer coefficients \( B_0 \) and \( B_1 \), but also on the phase equilibrium, reflected by the slope \( m \) of the equilibrium line, and the enhancement factor \( E \):

\[
\frac{1}{B_{0G}} = \frac{1}{B_G} \left( 1 + m \frac{s_G}{s_L} \frac{M_L}{M_G} \frac{B_G}{E B_L} \right)
\]  

Eq. (1) results from

\[
\dot{n} = B_{0G} \frac{s_G}{M_G} \left( \gamma - \gamma^* (\bar{x}) \right)
\]  

(2a)

\[
= B_G \frac{s_G}{M_G} \left( \gamma - \gamma^*_I \right)
\]  

(2b)

\[
= E B_L \frac{s_L}{M_L} \left( \bar{x}^*_I - \bar{x} \right)
\]  

(2c)

with

\[
\gamma^* = m \bar{x}^* + \text{const}
\]  

(3a)

and

\[
m = \frac{d\gamma^*}{d\bar{x}^*}
\]  

(3b)

It is obvious from the derivation of the equation for the overall mass transfer coefficient \( B_{0G} \) that the parameter describes the relationship between the true concentrations of the component being transferred (e.g., monomeric formaldehyde) in the gas and liquid phases. The frequently employed representations of phase equilibria on the basis of apparent mole fractions is not very helpful in such cases and, in fact, its use can result in substantial errors, as shown by the following example:

1) see list of symbols
Using a VLE representation based on apparent mole fractions $\bar{x}_F^A$, the slope $m$ of the equilibrium line becomes /14/:

$$\bar{y}_F = \frac{\bar{y}_{ref}^A}{F}$$

$$m = \frac{\bar{y}_{ref}^A}{p} = 0.55$$

On rearrangement of the VLE representation on the basis of true mole fractions $x_F$, the following is obtained:

$$\bar{y}_F = \frac{x_F^A}{F} f_F^{ref}$$

$$m = \frac{(1 + K_1) x_{ref}^A}{p} = 375$$

Strong chemical interactions also add to the difficulty of carrying out predictive calculations for separation processes involving carboxylic acids which show association in the gas phase. Chemical theory of fugacity coefficients under moderate pressures, which assumes the dimer to be the only associate, is of some help in the representation of phase equilibria /16/. Equilibrium constants for dimerization are available for only a few carboxylic acids /17/. Uncertainties remain in respect of crossdimers and the caloric data.

The example of a distillation column for acrylic acid shows the importance of correct consideration of association, even in a binary system (Fig. 2). As an approximation the dimerization constant of acrylic acid is assumed as equal to that of propionic acid. Dimerization affects the mean molar mass of the vapour phase and hence the vapour density. This shows clearly that the $F$-factor $w_{ref}$ which determines the column cross-section will be calculated 26% too high, if association is neglected and the vapour phase is assumed to be purely monomeric. If, on the other hand, a complete dimerization of the vapour phase is postulated, the calculation will result in a value of the load factor which is 11% too low. The differences are even more marked in performance calculations of overhead condenser. Taking association into account, the energy liberated per unit mass of condensed acid must be calculated from the heat of the dimerization reaction and latent heat of evaporation of the monomeric acid. The latter is obtained by the Clausius-Clapeyron equation from the slope of the vapour pressure curve of the monomeric acid. On the other hand, latent heats of evaporation calculated from the overall vapour pressure curves, normally measured, are between 129% and 257% of this value, depending on the assumed degree of dimerization. What sort of error can thus result in designing the equipment, becomes immediately clear.

These examples from distillation, absorption and extraction show that it is primarily the coupling of conventional physico-chemical interactions with chemical reactions which, on the one hand, produces favourable effects but, on the other hand, often cannot be used as a model to carry out computational process optimization since the requisite information is lacking.
3. Process Simulation

Given the knowledge of phase equilibria, process calculation and optimization can begin. In this respect, the authors are not aware of any outstanding questions. There is no need yet to add further methods to the large number already available for the simulation of countercurrent separation processes on the basis of theoretical stages /18 - 24/. The matrix methods, with Newton-Raphson iteration, have proved the most suitable for this purpose.

4. Distillation and Absorption/Desorption Equipment

4.1 Fluid Dynamics

In dimensioning of gas/liquid contact equipment for rectification, absorption and desorption the current practice is to ensure good separation efficiency by selecting dimensions which are completely satisfactory in respect of fluid dynamics. This presupposes a knowledge of the various capacity limits and pressure drops attributable to all types of mass transfer devices, as well as of their dependence on physical properties and geometrical values /25/. For cross-flow trays, some years ago Stichlmair /26/ reviewed the existing knowledge and, using physical models, placed some of the known, mostly empirically determined relationships on a new basis. Reichelt /27/ produced a similar compilation on packings. Unfortunately, on a closer look, these relationships proved far from being sufficiently reliable. With the aid of some examples, the authors now propose to indicate which problems, in their view, still remain unsolved.

Stichlmair gives a relation for calculating the pressure drop of sieve trays, consisting in the usual way of the dry pressure drop $\Delta p_d$, the hydrostatic pressure drop $\Delta p_h$ and the residual pressure drop $\Delta p_r$ which, inter alia, takes into account bubble formation at the aeration orifices, and the work done in accelerating the entrained droplets:

$$\Delta p = \Delta p_d + \Delta p_h + \Delta p_r$$

(6)

with

$$\Delta p_d = \frac{1}{2} \xi_G F_o$$

(7)

$$\Delta p_h = f_1 (h_w, \dot{V}_L / \dot{V}_G, \epsilon_L, F_\ldots)$$

(8)

$$\Delta p_r = f_2 (d_w, \sigma_L, \Delta \dot{V}_L / \dot{V}_G \ldots)$$

(9)
Comparison of this equation with own measurements and those of Fractionation Research Inc. (FRI) /28/ shows a useful agreement as far as the total pressure drop is concerned (Fig. 3a). However, if the individual pressure drop components are considered separately, the error diagram shows considerable systematic deviations: the calculated values of the dry pressure drop or friction factor are obviously too high (Fig. 3b); the static pressure drop shows wide scatter, and the individual series of measurements tend to deviate from calculations (Fig. 3c). This implies that the liquid level on a tray, and hence the parameters depending thereon, such as the transition from froth to spray regime, interfacial area and the lower capacity or weeping limit, will be calculated incorrectly.

I take a closer look, according to Mersmann /29/, a sieve tray with holes of \( d_0 \approx 2 \, \text{mm} \) should show no weeping if the condition

\[
F_o > \left\{ C d_0 (f_L - f_S) \right\}^{1/2} \tag{10}
\]

is satisfied, where \( i \leq 0.4 \). This relation results from setting up a balance of forces around two holes within the froth layer, one of them blowing and the other weeping. It shows that the weeping limit is independent of the liquid level on the tray and hence also of the liquid load. This does not agree with experimental findings (Fig. 4).

By analogy to Faris /30/, the authors arrived at a different result. The gas which flows through the holes and the froth layer undergoes a pressure drop \( \Delta p \) as discussed previously.

\[
\Delta p = \Delta p_t + \Delta p_L + \Delta p_R = p_1 - p_2 \tag{6a}
\]

At the feed inlet, clear non-aerated liquid flows onto the tray and over the first row of holes, where it becomes agitated. The height \( h_0 \) of this liquid corresponds to the liquid hold-up in the froth layer, i.e., to the hydrostatic pressure drop \( p_L \) due to a forces balance /31/:

\[
g f_L h_L = \frac{\Delta p_L}{\beta} = f \left( h_0, \dot{V}_L/L_w, \ldots \right) \tag{11}
\]

where \( \beta \) is the load dependent aeration factor. In order to prevent weeping, the total pressure drop \( \Delta p \) must not fall below this height of liquid

\[
\Delta p \geq g f_L h_L \tag{12}
\]
Accordingly, for the gas load at the weeping limit \( F_{\text{G, weep}} \), with \( \Delta P_R = 0 \), the observed dependence on the liquid load is as follows:

\[
\frac{G R}{2 F_{\text{G, weep}}} \geq \frac{1 - B_{\text{o, weep}} v_{\text{p}}}{B_{\text{o}} \Delta P_L}.
\]

Incorrect allocation of the total pressure drop leads therefore to considerable errors in predicting the weeping limit. These, in turn, result in uncertainty of prediction of the expected behaviour under partial load, and hence also of the flexibility of a column, and in possibly unfavourably high pressure drops or bottom temperatures, etc., being required.

With packed columns, surprising gaps in knowledge and contradictions, in calculating their performance, are also encountered. This is all the more regrettable since it is to be expected that with the constantly increasing demand for energy-saving measures, and the trend towards energy integration, the use of mass transfer devices, which produce a low pressure drop, will increase.

A commonly employed method for calculating the pressure drop \( \Delta P/H \) and the flooding velocity \( w_f \) of packed columns was put forward by Sherwood /32/ and Eckert /33, 34/. It makes use of a generalized representation of pressure drop phenomena in packed beds and employs, as an empirical adjustment factor, the so-called packing factor \( F_E \) (Fig. 5):

\[
\Delta P = f \left( F_E W_G^2 C ; F_{L G} \right) \quad (14)
\]

\[
w_{G, \text{flood}} = \left\{ \frac{y (F_{LG})}{(F_{EC})} \right\}^{1/2}, \quad (15)
\]

where the constant \( C \) includes the physical properties of the ordinate term \( y \) of Fig. 5.

As early as 1969, Billet /35/ showed that, at least in the case of metallic Pall rings, the packing factors given by Eckert are too low and do not correctly indicate the flooding velocity (Table 2). Krötzsch and Kürten /36/ arrived at similar packing factors from an evaluation of their pressure drop measurements. In the authors' experience, on the other hand, the pressure drop measurements of Teutsch /37/, Billet /38/ and FRI /39/ can be best represented in terms of the original Eckert constants, whilst for the flooding limit, packing factors which are calculated from the geometrical data of the packings (geometrical surface area \( a \) and void fraction \( \varepsilon \)), in accordance with Sherwood's original model, are appropriate (Fig. 6).
It can be seen from this example that performance calculations of packed columns based on empirical correlations are misleading. Unfortunately, even semi-empirical equations, based on two-phase flow models, are no more reliable, even if their parameters are adjusted to measurements. A comparison of the flooding limit and pressure drop correlations, published by Reichelt and Blaß /40/, which merely require the dimensions of the packings in order to characterize the packed column, with the measured values of Teutsch, Billet and FRi confirms this conclusion (Fig. 7).

Summarizing, it can be said that the fluid-dynamic basis of dimensioning of gas/liquid contacting equipment definitely needs further improvement.

4.2 Mass Transfer

The starting point for determination of the number of actual trays or height of a packed column is usually the number of theoretical stages required for the actual separation problem. The relationship between the actually achieved concentration change and that effected in one theoretical stage is expressed as the Murphree tray efficiency $E_{MG}$, which, in turn, is related to the point efficiency $E_0$ and to the number of transfer units $N_{fG}$ or $N_G$ and $N_L$, obtained in the froth layer:

$$E_{MG} / E_{0G} = f (E_{0G}, \lambda, Pe)$$ (16)

$$E_{0G} = 1 - \exp (-N_{0G})$$ (17)

$$\frac{1}{N_{0G}} = \frac{1}{N_G} (1 + \lambda \frac{N_G}{N_L})$$ (18a)

$$= \frac{1}{N_G} (1 + m \frac{S_G}{S_L} \frac{M_L}{M_G} \frac{D_G}{D_L})$$ (18b)

Since, in most distillation problems, the slope $m$ of the equilibrium curve for all components differs only slightly from unity, the resistance lies predominantly in the vapour phase, i.e., $N_{0G} \approx N_G$. The two-phase flow on a tray exhibits, at least under froth conditions, a wide bubble size distribution: As Schlünder /41/ has shown, mass transfer under these conditions is essentially determined by the structure of the two-phase dispersion. With $N_{0G} \approx N_G \approx 1$, it follows that $E_{0G}$ is about 70%. The search for a theoretical confirmation of a numerical value which has, for more than half a century, been known from practical experience, can thus be regarded as successfully concluded.
Experience also shows that the numerical value of $E_{MG}$ differs only slightly from $E_{QG}$; theoretically, it could assume values far in excess of 100% under froth conditions and with large column diameters, i.e., long flow paths of the liquid. But the value of $E_{MG}$ is affected by fluctuations in aeration and in liquid flow, caused in turn by fabrication tolerances, by entrainment or weeping of liquid, especially at low liquid loads, and, in particular, by stagnant regions /42/ (Fig. 8). Recognition of unfavourable geometrical configurations and their replacement by better equipment design is of greater importance than the correlation of the Peclet numbers for mixing in the non-stagnant region.

In contrast to the case of tray-type multistage equipment, calculations of continuous mass transfer equipment, such as packed columns, are better carried out according to the $H_{OTP}-N_{OTP}$ concept. If the operating and equilibrium curves are parallel, the height of one theoretical plate HETP is equal to that of one transfer unit $H_{QG}$. The latter increases with increasing gas throughput /43/. The fact that the frequently measured HETP values fail to do so, over a wide range (Fig. 9), again indicates that the two-phase flow is of highly heterogeneous structure. Therefore, in practice, empirical HETP values are usually employed, and since these are doubtful, considerable safety margins have to be applied. In this context, the authors agree with Schlünder /44/ that it would be desirable to set up a model which, for irregular channeling systems, does not rely on the conventional mean values but bases the description of macroscopic effects on the analysis of microscopic phenomena.

With increasing effect of the liquid phase resistance on mass transfer, the situation changes. In tray columns, $E_{QG}$ is substantially less than the standard value of about 70%. Early recognition of these conditions is very important in industrial practice. In the past, the empirical relationship of O'Connell /45/, which Stichlmair /46/ explained theoretically and also improved, has been of help:

The term of main influence on point efficiency $E_{QG}$ (Eqs 17 and 18) is:

$$T = \frac{m}{S_{L}} \frac{S_{G}}{S_{L}} \frac{M_{L}}{M_{G}} \frac{S_{L}}{S_{L}}$$  \hspace{1cm} (19)

With simplifications

$$T \gg 1; \quad S_{L} \sim \frac{S_{L}}{S_{L}} \sim \gamma_{L} \exp \gamma_{G}$$

$$S_{L} \sim M_{G}$$

it follows that

$$N_{QG} \sim \left( m \eta_{L} 0.5 \frac{M_{L}}{S_{L}} \right)^{-1}$$  \hspace{1cm} (20)
and

\[ E_{OG} = f \left( m \eta L, 0.5 \frac{M_L}{s_L} \right). \]

(21)

O'Connell found empirically:

\[ E_{OG} = f \left( m \eta L, \frac{M_L}{s_L} \right). \]

(22)

When the liquid phase resistance predominates, and hence very low values of \( E_{OG} \) are attained, caution is recommended in applying the concept of an equilibrium stage. This is usually the case with absorption or desorption of a slightly soluble gas (i.e., with a high Henry constant). Then the equilibrium stage model leads to incorrect concentration and temperature profiles, especially when two or more components of different solubilities and hence different resistance distributions are being transferred. In such cases, the system of differential equations for simultaneous mass and heat transfer in countercurrent equipment must be solved for each individual component /47, 48/.

In industrial practice, it is nevertheless often necessary to apply an outdated method, namely experiments in a pilot plant and scale-up to production plant. This is partly due to insufficient reliability of the parameters required for a numerical calculation, such as the liquid mass transfer coefficient \( \beta_L \) and the interfacial area \( a \).

Undoubtedly, effort and experience have not been spared in trying to measure the interfacial area; the number of contradictory data presented in literature is truly confusing; some people can still remember the discussion of the correct interfacial area or, rather the correct method of its measurement, at various meetings of the GVC-subject-group. Looking back, it is fair to say that more care and self-critical examination would not be amiss when publishing the results, especially in the case of research institutes. In this light, the work of Hofer and Mersmann /49/ is of merit. It shows that large errors can occur under unfavourable conditions when applying a chemical method (bubble size distribution, depletion of solute in small bubbles; Fig. 10). Equally welcome would be work providing data required for practical use, for example, sufficiently accurate interfacial areas of packings of sizes used in industry.

Chemical scrubbing operations, i.e., the absorption of one or more components of a gas mixture by a chemically reacting solvent are again of particular interest. Examples encountered in industry include the removal of \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) from synthesis gas, the purification of Claus tail gas and the separation of \( \text{CO}_2 \) and \( \text{NH}_3 \). The latter is an example of selective absorption and desorption, with water as the solvent; for this separation, both the temperature dependence of the decomposition of carbonates and carbamate, and the different rates of absorption of \( \text{CO}_2 \) and \( \text{NH}_3 \), are utilized.
Fig. 11 shows the principle of this separation process /47/. In the first stage, about 98% of the ammonia is absorbed by water. These absorbers are designed in such a way that whilst ammonia is absorbed, the amount of carbon dioxide taken up is substantially less than that corresponding to equilibrium. In the second stage, the ammonia absorbed in excess over the carbon dioxide is stripped off. A more detailed analysis of this stage /48/ shows that, in fact, not the desorption of ammonia but rather the absorption of carbon dioxide by aqueous ammonia from a CO₂/NH₃/water vapour mixture formed by the decomposition of the carbonates and the carbamate is involved. A comparison of a simulation, based on the equilibrium stage model, with the actually measured concentration profiles clearly shows the errors entailed in the former. In contrast, a mass transfer simulation gives profiles which fit the measured results very well (Fig. 12).

These comments once again show how widely the field of mass transfer separation engineering overlaps that of chemical reaction engineering. The basic relationships between mass transfer and chemical reaction kinetics have been known since the work of Danckwerts et al. /51/. The literature on this subject is very extensive but such that a chemical engineer working in industry can hardly gain an overall picture. In the authors' opinion, here again a state of development has been reached which merits a critical screening of existing information, in order to process and present it in a form permitting not only a physical understanding of the phenomena involved but also allowing the practical utilization in the solution of problems.

5. Extraction Equipment

In view of the problems which a chemical engineer faces in working on extraction projects, the initial question, whether there is any scope for research left, must appear frivolous.

Reissinger et al. /52/ presented a review of the capabilities and problems of extraction process design. They concluded that a prediction of fluid dynamics and mass transfer on the basis of existing models is, as a rule, not possible and that, therefore, design without experiments is inconceivable. Given this situation, it is right to ask which of the problems require the most urgent attention from the industrial viewpoint.

5.1 Phase Equilibrium

The question of phase equilibrium and of solvent selection has already been discussed. It should be added that the physical properties of the solvent, such as density, surface tension and coalescence characteristics, also play a part in the selection and design of equipment and can therefore affect the choice of solvent.

5.2 Choice of Equipment

In selecting the most suitable extractor for a particular problem, one faces a multitude of very diverse types (Table 3). Each of these can be modified in respect of its performance, sometimes within quite wide
limits, and fitted to the particular problem and principal system in question by varying the geometry of mass transfer devices inserts, the material of their construction and the intensity of energy input /53-56/. The general criteria in selecting equipment include performance, i.e., throughput and separation efficiency, as well as behaviour under partial load (Table 4). These parameters are determined by the fluid-dynamic characteristics of the system and by the design data of the extractor. The fluid-dynamic characteristics depend not only on the density difference, viscosity and interfacial tension, but also on the coalescence characteristics, the mass transfer itself and its direction, as shown by Bender et al. /56/, and other interfacial phenomena. Apart from a rough empirical matrix which permits a certain degree of preselection, systematic criteria which could be assessed objectively, i.e., are measurable, are lacking. Hence, the only possibility left open is to carry out experiments in the equipment to be used in order to match the geometry to the particular system by trial and error. This is extremely time-consuming and expensive, and accordingly individual users tend to confine themselves to a small number of types which are generally accepted within their company.

Therefore, an important role of all the research establishments should be the investigation of performance characteristics of various existing types of equipment, including the variation of geometrical parameters, and an analysis of the factors affecting this variation. Even though accurate predictions will not be made for a long time, it should be possible, through mutual coordination of research work, to define systematic criteria for the selection of equipment. Since physical properties exert a decisive influence, emphasis should be put on the use of test mixtures recommended by the EFCE /57, 58/ (Table 5). Documentary information which permits a comparative assessment /57, 58/ can only be obtained in this way.

5.3 Design of Equipment

In the absence of well-established correlations which permit the prediction of fluid dynamics and mass transfer, the question of scaling up extractors from experimental to production scale is seen to be the key problem. The reliability with which this scale-up question can be answered for a given type of equipment is also a criterion for the selection of equipment.

Complete concepts are available only for stirred columns, RDC /59/, ARD /60/ and the Kühni column /61/, as well as with certain restrictions, for unpulsed sieve-tray extraction columns with downcomers /54, 62/. Such concepts are lacking, in particular, for the industrially widely used pulsed packed columns and sieve-tray columns. With these types of equipment the common practice is to retain the geometry of the mass transfer devices on scaling up from experimental stage and to assume that at the same pulsation intensity, the volume throughput per unit cross-sectional area can remain constant. This implies that droplet size and size distribution, hold-up, interfacial area and mass transfer coefficients, on both experimental and production scale, are identical.

---

a) European Federation of Chemical Engineering
The concentration profile which is set up in the column is, however, also considerably affected by the mixing phenomena in the continuous and dispersed phases, as a result of different paths and velocities of the liquid particles. This axial mixing reduces the driving concentration gradient (Fig. 13). Since these mixing phenomena depend on the diameter, on increase of diameter lengthening of the column is required.

Table 6 presents some well-known scale-up equations for pulsed sieve-tray columns /63, 52/, reciprocating plate columns /64/ and pulsed packed columns /65/. These relationships which, for the most part, are only very inadequately substantiated, do not reflect the fact that the effect of axial mixing on the scale-up factor depends on mass transfer kinetics. According to Miyauchi and Vermeulen /64/, the height of a transfer unit, \( H_{OC} \), under conditions of axial mixing, but assuming plug flow, is approximately made up of the height of a true mass transfer unit \( H^* \) and that of a dispersion unit \( H_{OD} \):

\[
H_{OC,P} = H_{OC} \left(1 + \frac{H_{OD}}{H_{OC}}\right).
\]  

This equation shows clearly that axial mixing is particularly unfavourable where, due to the nature of the system and fluid-dynamic conditions, the parameter which determines pure mass transfer, namely \( \beta_{OC} \), is large, i.e., \( H^* \) becomes small.

More reliable values are obtained with the aid of a scale-up concept, again based on the assumption that on increasing the diameter, the hold-up, interfacial area and mass transfer coefficients remain unchanged, if the geometry of the mass transfer devices stays the same and only the concentration gradient varies as a result of different axial mixing of the two phases. Experimentally, this axial mixing can be investigated, as a purely fluid-dynamic effect, by measuring the residence time distribution of the two phases. In contrast to the procedure for calculating the height of a distillation or an absorption column, calculation of the height of an extraction column must be based on a flow model which describes axial mixing. When using a dispersion model, the following set of differential equations is obtained for the calculation of concentration profiles along the column:

**Dispersed phase:**

\[
\frac{\partial}{\partial t} \left( \varepsilon_d \frac{d c_d}{d t} \right) - \frac{\varepsilon_d}{\varepsilon_d} \frac{d c_d}{d t} - \frac{\beta_{OC}}{\varepsilon_d} \left( c_d - c^*(c_c) \right) = 0
\]  

**Continuous phase:**

\[
\frac{\partial}{\partial t} \left( \varepsilon_c \frac{d c_c}{d t} \right) + \frac{\varepsilon_c}{(1-\varepsilon_d)} \frac{d c_c}{d t} + \frac{\beta_{OC}}{(1-\varepsilon_d)} \left( c_d - c^*(c_c) \right) = 0
\]
Boundary conditions:

\[
\begin{align*}
    z = 0 : & \quad c_c - c_c(0) = -\frac{\partial c_c}{\partial t} = 0 \\
    z = H : & \quad c_c - c_c(H) = +\frac{\partial c_c}{\partial t} = 0
\end{align*}
\]  

(26a, 26b)

(27a, 27b)

With the exception of RDC /67, 68/ and ARD /69/, no measurements of dispersion coefficients exist for any other type of column, which would permit the application of this concept to scale-up. In particular, there is a complete lack of investigations on the effect of the diameter.

Moreover, the most frequently quoted investigations on the subject of axial mixing in pulsed sieve-tray columns, namely the investigations of Miyauchi and Oya /70/, Rozen et al. /71/ and Kagan et al. /72/ do not touch the real problem. These investigations are based mainly on the phenomena in single-phase flow and therefore exclusively consider mixing attributable to the pulsing motion of the continuous phase through the holes. However, under the operating conditions of an extraction column, which are of industrial interest, namely with a substantial content of the dispersed phase, axial mixing is predominantly determined by the state of the droplet dispersion between trays. Here, the local fluctuations in droplet motion, their size distribution and hold-up are primarily responsible for inducing unfavourable circulatory motions. And it is to these circulatory motions that the diameter dependence of performance is attributed. This influence of the dispersed phase, which was not reflected by the above-mentioned publications, is shown clearly by the investigations of Niebuhr and Vogelpohl /73/ (Fig. 14).

Nemeček and Prochazka /74/ have introduced a model (Fig. 15) in which the space between trays is divided into a zone of almost ideal mixing on both sides of the tray with height \( h_1 \), and another zone of height \( h_2 = H_2 - 2 h_1 \), in which mixing is determined by the state of droplet dispersion. The latter constitutes the region which requires attention when increasing the diameter.

Summarizing, it can be said that a purely theoretical prediction, with no experimental support work, is still far away. This is a long-term objective, and research work should not be immediately directed towards it. There are many technological reasons why, in any case, extraction experiments on a pilot scale can never be completely dispensed with. A deeper insight into the complex relationships may help in designing experiments with more specific aims and to reduce the effort involved. However, the primary objective is to make the scale-up risk, entailed in employing an extraction process in industrial production, calculable. This requires two things: i.e., investigation of fluid-dynamic phenomena in a droplet dispersion in industrial equipment and the development of physical model concepts.
6. Concluding Comment

In order to keep up with the progress of knowledge, a chemical engineer must devote a considerable part of his time to the study of literature. Therefore, publications which, from time to time, provide a review of the current state of knowledge, are particularly welcome. In preparing such surveys, the correct scientific practice is to quote the work of others in the same field; however, a multitude of literature reports is often more an expression of lack of knowledge than a provision of well-established information. There is a need to exclude publications which have not contributed any relevant new knowledge, from the reference lists which tend to be universally quoted, over and over again. A chemical engineer concerned with separation processes should be familiar with such a task. Not least of all, this might prevent a situation where an objective reader, e.g., a manager when looking at the sheer column of existing literature, may ask the research workers: "Is there any scope for research left?"

Symbols Used

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Indices
- c: continuous phase
- d: dispersed phase
- G: gas phase
- L: liquid phase
- O: overall based on one phase
- I: interface
- W: water
- *: equilibrium

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1971, paper No. 218.
(65) Spaay, N.A.; Simons, A.J.E.; ten Brink, G.P.: Int. Solvent Extrac-
Nr. 2, pp 113-126.
Nr. 12, pp 844-850.
Fig. 1: Mechanisms of the reactions between formaldehyde and water. Model 1: formaldehyde (F) reacts with water (W) and oligomers (WF).: Model 2: formaldehyde reacts primarily to methylene-glycol (WF), which reacts with other oligomers (WF) under formation of water.

Vapour phase chemical equilibrium:

\[ F + W \rightleftharpoons K_v WF \]

Vapour-liquid equilibrium:

\[ (F)_v \rightleftharpoons (F)_L \]

\[ (W)_v \rightleftharpoons (W)_L \]

Liquid phase chemical equilibrium:

<table>
<thead>
<tr>
<th>model 1</th>
<th>model 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ F + W \rightleftharpoons K_1 WF ]</td>
<td>[ F + W \rightleftharpoons K_1 WF ]</td>
</tr>
<tr>
<td>[ F + WF_1 \rightleftharpoons K_2 WF_2 ]</td>
<td>[ WF_1 + WF_1 \rightleftharpoons K_2 WF_2 + W ]</td>
</tr>
<tr>
<td>[ F + WF_{n-1} \rightleftharpoons K_n WF_n ]</td>
<td>[ WF_1 + WF_{n-1} \rightleftharpoons K_n WF_n + W ]</td>
</tr>
</tbody>
</table>

acrylic acid association \[ CH_2 = CH-COOH \]

association \[ A + A \rightleftharpoons K_a A_2 \Delta h_R \]

Fig. 2: Influence of different assumptions on the grade of vapour-phase-association on the vapour-flow-rate (F-Factor) and condenser-duty (Q_K) of an acrylic-acid-distillation-column.
Fig. 3: Sieve tray pressure drop: Comparison between experiment /28/; this work/ and calculation /26/.
(a) Total pressure drop, (b) dry tray pressure drop (friction factor), (c) static pressure drop
Fig. 4: Performance diagram of a sieve tray with most important capacity limits. Comparison between experimental and calculated (Eq. (10)) weeping limit.

Fig. 5: Generalized pressure drop diagram for packings with flood line (Eckert /33/).
Fig. 6: Flooding velocity and pressure drop of metal Pall rings. Comparison between experiment (Billet /38/, FRI /39/, Teutsch /37/) and calculation (Eckert /33/).

(a) and (c): $F_E$ (Eckert /33/); (b) and (d): $F_E = \frac{a_p}{\varepsilon^3 p}$. 
Fig. 7: Flooding velocity and pressure drop of metal Pall rings. Comparison between experiment (same as Fig. 6) and calculation (Reichelt and Blaß /40/).

Fig. 8: Influence of stagnant regions on column efficiency of one pass cross flow trays /42/ (N: Number of trays).
Fig. 9: Height equivalent to a theoretical plate (HETP) and height of a gas phase transfer unit (H_{0G}) in a Pall-ring packing with gas phase mass transfer resistance dominating (HETP-values experimental: Billet /38/; H_{0G}-values calculated: Onda /43/)

Theoretically (\lambda = 1):

\[ \text{HETP} = H_{0G} \]

\[ H_{0G} = H_0 \cdot (1 + \lambda \cdot \frac{H}{H_0}) \]

Onda:

\[ H_0 = \frac{V_G}{P_G} - F \cdot 0.30 \]

\[ H_{0G} = F \cdot 0.30 \]

Fig. 10: Deviation between chemically determined and geometrical interfacial area on sieve trays because of depletion of solute in the gas phase and bubble size distribution (Hofer and Mersmann /49/).
**Fig. 11:** BASF process for \( \text{NH}_3/\text{CO}_2 \)-separation /50/.

**Fig. 12:** \( \text{NH}_3 \)-desorption in the BASF process. Measured and calculated temperature and concentration profiles (/48/; ○ experimental; — simulation with a mass- and heat-transfer model; --- simulation with an equilibrium-stage model).
Fig. 13: Deformation of the operating line when axial mixing occurs

Fig. 14: Influence of the dispersed phase on the axial mixing of the coherent phase in a pulsed sieve-tray extractor /73/.

Fig. 15: Mixing model of a pulsed sieve-tray extractor /74/.
Table 1: Distribution coefficient $K_g$ in the system solvent (1)/water (2)/acetic acid (3). Comparison between values extrapolated from experimental data and values estimated by UNIFAC-VLE /9/ and UNIFAC-LLE parameters /10/.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>$\gamma$ [°C]</th>
<th>Exp.</th>
<th>UNIFAC VLE</th>
<th>UNIFAC LLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acetate</td>
<td>30</td>
<td>3.47</td>
<td>1.54</td>
<td>0.98</td>
</tr>
<tr>
<td>i-Propyl acetate</td>
<td>70</td>
<td>2.30</td>
<td>1.49</td>
<td>1.24</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>25</td>
<td>3.30</td>
<td>1.44</td>
<td>1.48</td>
</tr>
<tr>
<td>i-Butyl acetate</td>
<td>20</td>
<td>2.46</td>
<td>1.44</td>
<td>1.48</td>
</tr>
<tr>
<td>Ethyl acetoacetate</td>
<td>25</td>
<td>3.90</td>
<td>3.67</td>
<td>1.25</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>27</td>
<td>4.60</td>
<td>3.81</td>
<td>3.02</td>
</tr>
<tr>
<td>Methyl-i-butyl ketone</td>
<td>30</td>
<td>2.97</td>
<td>2.73</td>
<td>2.16</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>20</td>
<td>0.05</td>
<td>0.30</td>
<td>0.75</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>20</td>
<td>0.15</td>
<td>0.49</td>
<td>0.95</td>
</tr>
<tr>
<td>Toluene</td>
<td>25</td>
<td>0.26</td>
<td>0.51</td>
<td>0.79</td>
</tr>
<tr>
<td>Dibutyl formamide</td>
<td>25</td>
<td>18.8</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Tributyl phosphate</td>
<td>25</td>
<td>22.5</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

Table 2: Packing factors $F_E$ for metal Pall-rings.
1: Eckert's (original) factors /33/; 2: Billet /35/, evaluated from flooding data; 3: Krötzsch and Kürten /36/, evaluated from pressure drop data; 4: this work, flooding data (Fig. 6 b); 5: this work, pressure drop data (Fig. 6 c).

<table>
<thead>
<tr>
<th>Pall-Ring Size</th>
<th>Packing Factors</th>
<th>$F_E$ [1/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>25 x 25</td>
<td>157</td>
<td>202</td>
</tr>
<tr>
<td>35 x 35</td>
<td>92</td>
<td>161</td>
</tr>
<tr>
<td>50 x 50</td>
<td>66</td>
<td>115</td>
</tr>
</tbody>
</table>
Table 3: Liquid/liquid extractors

<table>
<thead>
<tr>
<th>Mixer - settler</th>
<th>Box type, Tower type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centrifugal</td>
<td>Podbielniak</td>
</tr>
<tr>
<td>Columns (without energy input)</td>
<td>Spray column, Packed column,</td>
</tr>
<tr>
<td></td>
<td>Sieve-tray column (with downcomers)</td>
</tr>
<tr>
<td>Columns (with energy input)</td>
<td>Oldshue-Rushton, Kühni, RDC, ARD</td>
</tr>
<tr>
<td>a) rotating:</td>
<td>Packed column, Sieve-tray column</td>
</tr>
<tr>
<td>b) pulsed:</td>
<td>Karr column</td>
</tr>
<tr>
<td>c) reciprocating:</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Some criteria for selection of extraction equipment

1. Number of theoretical stages to be realized
2. Throughput, phase-ratio
3. Reliability on scale-up
4. Flexibility
5. System properties: Density difference, Interfacial tension, Viscosity, Coalescence, Corrosivity, Wettability ...
6. Hold-up of dispersed phase
7. Requirements of area or height
8. Maintenance requirements
9. Price
### Table 5: Recommended systems for liquid/liquid extraction studies: important properties at 20° C

<table>
<thead>
<tr>
<th>System</th>
<th>$\sigma$ [mN/m]</th>
<th>$\Delta g$ [kg/m²]</th>
<th>$\gamma_{org}$ [m Pas]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene / Water / Acetone</td>
<td>36.1</td>
<td>133.0</td>
<td>0.584</td>
</tr>
<tr>
<td>Butyl acetate / Water / Acetone</td>
<td>13.5</td>
<td>116.7</td>
<td>0.735</td>
</tr>
<tr>
<td>Butanol / Water / Succinic Acid</td>
<td>1.8</td>
<td>139.6</td>
<td>3.364</td>
</tr>
</tbody>
</table>

### Table 6: Scale-up proposals for pulsed extractors (scale-up from $D_1$ to $D_2$)

<table>
<thead>
<tr>
<th>Extractor</th>
<th>Author</th>
<th>Proposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsed tray column</td>
<td>Logsdail, Thornton /63/</td>
<td>$H_2 / H_1 = \exp (1.64 (D_2 - D_1))$</td>
</tr>
<tr>
<td>Pulsed tray column</td>
<td>Reissinger, Schröter, Bäcker /52/</td>
<td>$H_2 / H_1 = \left( \frac{D_2}{D_1} \right)^{4/3}$</td>
</tr>
<tr>
<td>Reciprocating plate column</td>
<td>Karr, Lo /64/</td>
<td>$H_2 / H_1 = \left( \frac{D_2}{D_1} \right)^{4/3}$</td>
</tr>
<tr>
<td>Pulsed packed column</td>
<td>Spaay, Simons, ten Brink /65/</td>
<td>$H_2 / H_1 = 1.0$</td>
</tr>
</tbody>
</table>
DESIGN ASPECTS OF A CONTINUOUS STRIPPING PROCESS

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Summary: In production of polycondensation products stripping of the excess volatile reactants from the final nonvolatile product is an important separation process in order to assure product's demanded purity. Continuous vacuum steam stripping operation in a multistage column is an effective method to achieve this task. In this work vapour-liquid equilibrium of the system consisted of volatile and non-volatile component is given in form of vaporisation ratio. The comparison between commonly used semi-batch stripping and continuous operation is discussed. The results of the continuous steam stripping operation obtained on adiabatically operating QUICKFIT bubble cap column are presented in form of average stage efficiency with respect to stripping factor.
INTRODUCTION

Steam stripping is a separation process where steam is in direct contact with the system for distillation in either a batch or a continuous operation. The broad use of this separation technique, including theoretical background and experimental results is given in some publications (1-6). Among separation or purification problems where this operation is involved, the separation of relatively small amounts of the volatile component from large amount of nonvolatile liquid component is used. One of the goals of this operation lies either in deodoration of the components with high boiling point, or regeneration of the excess component with low boiling point. In production of different polycondensates the stripping of the excess volatile reactants from final non-volatile product is an example of the use of this technique. The term nonvolatile is applied to polycondensate, having normal boiling temperature over 600 K, and the term volatile component (such as organic alcohols, acids, amines) with the boiling temperature not higher than 450K. When batch reactors are used for polycondensation-reaction the same reactor may serve as batch steam stripper after the reaction is finished.

The additional operation time for stripping, great power input for agitation of viscous liquids and heat losses during the operation are disadvantages of this process. The continuous stripping is an alternative separation technique, which is carried over in a separate apparatus, usually column with plates or packings. The disadvantages from batch process are not so evident in the continuous case, but additional apparatus involves investment costs.

The literature data on batch stripping show that specific steam consumption lies between 0.2-0.6 kg steam per kg organic, when vacuum is applied. Use of vacuum reduces operating costs for steam but demands energy for producing vacuum, so that real comparison between the operation costs at normal and vacuum conditions cannot be done on steam consumption but on energy consumption basis.
FUNDAMENTALS

The system is composed of completely immiscible volatile component (a), nonvolatile component (b) and steam (s). In stripping operations the partial pressure of the distilling component is low. The general equation for the actual mol fraction of volatile component in the vapor phase is given by the equation

\[ y_a = \frac{E \gamma_a P_a X_a}{P_{tot}} \]

where:
- \( E \) - denotes vaporisation efficiency dependent on heat and mass transfer
- \( \gamma_a \) - activity coefficient of component a, measuring the deviation from Raoults law
- \( P_a \) - vapor pressure of pure component a
- \( P_{tot} \) - system total pressure
- \( X_a \) - mol fraction of component a in liquid phase

The equation shows that the concentration of volatile component in vapor phase is directly proportional to the vapor pressure of the pure component a and inversely proportional to the system pressure. In computation of equilibrium composition the variation of activity coefficient \( \gamma_a \) with liquid composition must also be known and taken into account. Ratio \( \gamma_a P_a / P_{tot} = K \) is known as vaporisation ratio and determines the shape of the equilibrium curve in \( y - x \) diagram. It has to be determined experimentaly for the system under consideration.

The design of the stripping column is based on steam consumption and the number of contact stages. The determination of the number of theoretical contact stages is a well known procedure (graphical or numerical). Determination of the number of practical stages demands knowledge of the vaporisation efficiency which has to be obtained on a pilot plant with
the same physical systems and under similar operating conditions. The stripping process on a pilot column must be conducted under specified thermal conditions: the adiabatic operation is an advantageous choice to isothermal operation, because it needs only good thermal insulation. The compilation of the heat balance of the process is done under the assumption that the vaporisation enthalpy of volatile component is provided by the sensible heat of preheated steam and organic phase given by equation

$$b\Delta X_a \cdot \Delta H_a = B c_p b \Delta T_b + S c_p s \Delta T_s$$

where: 
b- flow of nonvolatile component 
s- flow of steam 
c_p- specific heat capacity of b and s respectively 
$\Delta X_a$- composition difference of a per unit of b 
$\Delta T$- difference between inlet and outlet temperature of b and s respectively

EXPERIMENTAL WORK AND RESULTS

Preliminary experiments were carried out in order to eliminate 2-ethyl hexanol (a volatile compound) from dioctyl phthalate (DOP) by preheated vapour steam. Some properties of the above noted components are given.

<table>
<thead>
<tr>
<th>Component</th>
<th>Molar Weight (g/mol)</th>
<th>Boiling Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ethyl hexanol</td>
<td>130</td>
<td>180</td>
</tr>
<tr>
<td>dioctyl phthalate</td>
<td>390</td>
<td>450</td>
</tr>
</tbody>
</table>

Equilibrium partial vapour pressure was determined by means of isosteric scop, while the liquid phase composition by gas chromatographic method.
The process was studied on the pilot scale continuous stripping apparatus, shown in Figure 1. The main part of it represents a bubble cap column \( \phi = 100 \text{ mm} \), with nine stages, made by QUICKFIT, Glastechnik GmbH. Adiabatic conditions were established using good thermal insulation. It was connected to storage tanks for fresh and treated liquid phase, steam preheater and the condenser. Temperatures were measured at various locations of the apparatus and samples of the liquid phase taken before and after stripping. Inlet liquid concentration was held constant, mass fluxes of both phases varied from 0,03-0,3 kg/s m².

Stripping factor, defined as \( KV/L \) at the liquid inlet was taken as a characteristic operating variable. The vapour-liquid equilibrium curve as well as the operating line were plotted in the x-y diagram and the number of theoretical stages determined by graphical method (Fig.2). The obtained number \( n_t \) was divided by the number of practical stages, i.e. 9, to get the average stage efficiency. The relationship between stage efficiency \( E \) and stripping factor \( S \) obtained in a limited number of experiments is presented in Fig.3. The efficiencies are relatively low, probably due to large differences in transport properties of components. The increasing trend with increasing stripping factor was observed, which can be explained with greater transfer coefficients at higher steam rates. More data with improved accuracy is expected in following experiments.

Acknowledgement: The authors express their gratitude to QUICKFIT Glastechnik GmbH, W.Germany for their material support.

Literature index

Figure 1: Stripping apparatus
Figure 2: Determination of number of theoretical stripping stages.

Figure 3: Relation between stripping factor and average stage efficiency.
PRESSURE AND GAS-LIQUID MIXTURE OSCILLATIONS ON SIEVE TRAYS

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Dipartimento di Ingegneria Chimica - PISA (Italia)

SUMMARY

Amplitude and frequency of pressure and gas-liquid oscillations on sieve trays have been characterized in order to point out some aspects and to investigate mutual influence. By means of statistical analysis of experimental data a sharp distinction between two types of the gas-liquid mixture oscillation is possible: Casual Waves (local phenomenon), transverse Waves (involving the whole mixture). Their range of existence is compared with that indicated by other authors. Pressure oscillations ($h_p$) are influenced by the presence of liquid and can be directly correlated with two-phase layer oscillations ($h_L$) when T.W. are present even if $h_L$ is a function of time and space, while $h_p$ is only a function of time.

LIST OF SYMBOLS

\begin{align*}
A &= \text{active area of the plate} \\
A_h &= \text{hole area of the plate} \\
B_s &= \text{Biddulph's parameter (equation |2|)} \\
C &= \text{constant (equation |7|)} \\
D &= \text{column diameter} \\
d &= \text{specific gravity: } d_f, d_g, d_L \\
E &= \text{eddy kinematic viscosity} \\
f &= \text{natural frequency of oscillation} \\
f_o &= \text{observed frequency} \\
g &= \text{acceleration of gravity} \\
G &= \text{gas rate} \\
h &= \text{height: } h_f, h_L \text{ (clear liquid)} \\
h_p &= \text{pressure drop across the plates} \\
h_s &= \text{superficial tension} \\
K_p &= \text{gas flow resistance of holes} \\
K &= \text{ratio of gas specific heats} \\
L &= \text{specific liquid rate (for unit of weir length)} \\
L_p &= \text{plate width} \\
L' &= \text{liquid rate} \\
L_B &= \text{buffer number (equation |5|)} \\
L_d &= \text{damping number (equation |6|)} \\
N_p &= \text{number of plates} \\
P &= \text{absolute pressure in buffer volume} \\
N &= \text{buffer number} \\
P &= \text{buffer volume} \\
w &= \text{wave length} \\
\bar{h} &= \text{mean value of } h \\
\eta_i &= \text{oscillating component of } h \\
\bar{h}_L &= \text{mean value of } h_L \\
\bar{h}_p &= \text{oscillating component of } h_p
\end{align*}
INTRODUCTION

The hydrodynamic behaviour of sieve trays is influenced by the fluctuations of gas pressure and of liquid-vapour holdup. At low gas flow rates the oscillations certainly affect tray weeping, while at higher gas flow rates they can produce an increase of liquid entrainment and even mechanical damages (1,2,3).

Mc Allister (4) identified fluctuations of the vapour-liquid mixture perpendicular to the liquid flow, with wave length equal to one or twice the plate width (Transverse Waves). Other authors (1,5) identified oscillations of the liquid hydrostatic head, with wave length much smaller than tray dimension. A criterion to predict the onset of T.W. was given by Biddulph (6). Recently Wijn proposes a distinction between "oscillations" of the two-phase layer (transverse standing waves) and "pulsations" (with variable amplitude).

Chan and Prince (8) shown the existence of stables gas pressure oscillations at low frequency by the analysis of the dynamic equations of the system, while Priestman and Brown (9) studied the influence of some variables of the system on higher frequency pressure pulsations.

In this work liquid oscillation are characterized by means of statistical analysis, Biddulph's and Wijn's criteria are applied to our experimental data and mutual influence of oscillations is investigated.

EXPERIMENTAL

Experimental runs have been carried out on a rectangular column, made of perspex (PMMA) to permit direct observation of phenomena, using air and water as operating fluids. Details of the experimental apparatus are reported in (1,10,11). In the case of the column operating in the more usual way (that is plate with downcomer), two plates have been used: the lower one had the function of distributing the gas uniformly under the upper plate on which measurements were performed. In the case of operation in the dual flow regime (plate without downcomer), some mo
Difications have been made in the upper part of the column. A toroidal
distribution and a third plate with holes larger than the measurement
plate have been used to achieve a better distribution of liquid. The di-
mensions of column and plate (the same for the two cases) are shown in
Table 1.

Water and gas rates were measured by means of nozzles fitted on the
feed line. Mean values of hydrostatic head ($\bar{h}_L$) and of pressure drop
($\bar{h}_P$) were obtained by the use of several water manometers, while instan-
taneous values of $h_L$ and $h_P$ were measured, at one or two points respec-
tively, by means of differential pressure transducers. In this case, vo-
lumes of connecting tubes were chosen small enough so as not to introdu-
ce phase lag or damping of pulsation. Measurement points under the plate
are: inside the hole for $\bar{h}_L$ and $\bar{h}_P$ measurements and in the gas under
the plate for $h_L$ and $h_P$ measurements. All measurements are referred to
the pressure above the plate.

A statistical analysis of experimental data has been performed by
means of autocorrelation, crosscorrelation and power spectrum of vari-
bles; experimental data were recorder on magnetic tape and then sampled
and transformed by means of a D.E.C. PDP 11/40 computer. Details about
statistical analysis are reported in (10).

**FLUCTUATIONS OF THE TWO-PHASE MIXTURE**

Our experimental data permit us to assert that it is possible to
characterize the oscillating behaviour of the gas-liquid mixture in ter-
ms of two quite different types of fluctuations.

**Casual Waves (C.W.)** appear as irregular variations of two-phase hei-
ght, with low amplitude, with a frequency and wave-length not clearly
determinable and are present in all operating conditions.

**Transverse Waves (T.W.)** may appear on the plate at higher gas rates
and involve the whole mixture which oscillates between the walls paral-
ellel to liquid flow. Those T.W., which have a considerably higher ampli-
tude and dominate the others, have a typical frequency and a wave-length
equal to once or twice the plate width.

A statistical analysis of experimental data confirms the difference between the two types of oscillations. In figure 1 two typical examples of power spectrum of the hydrostatic head, obtained under two different conditions, are shown. In presence of C.W. (figure 1A), there is no dominant frequency and this indicates an oscillation with casual characteristics, while in presence of T.W. (figure 2a) a typical frequency (about 1.75 Hz) is observed.

Thus C.W. are a local phenomenon associated with the passage of the gas through the liquid: bubbling determines lightening of hydrostatic head over the hole and liquid moves from points with higher density towards the hole. T.W. can be seen as an instability phenomenon which involves the plate as a whole: it is possible to characterize frequency, amplitude and onset of T.W.

The frequency of T.W. is well correlated with the natural frequency of steady waves in a homogeneous and inviscid fluid (12):

$$f_N = \sqrt{\frac{g}{2\pi w}} \tanh \left( \frac{2\pi h}{w} \right)$$

if the value $$h = h_f$$ is used; details are given in (13).

The amplitude of T.W. vs. gas rate is shown in figures 2 and 3 for plate with and without downcomer, for different liquid rates; data from (10). The main difference is in the value of T.W. amplitude which for equal gas rates is much lower for the plate with downcomer. A damping of the waves can be presumed, owing to the flow of liquid on the plate in a longitudinal direction and to the flow over the weir into the downcomer, where a part of the energy, given by the gas to the liquid during the bubbling, is dissipated. Another reason for the different amplitude is that the mean value of liquid head on the plate ($$h_L$$) is generally larger for the dual flow operation.

In the case illustrated (10) T.W. appear on the plate with downcomer within the weeping range, while in other cases T.W. appear beyond
the weep point; the two different possibilities depend on dimensions of holes on the plate (13). The onset of T.W. can be located as corresponding to the point of inflection of the curves $|h_L|$ vs. $V$.

Biddulph's criterion, which permits the prediction of the onset of T.W. using a parameter $B_s$, has been applied to experimental data from (10) and (11) for two different column geometries. 

$$B_s = (VE h_f d_g) / (g D^3 d_L d_f)^2$$

with $E = \text{eddy kinematic viscosity calculated according to (14)}$, 

$$d_f = 0.272 V^{-0.61}$$

In particular may be distinguished:

- **Full-wave oscillations** ($W = D$) for $B_s \geq 0.5 \times 10^{-5}$
- **Half-wave oscillations** ($W = 2D$) for $B_s \geq 2.5 \times 10^{-5}$

The test has been performed by calculating the parameter $B_s$ for conditions in which T.W. were obviously present (for the case (10) by statistical analysis of the data, and for the case (11) by visual observation). Under these conditions a value of $B_s$ greater than $B_s^*$, given from equations /4/, ought to result. As can be seen from the table 2 these is a good agreement for case (11), but not good for case (10). This may be due to the fact that in (10) experimental conditions (and in particular hole diameter $D_h = 10$ mm) were very different from those for which had been previously calculated (14) and the criterion itself verified (6) ($D_h \leq 6.35$ m).

Wijn proposes to characterize the macroscale fluctuations of two-phase layer on the plate by means of two dimensionless parameters: $N_B$ (buffer number) and $N_D$ (damping number); defined as

$$N_B = (k \rho_a A / \rho_b A_b) / (n_v d_L g)$$

$$N_D = \kappa (d_f / d_L) (A / A_h)^2 (V / \sqrt{g h_L})$$

Oscillating behaviour, with a typical frequency (function of $N_B$ and
is possible if:

\[ N_D < C \sqrt{\frac{N^*}{N_B}} \] /7/

\( (C = 1.41 \text{ from a theoretical model, } C = 0.35 \text{ from experimental results}), \)
Wijn's criterion has been applied to data for sieve plate with downcomer from (10) and (11) (experimental conditions rather different from Wijn's) and has not given significant results. As it is seen from table 3, Wijn's pulsations are present on the plate in all operating conditions, whether or not there are T.W. Thus with regard to their range of existence, they might be compared with our C.W., but these do not have a typical frequency (see figure 1). Moreover \( N_D \) increases with \( V \) and this fact would lead to a disappear of oscillations at higher gas rates, while in our runs this has never been observed.

**PRESSURE FLUCTUATIONS**

Typical trends of pressure fluctuations, measured in two point anywhere under the plate, are shown in figure 4 A (dry plate) and in figure 4 B (wet plate).

Comparing the two signals recorded in different points (figure 4 A and figure 4 B separately) it is noted that they have the same amplitude and frequency and that there is no lag between them, showing that pressure oscillation have the same value in every point under the plate, whether or not there is liquid.

Comparing the two signals recorded in the same point (figure 4 A vs. figure 4 B) it is noted that at wet plate frequency diminishes and also amplitude results lower, pointing out that presence of liquid on the plate affects pressure drop fluctuations.

To verify if the two oscillating phenomena are directly correlated, a statistical analysis of experimental data has been performed, in terms of crosscorrelations between pressure drop and liquid height oscillations and in terms of power spectra of pressure drop oscillations.
By inspecting power spectra of pressure drops it results that in many cases of operations in presence of T.W., pulsating components at low frequency \( f \approx 2 \text{Hz} \), figure 5 B) are introduced; pressure oscillations at higher frequency, caused by the gas feeding system, are superimposed on them. These components are not found when only Casual Oscillations of \( h_L \) are present (figure 5 A); analogous observations are drawn from crosscorrelations (not shown here).

Thus pressure fluctuations, which are constant in space and variable in time, are influenced by liquid fluctuations, which are variable in space and in time and are responsible for local phenomena, e.g. hole weeping: the hole will be active, with constant pressure in every point under the plate, if:

\[
{h_L} < h_p + h_s
\]

(Analogous considerations apply to the distribution of gas flow rate through single holes).

The low frequency induced on \( h_p \) by \( h_L \) lead us to exclude an influence of liquid oscillations on plate vibration, characterized by higher frequencies (3).

CONCLUSIONS

The fluid dynamic behaviour of sieve plates is influenced both by pressure and two-phase mixture oscillations which can be clearly distinguished in local oscillations (Casual Waves) and oscillations of the whole gas liquid mixture (Transverse Waves).

The onset of T.W. is located experimentally as corresponding to the point of inflection of the curves \( |h_L| \) vs. \( V \); the prediction by means of Biddulph's criterion has been demonstrated valid enough for plates with relatively small holes \( (D_h = 4 \text{ mm}) \), but not so for larger diameters; the application of Wijn's criterion has not given significant results.

The two-phase mixture oscillations affect pressure oscillation and
in presence of T.W. a fluctuating component in the low frequency range is induces, but, while \( h_L \) is a function of space and of time, \( h_P \) is only a function of time.

**LITERATURE CITED**

(2) W.V.PINCEWSKII, C.J.D.FELL - A.I.Ch.E. J. 21(5), 1019 (1975)
(10) A.FRANCHI - Tesi di laurea in Ing. Chimica - Pisa (1979)
(11) R.DEL BIANCO - " " " - Pisa (1971)
### Table 1: Geometrical characteristics of the column used in (10) e (11)

<table>
<thead>
<tr>
<th>Dimension of the plate</th>
<th>Further details</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10)-(11)</td>
<td>(10)-(11)</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>520 415</td>
</tr>
<tr>
<td>Width (mm)</td>
<td>342 190</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>4 4</td>
</tr>
<tr>
<td>Hole diameter (mm)</td>
<td>10 4</td>
</tr>
<tr>
<td>Number of holes</td>
<td>173 278</td>
</tr>
<tr>
<td>Hole area (cm²)</td>
<td>937 263</td>
</tr>
<tr>
<td>Active area (cm²)</td>
<td></td>
</tr>
<tr>
<td>Plate spacing (mm)</td>
<td>300 600</td>
</tr>
<tr>
<td>Weir height (mm)</td>
<td>40 30-50</td>
</tr>
<tr>
<td>Weir length (mm)</td>
<td>342 190</td>
</tr>
<tr>
<td>Column dimension (mm)</td>
<td>642x342 470x190</td>
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<tr>
<td>Downcomer area (cm²)</td>
<td>393 104</td>
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<tr>
<td>Number of plates</td>
<td>2 2</td>
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<tr>
<td>Column area (cm²)</td>
<td>2196 893</td>
</tr>
<tr>
<td>Buffer volume (m³)</td>
<td>0.153 0.036</td>
</tr>
</tbody>
</table>

### Table 2: Verify of Biddulph's criterion

(A) data from (10): F.W. \( w/l_p=342 \text{mm} \), \( B_S=0.5\times10^{-5} \), \( De=400 \text{mm} \)

(B) data from (11): H.W. \( w=2 \) \( l_p=380 \text{mm} \), \( B_S=2.5\times10^{-5} \), \( De=278 \text{mm} \)

<table>
<thead>
<tr>
<th>( lw ) (mm)</th>
<th>( L ) (l/h cm)</th>
<th>( G ) (m³/h)</th>
<th>( V ) (m/s)</th>
<th>( \Delta f )</th>
<th>( \bar{h}_L ) (mm)</th>
<th>( \bar{h}_f ) (mm)</th>
<th>( E \times 10^3 )</th>
<th>( B_S \times 10^5 )</th>
<th>( B_S^* \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) 40</td>
<td>29.24 58.48</td>
<td>360</td>
<td>1.07</td>
<td>0.261</td>
<td>29.3 32.3</td>
<td>112.2 123</td>
<td>4.5 4.78</td>
<td>0.33 0.38</td>
<td>0.5 0.5</td>
</tr>
<tr>
<td>(B) 40</td>
<td>52.5 210</td>
<td>120</td>
<td>1.48</td>
<td>0.217</td>
<td>28 41</td>
<td>128.2 172</td>
<td>8.76 8.07</td>
<td>3.6 3.18</td>
<td>2.5 2.5</td>
</tr>
<tr>
<td>(A) 40</td>
<td>52.5 210</td>
<td>120</td>
<td>1.48</td>
<td>0.217</td>
<td>28 41</td>
<td>128.2 172</td>
<td>8.76 8.07</td>
<td>3.6 3.18</td>
<td>2.5 2.5</td>
</tr>
<tr>
<td>(B) 50</td>
<td>52.5 210</td>
<td>120</td>
<td>1.48</td>
<td>0.217</td>
<td>28 41</td>
<td>128.2 172</td>
<td>8.76 8.07</td>
<td>3.6 3.18</td>
<td>2.5 2.5</td>
</tr>
</tbody>
</table>

### Table 3: Verify of Wijn's criterion

(A) data from (10): \( N=4.34 \), \( N^*=0.729 \)

(B) data from (11): \( N^*=5.26 \), \( N^*=0.802 \)

<table>
<thead>
<tr>
<th>( L ) (l/h cm)</th>
<th>( G ) (m³/h)</th>
<th>( V ) (m/s)</th>
<th>( \bar{h}_L ) (mm)</th>
<th>( N_D )</th>
<th>&quot;Pulsation&quot;?</th>
<th>T.W.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) 29.24 58.48</td>
<td>180 180</td>
<td>0.71 0.71</td>
<td>10 20</td>
<td>0.167 0.118 0.226</td>
<td>YES YES YES</td>
<td>NO NO YES</td>
</tr>
<tr>
<td>(B) 29.24 58.48</td>
<td>180 180 560</td>
<td>0.71 1.66</td>
<td>10 20</td>
<td>0.167 0.118 0.226</td>
<td>YES YES YES</td>
<td>NO NO YES</td>
</tr>
</tbody>
</table>
Figure 1: Power spectrum of liquid oscillation
(A): Casual Waves
(B): Transverse Waves

Figure 4: Instantaneous values of pressure drop across the plate; (A): Dry plate \( (G=360\text{m}^3/\text{h}) \)
(B): Wet plate \( (G=360\text{m}^3/\text{h}, L=29.24 \text{ l/h cm}) \)

Figure 5: Power spectrum of pressure oscillation in presence of liquid:
(A): Casual Waves
(B): Transverse Waves
Figure 2: Amplitude of liquid oscillation for sieve plate with downcomer

Figure 3: Amplitude of liquid oscillation for sieve plate without downcomer
The efficiency of a distillation or absorption column can theoretically be doubled by operating the column in a periodically cycled mode provided that the liquid of each plate is transferred exactly to the plate below during the liquid drain period and without mixing. The experimental study of liquid flow through a single stage column showed that a short packing fitted between adjacent downcomerless sieve plates significantly improves the liquid transport with respect to mixing compared with a sieve plate column without downcomer. A mathematical model for the instantaneous mass transfer in such a single packing sieve plate unit is proposed and the model parameters are evaluated from the experimental data obtained by desorbing ammonia from water by air. The results show an improved mass transfer efficiency in comparison with the single sieve plate without packing. Thus, the investigated construction essentially fulfills the requirements for operating a column successfully in the cycled mode.

INTRODUCTION

In absorption or distillation columns operated with periodic cycling, the continuous counter-current flow of the phases is replaced by an alternate flow of gas and liquid through the column. Two modes of operation exist: the gas flow period (GFP) during which an instationary mass transfer occurs on each plate and the liquid drain period (LDP) during which the gas flow is interrupted and the liquid on each plate is allowed to flow to the plates below. The reported duration of the flow periods ranges from 5 to 80 seconds for the GFP and from 1 to 3 seconds for the LDP. Alternating mass transfer and liquid movement in a periodically cycled column avoid backmixing of the liquid influenced by the gas phase which occurs in conventional sieve plate columns with downcomers. Therefore, larger mass transfer driving forces are available than with steady state operation.

The mass transfer theory of a periodically cycled plate column based on a linear mathematical model from Duffy and Furzer (1) indicates that the cycled column should operate with separations equivalent to a conventional column containing twice the number of plates. Experimental results of McWhirter and Lloyd (2) showed these high levels of performance in a periodically cycled
column of 150mm in diameter. Other results failed to meet the theoretical improvements in performance (3), (4), (5). It is obvious that the predominant reason for only moderate improvements is the use of simple downcomerless sieve plates. At the begin of the liquid drain period the liquid falls down rapidly from each plate and mixes with the liquid on the plate below. This produces strong axial mixing of the liquid and decreases the potential improvement in efficiency of a cycled column. For a liquid flow without mixing the tray construction must fulfil two requirements:

1. the liquid of each plate must drain rapidly,
2. subsequently the liquid flow must be delayed and damped to avoid liquid mixing between adjacent plates.

These requirements can be fulfilled easily by fitting a packing in the free space between two sieve plates.

**MATHEMATICAL MODEL**

Figure 1 shows schematically the single packing sieve plate unit during the gas flow period. At the beginning of the gas flow liquid accumulated during the previous LDP is present in the packing and drains slowly to the sieve plate below due to the counter-current gas flow. Mass transfer occurs both in the froth - signed 1 - and in the packing section - signed 2. An unsteady state mass balance including weeping can be written for section 1. Due to the counter-current flow of gas and liquid, time-dependent concentration changes are present in the packing along the z-axis.

![Figure 1: The single packing sieve plate unit during the gas flow period](image)

Figure 2 presents the mathematical model for calculating the composition profiles of gas and liquid through the packing section. The packing is divided into a number of segments of equal volumes which depleted from liquid successively as a
result of the downward motion of the liquid from the packing - in form of a trickle flow with constant film-thickness - to the sieve plate below. Unsteady state mass balances are written separately for each segment (cell) assuming a total mixed liquid holdup. The following equation holds for a selected segment $k$, and contains the overall liquid mass transfer coefficient, the specific interfacial area, the packing volume, the molar density, and the driving force of the liquid concentration:

$$\dot{N}_k = \beta_{\lambda k} \cdot \alpha_{k} \cdot \dot{V}_{\text{ch}} \cdot \bar{p} \cdot \frac{\Delta h_{c,k}}{N_p} \cdot [x_{z,k}(t) - x^* \cdot y_{z,k-1}(t)] \quad \text{(1)}$$

The term $\frac{\Delta h_{c,k}}{N_p}$ is the momentary fraction of the total interfacial area for the segment $k$ at the begin of the gas flow and is given by different equations depending whether a full cell, a partial filled cell or an empty cell is considered.

$$\frac{\Delta h_{c,k}}{N_p} = \begin{cases} \frac{1}{N_c}, & \text{full cell (} k < N_p) \\ \frac{H_2(t)}{H_1(t)} \cdot \frac{N_{p-1}}{N_c}, & \text{partial filled cell (} k = N_p) \\ 0, & \text{empty cell (} k > N_p) \end{cases} \quad \text{(2)}$$

The model consists of a system of nonlinear first order differential equations which must be solved numerically on a computer. The solution can be expressed as a function of the plate efficiency, the mass transfer coefficient for the packing, the modified stripping-factor, the time dependent normalized liquid holdup on the sieve plate, and the weeping-rate.

$$y_{z,k}(t) = f(\varepsilon_k, \beta_{\lambda k}, x^*, H_1(t), \dot{W}') \quad \text{(5)}$$

Several experiments are required to determine the numerical values of the afore-mentioned parameters.
Measurements of the liquid residence time in a single packing sieve plate unit show which kind of packing, regular and irregular, is more suitable to obtain an almost ideal liquid movement from one plate to the plate below without mixing during the LDP. Figures 3 and 4 show the measured residence time, the experimental procedure, and the geometry used in the experiments.

Using an irregular packing of Raschig-rings 15x15x0.4 retarded the liquid motion in the investigated unit; the constant time delay was about 1.2 seconds. The free spaces and the gussets in or between the Raschig-rings have an additional damping effect on the liquid flow like a storage tank. Therefore, at short times, the shape of the curves in figure 3 is independent of the mass of liquid drained to plate.

**Figure 3:** Liquid flow through the sieve plate and the Raschig ring-packing

**Figure 4:** Liquid flow through the sieve plate and the MELLAPAK
Similar plug flow conditions are obtained by using a regular packing e.g. the SULZER-MELLAPAK (figure 4). However, the time delays of the liquid flow attainable by such regular packing were significantly lower than those obtained with the irregular packing and were dependent on the loading. This may be attributed to the smooth surface of the MELLAPAK causing a considerable lower storage capacity.

The liquid motion from the packing to the bubbling zone between the sieve plate and the packing during the GFP can be determined by continuous measurements of the liquid holdup in the packing. Figure 5 shows measured and recalculated time-dependent holdups in the packing. The shapes of the curves are mathematically expressed in the form:

$$\frac{H_2(t)}{H_2(0)} = (1+a_1 t + a_2 t^2 - a_3) e^{-a_4 t}$$

(6)

The coefficients $a_1$ to $a_4$ of the equation are optimized by minimizing the sum of least squares between experimental and analytical values.

![Figure 5: Liquid holdup of the packing vs. time](image-url)
MASS TRANSFER RESULTS

A series of experiments were carried out with the system ammonia/water/air under various operating conditions and with different constructions of the single packing sieve plate unit. In each experiment the average concentration of the liquid was measured for different gas flow periods. The measured instantaneous composition profile can be used to obtain the plate efficiency and the mass transfer coefficient as well as the unknown parameters in the mathematical model.

Figure 6 gives the results of an evaluated experiment for a single stage unit equipped with a downcomerless sieve plate and a 200 mm packing of Raschig rings. The upper diagram shows the measured values and the calculated concentration profile with optimal parameters $\epsilon_1$ and $\beta$. A plot of the normalized holdup on the sieve plate including the measured weeping-rate is also shown. The lower diagram shows the time dependent overall efficiency of the single unit which describes the mass transfer performance both on the sieve plate and in the packing as well as the time-averaged overall efficiency $\bar{\epsilon}_{ol}(t_{av})$ of the single unit which is a function of the duration of the gas flow period.

![Diagram](image-url)

**Figure 6:** Instantaneous mass transfer results
The high values of the overall efficiency at the begin of the GFP can be explained as follows: At short times the investigated construction works practically as a column with two separation units. The separation ability of the upper mass transfer unit – namely the packing – is reduced in accordance with the depletion of the packing from the liquid. However, when there is no more flow to the sieve plate section, the overall efficiency of the single unit approaches almost the efficiency of the single sieve plate under the same flow conditions.

The expected improvement in performance obtainable by operating a single packing sieve plate unit in a periodically cycled mode can be determined from the measured and evaluated overall efficiencies of the single unit using the ratio \( \frac{N_{ss}}{N_{pc}} \). 

\( N_{ss} \) is the number of equivalent steady state plates with the same efficiency and \( N_{pc} \) is the actual number of plates in a periodically cycled column (here: \( N_{pc} = 1 \)).

Figure 7 shows the calculated improvements in performance based on the measured overall efficiency (single unit) of the investigated constructions: single sieve plate without downcomer, a sieve plate combined with the SULZER-MELLAPAK and a sieve plate combined with an irregular packing of Raschig rings.

**Figure 7:** Effect of periodic cycling on mass transfer efficiency
The diagram is valid for $\lambda = m \cdot \frac{G}{L} = 1.0$ and for a complete replacement of the liquid of each stage during the LDP ($\phi = 1.0$). The mass transfer results lie between two curves which were calculated by the mathematical model assuming either no weeping or weeping of 25% of liquid holdup. The figure shows that higher overall efficiencies of the single packing sieve plate unit obtained with the combination sieve plate and Raschig-ring packing produces maximum increase in separating ability compared with a steady state column.

**SYMBOLS**

- $a_e$: specific interfacial area
- $G$: gas flow rate
- $H$: liquid holdup
- $m$: equilibrium coefficient
- $N_c$: total number of cells
- $N$: mass transfer rate
- $V$: volume
- $\dot{W}$: weeping-rate
- $x, y$: concentration

- $\beta_{ol}$: mass transfer coefficient
- $\lambda'$: modified stripping-factor
- $\varepsilon_{og}$: overall (gas) efficiency
- $\varepsilon_1$: sieve plate efficiency
- $\phi$: liquid holdup replaced per cycle

**REFERENCES**

In this paper the mathematical model of unsteady state distillation column with bell-plates for association reaction was developed and verified. The effects of association reaction of the binary systems with association one component in both phases taking into account a concentration-dependent liquid phase association constant were investigated. The experiments were carried out at atmosphere pressure by the acetic acid-benzene and acetic acid-toluene systems. The obtained experimental results were compared to computed ones.

INTRODUCTION

Reaction columns are an interesting alternative for numerous reactions, and they have often proved economically advantageous. The effects resulting from superposition of reaction and distillation are demonstrated for a few examples Block-Hegner (1, 2), Suzuki et al. (3), Kaibel et al. (4), Mayer-Wörz (5) and Izarraraz et al. (6).

In comparison to the processes in actual distillation columns the processes in reaction columns are extremely complex. It is therefore advantageous in industrial engineering design to have suitable mathematical models at hand.

In the present paper the mathematical model of unsteady state distillation column with bell-plates was developed for association reaction in binary systems with association one component in both phases.

The effects of association constant to the design of separation systems with association reaction in distillation packed column are studied in the paper (7). The effects of association reaction on the mass transfer, according to the model of two-film theory in packed distillation column are investigated in the paper (8).

The aim of this work was deriving of mathematical model of unsteady state distillation column in which one association reaction occurs on each bell-plate.

MATHEMATICAL MODEL

The model for the simulation of a batchwise operation reaction columns was developed from that of a theoretical plate for pure
distillation, by incorporating the reaction terms into the mass balance and heat balance equations. The column model consists of plates in a counter-current operation (Fig. 1.). The following assumptions are made: phase equilibrium between the streams leaving any plate, complete mixing of the reaction phase, on each plate and equimolal overflow. Tray efficiency is 100%.

Based on these assumptions, the following model equations result for each plate, $1 \leq j \leq N$.

\[
\begin{align*}
\frac{d (v_j x_{ij})}{dt} &= L_{j+1} x_{i,j+1} - L_j x_{ij} - G_j y_{ij} + G_{j-1} y_{i-1} + \Delta R_{ij} \\
\text{or} \\
(L_{j+1} x_{i,j+1})_{t+\Delta t} - (L_j x_{ij})_{t+\Delta t} - (G_j y_{ij})_{t+\Delta t} &+ (G_{j-1} y_{i-1})_{t+\Delta t} + \frac{v_j}{\Delta t} x_{ij} = 0
\end{align*}
\]

Gas holdup is neglected.
Enthalpy balance:

\[
\left( L_{j+1} \right)_{t+\Delta t} - \left( L_{j} \right)_{t+\Delta t} = - \left( G_{j} \right)_{t+\Delta t} + \left( G_{j+1} \right)_{t+\Delta t}
\]

\[
(G_{j-1} H_{j-1})_{t+\Delta t} + (\Delta H_{R,j})_{t+\Delta t} + \left( \frac{v_i}{\Delta t} \right)_{t+\Delta t} = 0
\]

where

\[
\Delta R_i = R_{ij} v_i, \quad R_i = \sum P v_i r_p = k \cdot x_A
\]

and

\[
\Delta H_R = - \sum_{i=1}^{M} \Delta h_i^0 \Delta R_i
\]

Summation equations

\[
\sum_{i=1}^{M} x_{ij-1} = 0
\]

\[
\sum_{i=1}^{M} y_{ij-1} = 0
\]

Phase equilibrium

\[
y_{ij} = K_{ij} x_{ij}, \quad \text{and}
\]

\[
K_{ij} = \frac{y_i (x_{i1}, x_{i1}, T) P}{\rho_0 (T)/P}
\]

Activity coefficients, \( y_i \) by NRTL (9) correlation model are obtained. Reduction vapour – liquid equilibrium data of associated systems is shown in the paper (12).

The solution of the model equations achieved by means of Euler's method (10, 11). According to the developed algorithm a computer program was made.

EXPERIMENTS

The experiments were carried out in a ordinary laboratory.
column with bell-plates at atmosphere pressure by the acetic acid-
-benzene and acetic acid-toluene systems. Investigation was performed
in the glass column of 50 mm inside diameter with ten real bell-plates.
Outside diameter of bell is amounted 30 mm and bell height 25 mm.
The charge consisted from 90 mole per cent of acetic acid.
The composition of the distillate and bottom product were determined
by measurements of the refractive indices by Zeiss refractometer
with an accuracy ± 0.01°C. The distillation was made at different reflux ratio and flow rate through column. Previously, hydrodynamic conditions and optimal vapour velocities through column were investigated.

RESULTS AND DISCUSSION

The obtained experimental and calculated results are presented in Fig. 2 and 3. Comparison experimental and calculated values of the composition through the column vs. time for acetic acid-benzene system is shown in Fig. 2. The comparison calculated and experimental values of the composition vs. time for acetic acid-toluene system is shown in Fig. 3.

CONCLUSIONS

The analysis of the obtained results showed that the developed mathematical model in a good agreement with real distillation column. The derived algorithm with the Euler’s method given a good results and adequately represents the experimental data.

ACKNOWLEDGMENT. The Research Council of Serbia, through Grant provided partial financial assistance for this work. The author wishes to express her gratitude to the Institute THAT, TU Berlin (West) Germany, and DAAD of Germany for a grant which have made this research possible.

NOTATION

N - total number of theoretical plates
M - total number of component
P - total number of reactant
t - time, s
v - volume holdup on plate j
x - mole fraction of associating component
\( x_{ij} \) - mole fraction of component i in the liquid phase on plate j, mol/mol

\( y_{ij} \) - mole fraction of component i in the gas phase on plate j

\( L_j \) - liquid stream from plate j, mol/s

\( G_j \) - vapour stream from plate j, mol/s

\( H_j \) - vapour phase enthalpy on plate j, J/mol

\( h_j \) - liquid phase enthalpy on plate j, J/mol

\( \Delta h_i^o \) - standard enthalpy

\( r_p \) - association reaction rate

\( k \) - association constant

\( P \) - pressure

\( P_{ij}^o \) - saturated vapour pressure

\( T \) - temperature

Greek symbols

\( \nu \) - stoichiometric ratio

\( \gamma \) - activity coefficient

REFERENCES


Fig. 2. The composition of the distillate and bottom product vs. time for acetic acid-benzene.

Fig. 3. The composition of the distillate and bottom product vs. time for acetic acid-toluene.
"HOW TO IMPROVE THE PERFORMANCE OF DUAL FLOW TRAYS"

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Technical University of Vienna, Austria

This article is a report on a new more efficient modification of a dual flow tray with an improved turn down ratio and stability (more adequate for scale-up), conceived and tested in authors laboratory. The tray contains two categories of holes with different diameters instead of openings of the same size.

INTRODUCTION

Dual flow trays possess apart from the "autocleaning property" the advantages of material saving simple construction, low pressure drop, high throughput and high efficiency. Despite of these intrinsic merits the field of application of this type of tray is rather limited because of low turn down ratio. In the last decade there have been some attempts to improve the performance of dual flow trays by modification of the tray deck (1).

For the purpose of improving the turn down ratio and stability of dual flow trays, a new modification of this type of tray was conceived and tested in authors laboratory. This tray contains two categories of holes with different diameters instead of openings of the same size. In the following a brief description of the operation of the tray is given and the influence of the hole diameter on the tray performance is discussed in order to explain the reasoning behind this modification.

The working region of dual flow trays lies between the hold-up point and the flooding point. At low gas velocities (i.e. near hold-up point), there is a significant
influence of the hole diameter on the tray behaviour. In the case of small holes (3 - 5 mm) the gas passes through some holes of the tray and the liquid flows through other holes, whereas in the case of wider holes there is a rather quite flow of both phases in parallel through the same openings; Van den Berg (2). At higher gas velocities there is no such influence of the hole diameter on the operation of the tray.

Due to surface tension effects the tray containing smaller holes starts operating at much lower gas velocities and therefore the operating region of a tray with smaller holes is broader than one with bigger holes. On the other hand a tray with wider holes is less susceptible to fouling and the distribution of the gas phase is more uniform in the liquid phase. The new modification of the dual flow tray thus combines the advantages of smaller holes with those of the bigger holes.

EXPERIMENTAL PROCEDURE

The experiments were conducted at a specially designed column with 310 mm in diameter. The apparatus and the experimental technique have been described in detail in previous papers (3,4). Fig. 1 shows the apparatus schematically.

For this study the column was adapted to carry out the efficiency measurements in addition to the usual hydraulic measurements. For determining efficiency O₂-stripping method was used. The measuring technique employed was similar to that used by Garner et al. (5) with the main difference that oxygen concentration in water was determined by means of an oxygen meter (6).

The oxygen contents of the water entering (which was enriched with oxygen) and of the water leaving the tray
Fig. 1a: Schematic view of the apparatus

b dual flow tray, d pressure transducer,
f liquid container, f' overhead container
i flow meter, k hydraulic section,
n level control o oxygen feed,
u metallic receiver, v liquid distributor,
w weighing arrangement, o1 oxygen meter

Fig. 1b: Modified dual flow tray
were measured. The efficiency was calculated by comparing the change in oxygen content with the maximum possible change, i.e. if the water were leaving with a dissolved oxygen content equivalent to that in equilibrium with the oxygen content of the air.

Altogether 7 different trays were tested (4 dual flow and 3 modified dual flow trays). The geometrical parameters of the tested trays are given in Table 1.

The measurements were made at a constant liquid feed by varying the gas feed as well as where a constant gas flow was maintained and the liquid feed was changed.

TABLE 1 - Geometrical Characteristics of Trays Tested

\[ D = 310 \text{ mm} \]

<table>
<thead>
<tr>
<th>Tray No.</th>
<th>( \phi )</th>
<th>( d )</th>
<th>No. of holes</th>
<th>( P )</th>
<th>( T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>modified dual flow trays</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.1304</td>
<td>( d_1 = 5 )</td>
<td>( n_1 = 206 )</td>
<td>( P_1 = 15 )</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( d_2 = 10 )</td>
<td>( n_2 = 73 )</td>
<td>( P_2 = 30 )</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.1877</td>
<td>( d_1 = 4 )</td>
<td>( n_1 = 484 )</td>
<td>( P_1 = 10 )</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( d_2 = 8 )</td>
<td>( n_2 = 159 )</td>
<td>( P_2 = 20 )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.1875</td>
<td>( d_1 = 4 )</td>
<td>( n_1 = 819 )</td>
<td>( P_1 = 9 )</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( d_2 = 10 )</td>
<td>( n_2 = 48 )</td>
<td>( P_2 = 36 )</td>
<td></td>
</tr>
<tr>
<td>dual flow trays</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.1372</td>
<td>4</td>
<td>819</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>0.1983</td>
<td>6.21</td>
<td>491</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>0.2361</td>
<td>3.91</td>
<td>1475</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>0.2650</td>
<td>14.09</td>
<td>127</td>
<td>24</td>
<td>4</td>
</tr>
</tbody>
</table>
RESULTS

In Fig. 2 and Fig. 3 efficiency $\eta$ and pressure drop $\Delta p$ respectively are plotted against linear gas velocity $v$ and liquid loading $L$ as parameter for tray No.3 (modified dual flow tray). As it can be seen the efficiency $\eta$ increases at first with increasing gas velocity and then remains almost constant, whereas with increasing liquid loading the value of $\eta$ generally decreases. The pressure drop $\Delta p$ increases with increasing gas velocity; there is also an increase in $\Delta p$ as the liquid loading increases. This behaviour is in accordance with the behaviour of the usual type of dual flow trays.

Fig. 5 shows tray efficiencies for five different trays under the same flow conditions (linear gas velocity $v = 2$ m/s). It can be seen that the trays with smaller free area $\phi$ show higher efficiency than the trays having greater free area. The modified dual flow trays (Tray No. 2 and Tray No. 3) show better efficiencies than Tray No. 5, although all these three trays have approximately the same free area. The best values for efficiency shows Tray No. 3.

In Fig. 4 typical pressure drop data are presented for the above mentioned trays under the same flow conditions. It is to be noticed that trays showing higher efficiencies give higher pressure drops too. An exception is Tray No. 3, which shows higher values for efficiency but lower pressure drops than Tray No. 2.

CONCLUSION

The results have shown that the performance of dual flow can be improved significantly through simple constructional measures. The modified dual flow tray shows higher turn down ratio and better stability than the usual type of dual flow tray (more adequate for scale-up purposes).
Fig. 2: Efficiency against linear gas velocity

\[ \Delta_p \quad (kN/m^2) \]

Fig. 3: Pressure drop against linear gas velocity
Fig. 4: Comparison of pressure drops of different trays under the same flow conditions

Fig. 5: Comparison of tray efficiencies of different trays under the same flow conditions
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NOMENCLATURE

d = hole diameter (mm)
n = no. of holes
v = velocity of gas in cross section of the column (m/s)
D = column diameter (mm)
L = flow rate of liquid (m$^3$/m$^2$.h)
P = spacing of holes on a tray (mm)
T = tray thickness (mm)
η = tray efficiency (%)
Δp = total pressure drop across a tray (kN/m$^2$)
ϕ = relative free cross section of tray (m$^2$/m$^2$)

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R.F. PLASMA PREPARATION OF GAS SEPARATION MEMBRANES:
PRELIMINARY RESULTS

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Summary

A preliminary study is presented about the preparation of membranes for gas separation processes using a radio frequency plasma discharge.

The variation of permeability characteristics of a polymer support (Cellgard 2400) when exposed to plasma discharge was studied and correlated with the discharge parameters.
Introduction

Selective permeation of gases through membranes was considered from time to time as practical gas separation technique, and two patents on air separation were issued before the end of the last century (1-2).

No serious attempt was made to appraise the potential of gas separation on a large scale since 1950's when were examined the engineering aspects of several gas separation processes of industrial importance as the recovery of Helium from natural gas, the separation of Hydrogen from refinery gas, the separation of oxygen from air, etc. (3-4).

Since that time large progress has been made in all aspects of gas permeation technology, for example new membranes exhibiting higher permeabilities and selectivities were obtained, equipment for large-scale separation were developed and experience was made in processes design and optimization.

In our Institute people is involved in many research lines on membranes as gas separation, ultrafiltration, pervaporation and reverse osmosis processes; in this paper are outlined only the early results related to plasma R.F. prepared membranes and their application to gas separation.

The method of plasma polymerization is well-known to offer a combination advantages in the preparation of ultra-thin films (5) and although it has not yet been demonstrated, the plasma method should lend to the preparation of membranes in a variety of configurations such as hollow
fibers, tubes, and flat sheets.

Gas plasma generated by electrodeless flow discharge can be considered as a relatively mild radiation source in so far as the effect on many vinyl monomers and organic polymers are concerned (10-12); three major effects seem to be involved, i.e. polymerization of monomers, degradation and crosslinking of polymers.

The details of these effects depend on the experimental conditions such as mode of the discharge, frequency, power, pressure and position along the reactor, etc.

Consequently the results obtained with a particular experimental apparatus may not be generalized to other systems.

Among the various methods of producing a "plasma gas" the inductive one was chosen and a device was built up which allows a severe experimental parameters control.

The final purpose is to prepare membranes by plasma technique depositing ultrathin polymer film directly onto commercial porous supports.

Experimental

The schematic drawing of the apparatus used for R.F. discharges is shown in fig.1; the systems was designed for a severe control of the main discharge parameters and was previously described (6-9).

The R.F. generator, delivering an output power from 0 to 100 W, was operated at 13.5 MHz and connected to
the coil through a network of tunable capacitors.

The delivered and reflected power was monitored by a Wattmeter-SWRmeter mod.43 "Bird Electronic Co." (Cleveland, Ohio) 50-100 W ± 5% F.S.

The pressure in the reactor was measured with a capacitance monometer (Baratron MKS type 220, \(10^{-2}\) - \(10^0\) torr ± 1%) and the flow rate was monitored by using a thermoconductivity flowmeter; the detailed drawing of the cylindrical pyrex reactor is shown in fig.3.

The permeability parameters as selectivity coefficient and gas permeation rate were measured by the apparatus shown in fig.4; two permeability cells were used, with a membrane area of about 5 cm\(^2\), connected with a precision manometer (Budenberg 0-16 Atm. ± 1%) and with classic flowmeters.

To prepare a composite membrane by deposition of an ultrathin film from a plasma it is necessary to know what happens to the polymeric support exposed to the plasma. If the support is plasma susceptible, the degradation and the crosslinking of polymer may overwhelm the polymer deposition plasma and change the characteristics of the substrate polymer.

Due to this fact the first step of our work was to study the variation of the permeation characteristic of a commercial polymeric support when exposed to a plasma discharge.

Cellgard microporous polypropylene film by Celanese Company was chosen and its permeability characteristics are showed below:
Density 0.56 g/cc
Porosity 38 %
Pore density $10 \times 10^9$ pores/cm²
Pore dimension, max 0.02x0.2 μ
Permeability constant for air $4 \times 10^{-5}$ cm/sec.cm².cmHg

About two hundred circular films, with an area of 5 cm², were cut from a roll of Cellgard and were tested with Helium at a differential pressure of 1 Atm.

Only the films showing a permeability to Helium in the range of 10% than average permeability were used in this study. The measured average permeabilities to different gas of unmodified Cellgard 2400 films are showed below.

$$\phi = \frac{N_{cc}}{min \ cm^2 \ Atm}$$

<table>
<thead>
<tr>
<th>Gas</th>
<th>He</th>
<th>H₂</th>
<th>N₂</th>
<th>O₂</th>
<th>CH₄</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>75.0</td>
<td>102.6</td>
<td>28.6</td>
<td>26.4</td>
<td>36.0</td>
<td>23.8</td>
</tr>
</tbody>
</table>

The films were subjected to plasma discharges in Helium at different discharge conditions and the Helium flow rate at a differential pressure of 1 Atm was then measured. The results showed that a good reproducibility is obtained only for longer discharge times, higher reactor pressure and lower input power. Some typical results are listed below showing that with a simple Helium discharge the permeability of the polymer is reduced from 4 to 15 times.

Discharge parameters: He flow rate 15 Ncc/min
  - Power 50 Watt
  - Pressure 0.5 torr
<table>
<thead>
<tr>
<th>Discharge time (min)</th>
<th>R [φ₀/φ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>4.1</td>
</tr>
<tr>
<td>30</td>
<td>11.3</td>
</tr>
<tr>
<td>60</td>
<td>14.2</td>
</tr>
</tbody>
</table>

R is the ratio between the He initial flow rate and the He flow rate after R.F. discharge.

This fact means that in the synthesis of symmetric membranes by deposition of an ultrathin film from a plasma, on this kind of substrate, the variation of permeability characteristics are due both to the deposited film than to the modified substrate.

The results obtained with ethane as polymerizing monomer in the same discharge condition showed greater values of R increasing with discharge time.

Discharge conditions: \( \text{C}_2\text{H}_6 \) flow rate 15 Ncc/min

\[ \text{Power} \quad 50 \text{ Watt} \]
\[ \text{Pressure} \quad 0.5 \text{ torr} \]

<table>
<thead>
<tr>
<th>Discharge time (min)</th>
<th>R [φ₀/φ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>39.1</td>
</tr>
<tr>
<td>15</td>
<td>55.2</td>
</tr>
<tr>
<td>30</td>
<td>78.4</td>
</tr>
</tbody>
</table>

The research program foresees the definition of the permeability characteristics of the membrane to some gases as, \( \text{O}_2, \text{N}_2, \text{CH}_4, \text{CO}_2, \text{H}_2 \) and the synthesis of new films prepared by plasma R.F. discharge of ethane and \( \text{SO}_2 \) mixtures.
FIG. 1

FROM GAS SUPPLY

FLOW METER

PRESSURE REGULATION

FLOW METER

REMOVABLE END

PIRANI GAUGE

MAIN PUMP

CAPACITANCE MANOMETER

FIG. 2

FIG. 3
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LIQUID PERTRACTION OR LIQUID MEMBRANES

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SUMMARY

Some aspects of mass transfer phenomena in a three liquid phase system are discussed. A comparative study is made on double emulsion method and creeping film method using extraction of phenol and copper from diluted liquors as examples. It is shown that both methods are efficient, but the latter should be preferred to avoid negative effects like emulsion swelling and emulsion destruction. The creeping film pertraction is less complicated unit operation easy to be designed and scaled-up, but the pertractor productivity per unit volume is comparatively inferior.
INTRODUCTION

In the last decade one new separational process attracted the attention of many research laboratories. This process, known under several names as pertraction, liquid membranes, carrier mediated extraction, coupled transport, etc. [1,2,3,4,5] is as a matter of fact an integration in time and space between commonly applied in separational practice two consecutive operations: extraction and solvent stripping.

Simultaneous mass transfer in a three liquid phase system, with properly chosen equilibrium conditions, provides some interesting from practical point of view features and possibilities.

![Diagram](image)

The principal advantages of the schemes shown on Fig. 1 follow from the simple fact that combination of two almost freely chosen phase equilibria could provide practically complete removal of any species in a simple one-stage operation. Since the insoluble "membrane" liquid acts as a short time intermedier its capacity and left side distribution coefficient $m_{RS}$ of the solute are
not very important characteristics in cases b,c,d of the figure. This renders possible the introduction of various non-typical solvents or low concentrated solutions of tailor made liquid or solid "carriers" in neutral and harmful organic solvents.

Some examples demonstrating these advantages as well as some of the most reliable techniques for practical realization of the process are given in the experimental part of the paper.

TECHNIQUES FOR PRACTICAL REALIZATION

The integration of extraction and reextraction steps in a single operation using a three liquid phase system is probably very old idea. The absence of industrial processes based on this concept can be explained by the lack of practically suitable method to create a stable system of three liquids F, S and R using very small amount of S providing large interfacial areas and high mass transfer coefficients, and preventing in the same time any direct contact between F and R. In the last decade however, several methods meeting these conditions were developed. Two of them, the double emulsion technique and the creeping film pertraction will be discussed and compared only.

The first technique, proposed some 15 years ago by Li [6] and now widely studied is in fact a three-step procedure. Avoiding details of this method, the principal operation path is: Preparation of the R-in-S microemulsion using a proper emulsifier, treatment of the feed phase F by
this microemulsion in a conventional baffled agitator or extraction column, separation and destruction of saturated emulsion for removal of product liquor \( R \) and recycling the organic phase \( S \) for reuse. Since the typical ratios \( V_F:V_S:V_R \) are \( (10:100):1:1 \) the final product \( R \) is more concentrated solution of extracted solute \( A \). The process diagram is shown on fig. 2.

The creeping film pertractor \([7]\) represents a column packed with sandwich type hydrophylic vertical surfaces, separated by the organic phase \( S \). The feed liquid \( F \) enters the top part of the column, flows down the surfaces as thin creeping films and comes out of the apparatus after being collected in the bottom \( F \)-collector. The other aqueous phase \( R \) flows in parallel along the odd numbered surfaces and comes out from the \( R \)-collector outlet. All three liquids are in continuous movement; \( F \) and \( R \) aqueous solutions driven by gravitational and capillary forces, organic phase—by forced circulation. The simplified diagram of this arrangement is shown on fig. 3. Although the phase ratios \( V_F:V_S:V_R \) in the apparatus are roughly \( 1:2:1 \), the flowrate ratio \( Q_F:Q_R = \gamma \) can be easily controlled in a very wide range up to \( 1:100 \) or more, keeping both interfacial areas and mass transfer coefficients constant. Surfactants are not used in this one-step operation.

![Process Diagram](image-url)
EXPERIMENTAL RESULTS

A. Double emulsion method (DEM)

First studied example was removal of phenol from water. This classical example was chosen for comparison with the previous studies [8,9,10,11,12], as well as to demonstrate one of the advantages of the pertraction concept—the use of "unreasonable" solvents. The microemulsion was prepared mixing by centrifugal pump at 4000 rpm 0.5% (wt) water solution of sodium hydroxide (R) with equal volume middle fraction normal parafines (C_{11}-C_{15}) plus 5% (vol.) sorbitane monooleate (SPAO 30), added as emulsifier. An emulsion prepared in this way contained enormous number closely packed microdroplets of R-phase 1 \text{\mu m} in diameter. 0.5 or 1 l. emulsion E was poured into 20 l. baffled agitator of standard design with turbine impeller and gently stirred and dispersed into 10 liter phenolic water. The initial content of phenol was 100 \text{mg/l} and the pH value 5. The intensity of stirring was controlled in a way that nearly uniform emulsion globules 1 \text{mm}, in diameter were formed. The rate of transfer was measured by analysis of small samples of F-phase.

After some of the experiments recovered emulsion was separated and the amount of the swelled F-phase into emulsion was measured. The rate of emulsion destruction was taken into account also by parallel "blank" runs with destilled water as F-phase, measuring continuously in situ the pH values. Obtained results are shown on Fig. 4.
It is evident that the rate of removal expressed as
\[ r = \ln \left( \frac{C_0}{C_t} \right) / t = K_P \alpha \]
increases with stirring intensity and reduction of phase ratio \( \varphi = V_P / V_R \). The rate of emulsion break-up shows the same trend. The superposition of both phenomena results in typical for this method maximum of the efficiency curve. The position of this maximum depends on many factors and for each particular case should be found experimentally [13]. Another cause for peculiar curve pattern is the continuous change of interfacial area \( (\alpha_{AP}) \), which passes through a maximum too [5]. The mean measured values of \( K_P \) and \( \alpha_{AP} \) (with respect to feed phase) are \( 4 \times 8 \times 10^{-4} \) cm/s and 1 to 6 cm\(^2\)/cm\(^3\). The relatively high values of transfer coefficients \( K_P \) indicate that the liquid 3 is not stagnant inside of compact arrangement of encapsulated aqueous microdroplets of phase R. The amount of swelled water was less than 10 \% with respect to the initial R-phase volume after 35 minutes continuous agitation.

The second test system, illustrating the transfer mechanism shown in Fig. 1-d was: Phase F - solution of copper sulfate (initial concentration - 200 mg/l, initial pH value - 5.4); phase 3 - 2 \% (vol.) solution of ACOR-6100 (o-nonylalcohol) and o-nonylphenol) in the abovementioned paraffins plus 2 \% (vol.) SPA 80 as emulsifier; phase R - 3N sulfuric acid. Emulsion preparation procedure and feed phase treatment were the same as in the previous case. The copper content in F-phase can be analysed by means of atomic absorption spectrophotometer and pH values - by continuous measurement in situ using combined pH-electrode. Analogous procedures were applied to measure emulsion swelling and break-up.

Table 5 presents some typical data obtained with this system. In this case copper transport was accompanied by equivalent countercurrent flux hydrogen ions. The ion exchange mechanism provokes continuous decrease of pH value.
in $P$-phase and hence redution of initialy very high distribution coefficient $m_p$ which depends strongly on pH value (at pH=2 it is more than 200 at pH=0 it falls under 0.05). Nevertheless the mass transfer rates are high enough to provide acceptible very high efficiencies (99%) in a short time period. The swelling effect in this case is more pronounced. It increases with ion strenght of feed solution (for example presence of non extractable metal cations) and deteriorates to some extend separational selectivity. The final product liquor $R$ contents some amount of these non extractable metals too.

B. Creeping film method (CFM)

Both systems described in previous section were subject of second study concerning the creeping film method. The only difference in system formualtions was that in CF-method surfactants were not used. A CF laboratory type pertractor of 600 cm$^3$ volume, including 230 cm$^3$ $S$ phase, and 15 cm$^2$ total cross-section was used. The exposed vertical interfaces were: $a_{P/B}=340$ cm$^2$ and $a_{S/R}=510$ cm$^2$ respectively. The flowrate of receiving liquor $\omega_R$ was kept constant at 5 cm$^3$/h after obtaining that this parameter has no effect on pertraction efficiency until $R$-phase becomes saturated. Varying $P$-phase flowrates ($\omega_P$) in the range of 50 to 300 cm$^3$/h it was possible to produce relatively concentrated solutions of sodium phenolate.
and copper sulfate. The F-phase flowrate and intensity of circulation of organic phase were parameters affecting strongly removal efficiency. Fig. 6 presents the rates of pertraction versus mean residence time calculated from the equation $t = \frac{s_{co1}}{Q_F}$. Curves 1 and 2 correspond to the cases of stagnant organic liquids and curves 3 and 4 - circulating S-phase. The difference is obvious: The circulation controlled by an external pump, reduces several times overall diffusional resistences. The maximum transfer coefficients obtained are equivalent to the coefficients achieved using DE method.

It should be emphasized that phenomena like swelling and back transport inherent to DE technique are avoided as well as the auxiliary operations of emulsion preparation and thermal destruction.

CONCLUSIONS

Liquid pertraction is an efficient separational process, very promising for removal of valuable or toxic components from their diluted solutions. Both tested and compared techniques are suitable for removal of species of various type, using low capacity intermediate (membrane) phase.

The creeping film method, however shows advantages of avoiding the principal shortcomings of DE method as emulsion instability, emulsion swelling and multioperational mode.
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Continuous Extraction of Metals with Liquid Membrane Emulsions in a Kühni Extractor

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At low metal concentrations the solvent extraction technique is not economical. An alternative process is the extraction with liquid surfactant membrane emulsions with different carriers leading to high selectivity and enrichment of particular metal ions in the inner aqueous phase. We are working on separating leaching-liquors of the zinc industry by means of liquid membrane emulsions with several carriers. Especially Zn was separated from Cu and Co by means of Di-2-ethyl hexyl-phosphoric acid (D2EHP) at low pH values in a continuously operated multistage column. During the start-up and steady-state operations of the reactor the longitudinal concentration profiles of solutes were measured as functions of time at different flow rates of both phases and at different stirrer speeds. The multistage column was characterized during these runs by holdups of the phases, the droplet size distributions, longitudinal dispersion coefficients in both phases. Based on these reaction engineering investigations a mathe-
matical model was developed to simulate the reactive extraction process in the multistage column reactor.

Experimental

For industrial extraction with liquid membranes the liquid surfactant membrane system must be transferred from stirred cells to a continuous plant. We used a Kühni extractor which seems to be suitable for this purpose. The advantage of the Kühni extractor is the fact that the residence times and flows of the phases can be varied in a wide range. Furthermore the good dispersion of the emulsion is important because of the high viscosity of the emulsion. The liquid membrane emulsion was made using an Ultra Turrax 4 TS stirrer. The stirring time was 3 minutes at 10,000 rpm. It is important to standardize the production of the emulsion in order to get reproducible results. The metal concentration was analysed by a Perkin Elmer atom-absorption spectrophotometer equipped with an AS 1 autosampler and a teletype with a paper tape puncher. These paper tapes were read in a pdp 11-04 computer (Digital Equipment) and stored on a floppy disc. In order to compute the concentration from extinction a Fortran program was written.

In the following experiments zinc was separated from cobalt and copper with the carrier D2EHP. Initial conditions were:
- temperature: \(25^\circ\text{C}\)
- metal concentration: 100 ppm
- phase ratio org./strip: 1/2
The following parameters were varied:
- stirrer speed
- dispersed phase flow
- continuous phase flow

The axial concentration profile was measured and compared with the concentration profiles which were computed according to the cell model and the dispersion model. Using equation (1) we computed the $k_L$ values with a Fortran program. The $k_L$ value was varied until the resulting concentration profile corresponded to the marginal conditions.

\[
\frac{d^2 c_{zn1}}{dz^2} = \frac{Pe}{(1 - \varepsilon)} \frac{dc_{zn1}}{dz} + \frac{4 k_L L^2 \varepsilon C_{H2X2O}}{D_x d_32 (1 - \varepsilon)} \tag{1}
\]

The backmixing was computed from the distribution function of a Dirac impulse.

Backmixing can be described by two different models /1/:
- the dispersion model /2,3/
- the cell model /4,5/

Figures 1 and 2 show a plot of the dispersion coefficient and the number of cells vs. the continuous flow. The dispersion coefficient is independent of the continuous flow, the computed number of vessels increased from 4 at a flow rate of 50 l/h to 9 at 120 l/h.
The holdup of the extraction

The rate of extraction and the maximum flow of an extraction column are mainly given by the holdup under the respective conditions. The extraction rate is proportional to the specific interfacial area of the two phases, which can be calculated from the droplet size distribution and the holdup. The holdup is a function of the stirrer speed, the medium droplet size and the physical characteristics of the system.

For correlation of the flow rates of the two phases with the holdup a semiempirical equation (2) developed by Misek /6/ was used.

\[
u_r = \frac{u_d}{\xi} + \frac{u_c}{(1-\xi)} = u_o (1 - \xi) \exp \xi (z - 4.1) \quad (2)
\]

For computing the constants \( u_o \) and \( z \) the equation was linearized and \( \ln u_r / (1-\xi) \) is plotted versus \( \xi \).

The maximum holdup is given by equation (3):

\[
u_{df}^2 = \frac{2 \cdot \xi_f}{(1 - \xi_f + (z-4.1) \cdot \xi_f^2/2 - 1/2)} \quad (3)
\]

\[
u_{cf} = \frac{u_{df}^2}{(1-\xi_f)^2 (1-2 \xi_f + (z-4.1) \cdot (\xi_f^2 - \xi_f^2))}
\]

Figs. 3, 4 and 5 show the holdup as a function of the flows, of the continuous and dispersed phase and of the stirrer speed. The plots show the expected results. The holdup increases with the flow and the stirrer speed.
Continuous zinc extraction

The continuous extraction of zinc was studied to demonstrate that the Kühni extractor may be used with the liquid surfactant membrane system. The effects of the flow rate of the two phases and the stirrer speed on the extraction rate and the selectivity were tested.

In these experiments the temperature (25 °C), the initial metal concentration (c_{me0} = 100 ppm for Zn, Cu, Co) and the phase ratio (org/strip = 1/2) were kept constant.

Fig. 6 shows that the zinc extraction depends on the continuous flow rates (dispersed flow = 5 l/h, stirrer speed = 100 rpm). The extraction rate decreases from 60 % at a flow rate of \( v_c = 70 \) l/h to 35 % at 100 l/h.

Within the range from 100 l/h to 150 l/h the extraction rate remains nearly constant.

The concentration profiles computed with the dispersion model show good agreement with the experimental data (Fig. 7).

The \( k_L \) values obtained from the dispersion model were used to compute the extraction with the cell model.

Fig. 8 shows that an increase in the dispersed phase flow causes a linear increase in the extraction rate due to the higher holdup. A higher stirrer speed effects a strong increase in the extraction rate as well (Fig. 9) the reason being a smaller average droplet size and a higher interfacial area.
Fig. 1: Dispersion coefficient vs. continuous flow

Fig. 2: Number of vessels vs. continuous flow

Fig. 3: Holdup vs. continuous flow

Fig. 4: Holdup vs. disperse flow

Fig. 5: Holdup vs. stirrer speed
Fig. 6: Zinc extraction vs. continuous flow

Fig. 7: Comparison of computed axial concentration profiles
with experimental data
Fig. 8: Zinc extraction vs. dispersed flow

Fig. 9: Zinc extraction vs. stirrer speed
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CARRIER MEDITATED EXTRACTION IN A MIXER - DUAL FILTER SYSTEM

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ABSTRACT

A possibility to combine advantages of liquid-liquid extraction and liquid membrane systems was investigated. Using the principle of dual membrane separation, with simultaneous filtration of phases through a pair of hydrophilic - hydrophobic membranes, a new carrier mediated extraction unit was built. The unit represents one combined extraction-stripping stage, or a liquid membrane system with two water phases separated by an organic phase liquid membrane. By circulating the organic phase, through the membrane, between water phases and by the dispersion of organic phase in both water phases very high stage efficiencies were obtained. The possibility to connect such units into a battery was discussed.

Introduction

There are three basic types of carrier mediated extraction systems. The first "liquid membrane" system consists of two liquid-filled half-cells divided by an immiscible liquid film supported by a highly porous membrane\(^1,2\). The second "double emulsion" system consists of a column through which a continuous phase flows countercurrently to droplets formed of two immiscible phases\(^3,4\). The third system was developed by Boyadzhiev\(^5\) and Nakovar\(^6\). The unit consists of two aqueous phases divided by a porous hydrophobic membrane through which an organic phase is cycled using pressure pulsations. Basically all three types represent combined extraction-stripping systems with one or more extraction and stripping stages.

Using the principle of dual phase separation\(^7\) and data obtained on liquid phases separation, using hydrophilic and hydrophobic membranes\(^8\), a new type of the carrier mediated extraction system was developed and tested.

The system is based on an active transport of the carrier - organic phase, which is finely distributed in two aqueous phases and transported between them through a hydrophobic membrane. The organic phase is carrying a certain component from the extraction stage to the stripping stage of the system, and from the stripping stage is circulated back into the extraction stage, through another hydrophobic membrane. Aqueous phases are

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removed from the extraction and the stripping stages through two hydrophilic membranes, respectively. Flow diagram of the system is presented in the Figure 1.

Fig.1. Flow diagram of the mixer-dual filter system for a carrier mediated extraction

Experimental

To test the new system a laboratory scale extractor with one extraction and one stripping stage was built. The unit was machined from a block of plexiglass and membranes were produced from porous glass filters (G-2), by settling into the pores a suspension of graphitic oxide particles for hydrophilic membranes and graphite particles for hydrophobic membranes. As an alternative for hydrophobic filters, felt discs, based on polypropylene fibers, were used. The procedure of membranes preparing is given in the paper\(^9\). Both half cells were provided with stirrers. The construction of the unit is presented in the Figure 2.

Flows of both water phases was maintained by vacuum systems and flow of the organic phase, from the stripping section to the extraction section, by the piston metering pump. Pressure differences were measured by U manometers and flow rates of liquids by siphon elements.

To test the system a phenol solution in water was used as the first aqueous phase, kerosene, or diethyl ether in kerosene were used as the organic phase and a sodium hydroxide in water solution or water were used as the other aqueous phase.

Contents of phenol were measured using a spectrophotometric method\(^9\).
The feed solution, with the phenol concentration $C_1^0$ and flow rate $V_1$ flows through the half cell I and after mixing with the organic phase outlets through the hydrophilic membrane 1, with the phenol concentration $C_1$. The stripping solution, with the phenol concentration $C_2^0$ (usually equal to zero) and the flow rate $V_2$ flows through the half cell II and after mixing with the organic phase outlets through the membrane 3, with the phenol concentration $C_2$. The organic phase passes from the half cell I into the half cell II, through the hydrophobic membrane 4, with the phenol concentration $C_{or}^0$ and the flow rate $V_{or}$. From the half cell II the organic phase with the phenol concentration $C_{or}$ passes through the hydrophobic membrane 2 and is pumped into the half cell I.

Experiments were repeated with different flow rates and concentrations. Experimental runs were continuous and with constant flow rates and inlet concentrations for one run.

Maximal pressure differences at the graphitic oxide membranes were 20 kPa and at the polypropylene membranes 0.3 kPa.

Results and discussion
The results of experiments are presented in the Table 1.
Table 1. Experimental results of carrier-mediated extraction using two-cell mixer-filter

<table>
<thead>
<tr>
<th>No.</th>
<th>$C_1^O$ (ppm)</th>
<th>C.D.E. (V%)</th>
<th>$C_{NaOH}$ (%)</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$V_1$ (cm$^3$/sec)</th>
<th>$V_2$</th>
<th>$V_{or}$</th>
<th>$C_1$ (ppm)</th>
<th>$C_2$ (ppm)</th>
<th>$C_{or}$ (ppm)</th>
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<tr>
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<td>0.0017</td>
<td>0.05</td>
<td>0.017</td>
<td>0.17</td>
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<td>0.017</td>
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<td>0.4</td>
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<td>0.0017</td>
<td>0.03</td>
<td>0.012</td>
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<td>33.0</td>
<td>27.9</td>
<td>175</td>
</tr>
<tr>
<td>4</td>
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<td>0.4</td>
<td>0.16</td>
<td>0.0017</td>
<td>0.025</td>
<td>0.012</td>
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<td>27.0</td>
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<td>0.0017</td>
<td>0.013</td>
<td>0.012</td>
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<tr>
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<td>0.05</td>
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3rd CHEMICAL ENGINEERING CONFERENCE
Experimental results were compared with calculated values of concentrations \( C_1 \) and \( C_2 \), using expressions derived from material balance equations

\[
C_1 = \frac{1 + n_2 D_2}{1 + n_1 D_1 n_2 D_2} C^0
\]

(1)

\[
C_2 = \frac{n_2 D_1}{1 + n_1 D_1 n_2 D_2} C^0
\]

(2)

where \( n_1 = \frac{V_1}{V_1} \) and \( n_2 = \frac{V_2}{V_2} \) are distribution coefficients in half cells I and II. \( D_1 \) and \( D_2 \) are distribution coefficients.

From the Table 1 it is visible that errors are not large and are produced mostly by errors in measurements and controls of flow rates. In all experiments the loss of organic phase was negligible and both outlet aqueous phases were substantially without traces of organic phase.

From the results it can be seen that ratios \( n_1 \) and \( n_2 \) are acting as multiplying factors for distribution coefficients and that by proper adjustment of these ratios optimal concentrations \( C_1 \) and \( C_2 \) can be obtained.

Mixer-filter systems can be connected into a battery in different ways. Connection into a multistage extractor is presented in 7). Also, it is possible to connect single or double cells into a multistage carrier mediated extractor, or into a multistage fractional extractor. The Figure 3 shows a battery of three double cells with three extraction stages and three countercurrent stripping stages. There are three separate organic carrier streams in the crossflow. Methods of calculation for different mixer-filter batteries and numerical results obtained on computer are presented in 10). Using experimental data from the Table 1, for the battery presented, ratios \( C_2/C_1 \) for phenol in outlet streams was calculated and it was found that maximal practically possible value is

\[
C_2/C_1 = 54.700
\]

Conclusion

Experiments on a laboratory double cell mixer-dual filter system had shown high reliability, simplicity and flexibility of this system, compared to the existing liquid membranes and carrier mediated extraction systems. Very large contact areas between the organic and both aqueous phases ensure high mass transfer rates and dual membranes ensure an excellent phase separation. By the adjustment of flowrates ratios optimal enrichment and stripping factors can be obtained either for one double cell, or for different multistage batteries. Pressure differences at membranes were
rather small. The life of all membranes used was more than three months and settled membranes are easy for regeneration.

Fig.3. Carrier mediated extractor with three extraction and three stripping stages

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A COMPUTER CODE FOR CALCULATION OF SOLVENT-EXTRACTION SEPARATION IN A MULTICOMPONENT SYSTEM WITH REFERENCE TO NUCLEAR FUEL REPROCESSING.

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A B S T R A C T

Nuclear technology development pointed out the need for a new assessment of the fuel cycle back-end.

Treatment and disposal of radioactive wastes arising from nuclear fuel reprocessing is known as one of the problems not yet satisfactorily solved, together with separation process of uranium and plutonium from fission products in highly irradiated fuels.

Aim of this work is to present an improvement of the computer code for solvent extraction process calculation previously designed by the Authors.

The modeling of the extraction system has been modified by introducing a new method for calculating the distribution coefficients. The new correlations were based on deriving empirical functions for not only the apparent equilibrium constants, but also the solvation number.

The mathematical model derived for calculating separation performance has been then tested for up to ten components and twelve theoretical stages with minor modifications to the convergence criteria.

Suitable correlations for the calculation of the distribution coefficients of Uranium, Plutonium, Nitric Acid and fission products were constructed and used to successfully simulate several experimental conditions.
INTRODUCTION

After some years of standstill owing to the inability of industry to overcome the technical and economic problems associated with safeguarding and handling of highly radioactive materials, fissionable material recovery from spent nuclear fuel, or reprocessing, is now taken into account as a compulsory path to allow continued growth to the use of nuclear fission energy.

As far as the technical aspects are concerned, basic reprocessing technology for Light Water Reactor's fuels is that developed for the Hanford and Savannah River Plants by the U.S. Atomic Energy Commission (USAEC), and its main operation is a solvent extraction process from an aqueous solution.

This process (PUREX) has to be modified because the composition and exposure levels of the fuel to be processed by industry differ considerably from that processed by the USAEC. In addition, new safeguard problems aim at avoiding any purified Plutonium streams and new environmental rules stress the maximum recycle of aqueous effluents.

There are only a few computer codes available for the simulation of solvent extraction operation in the recovery of the fissionable material. This is based upon the formation of an extractable complex between the nitric salt of the cation and some extractant molecules at the interfaces. The simulation capacity of these computer codes should be improved not only to develop and analyse alternative flow-sheets but also to make possible the incorporation in automated systems for control of solvent extraction operations.

In this paper, two well-known computer codes are briefly compared to the one previously designed by the Authors. A new method to obtain empirical functions for the calculation of HNO₃, actinides, selected fission products distributions in the system metal nitrates-nitric acid/TBP-diluent is then illustrated. These empirical functions were utilized in the above mentioned computer code.
The most representative computer codes available in literature are the SEPHIS /7, 8/ and the REPROSY-P /9/.

The SEPHYS computer program models the stage-wise operation of one or more solvent extraction columns operating in series. The program works in term of solute-free-solvent basis and deals with three solutes: Uranyl nitrate, Plutonium IV nitrate (Plutonium III nitrate) and nitric acid between aqueous and TBP carbon-tetrachloride diluent organic phases.

The REPROSY-P code evaluates the Plutonium purification process for TBP-HNO₃-Pu system. It has been prepared on the basis of a batchwise counter-current extraction cascade model.

The code developed by the Authors allows a counter-current solvent extraction operation to be calculated, the component number N and stage number M being virtually unlimited.

The numerical solution of the N systems of M non-linear equations which take into account the material balances (1) and equilibrium relationships (2) for each stage and each component, is based upon the modified version of the Newton method according to Broyden. (Fig. 1).

\[ A_{j-1} x_{j-1,i} + F_{j,i} x_{j-1,i} + O_{j-1,i} y_{j-1,i} + S_{j,i} y_{j-1,i} = A_j x_j + O_j y_j + F_j x_j + S_j y_j \]  

(1)

\[ y_{j,i} = D_{j,i} x_{j,i} \]  

(2)

With reference to the typical extraction reaction

\[ M_{i}^{p+} + pNO_{3}^{-} + qE \rightleftharpoons M_{i}(NO_{3})_{p} \cdot qE \]  

(3)

where

- \( M_i \) = metal-containing cation
- \( NO_{3}^{-} \) = nitric ion
- \( E \) = extractant molecule
- \( p \) = charge of metal-containing cation
CHARACTERIZATION OF THE EXTRACTION SYSTEM

The distribution coefficient relative to eq.(2) can be theoretically expressed as follows:

\[ D_i = K_i \left( X_{NO_3} \right) P_i \left( Y_E \right)^q_i \]  \hspace{1cm} (4)

where

- $K_i$ = equilibrium constant of reaction (3)
- $X_{NO_3}$ = total $NO_3^-$ concentration in the aqueous phase
- $Y_E$ = free extractant concentration in the organic phase

In many practical conditions eq.(4) is not suitable for fitting the experimental observations thus leading to a large number of empirical functions.

The use of correlations chosen among the most representative ones based upon the ionic strength \cite{10,11,12}, total $NO_3^-$ \cite{8}, or the only nitric acid concentration in the aqueous phase \cite{20} was found to be inaccurate, especially in the case of high Uranium concentrations.

The empirical characterization of the system has been then improved assuming that not only $K$, but also $q$, might vary versus the phase composition. This assumption is well supported by several experimental results \cite{17,18}, which show that the number of extractant molecules taking place in the complex might vary within a certain range of the usually known value. A large number of experimental data were elaborated by using a direct-iteration method, where for each component the usually known value of the solvation number was chosen as a starting point.

In this way, the correlations obtained which are summarized in Table I, exhibit mean standard errors remarkably small, if we take into account some lack of precision in the experimental procedure.
The comparison between the correlations developed in this work and those selected in the literature for the same phase composition is shown in Fig. 2 for Uranium (low and medium concentrations), Zirconium and Nitric Acid. It is possible to notice the capacity of the new correlations to match experimental data of several Authors.

**CONCLUSIONS**

A computer code for calculation of solvent extraction separation in a multicomponent system has been modified in order to calculate distribution coefficient with whatever function. The utilization of the new correlations in the computer code for a 12-stage, 10-component run, which simulates the first column of a PUREX process operating with a feed composition typical of LWR's fuels, was found to be much more efficient than that of the other correlations, since it leads to a better reconstruction of the observed decontamination and recovery factors.

![Diagram](image)

**Fig. 1 - Material balance for the j-th stage**

- $A_j, X_j$ aqueous, organic flow (interstage)
- $F_j, S_j$ aqueous, organic feed
- $\bar{F}_j, \bar{S}_j$ aqueous, organic outflow
- $x_{j,i}, y_{j,i}$ aqueous, organic concentration for the $i$-th component
- $o_{j+1}, y_{j+1,i}$
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>RANGE</th>
<th>Ref.</th>
<th>K</th>
<th>q</th>
<th>p</th>
<th>H.E.E.</th>
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<tr>
<td>HNO₃</td>
<td>0-4 M HNO₃</td>
<td>13</td>
<td>0.5560-0.2753x+0.0411x²</td>
<td>1.61/(x+0.1419)-0.2055</td>
<td>1</td>
<td>8.5</td>
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<td></td>
<td>2.5-6 M HNO₃</td>
<td>13</td>
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<td>1.61/(x+0.1419)-0.2055</td>
<td>1</td>
<td>1.9</td>
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<td>UO₂(NO₃)₂</td>
<td>0-5 M HNO₃ 0-30 C g/l U</td>
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<td>16.70-3.371x+0.2951x²</td>
<td>2.286-0.1659x+0.0186x²</td>
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<td>16.8</td>
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<td>0-1 M HNO₃ 0-25 C g/l U</td>
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<td>16.07-16.24x+4.161x²</td>
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<td>1-2 M HNO₃ 0-200 g/l U</td>
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<td>15</td>
<td>2.566/(x+0.2122)-0.5742</td>
<td>1.971x+0.02038x+0.0457x²</td>
<td>4</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>1 M HNO₃ 0-300 g/l U 0-50 g/l Pu</td>
<td>15</td>
<td>1.559/(x+0.7021)-0.3595</td>
<td>1.338x+0.1658x+0.0265x²</td>
<td>4</td>
<td>12.2</td>
</tr>
<tr>
<td>Pu(NO₃)₂</td>
<td>0-1 M HNO₃ 0-300 g/l U 0-50 g/l Pu</td>
<td>14</td>
<td>5.401/(x+0.4926)-0.9483</td>
<td>3.262x+0.867x+0.1065x²</td>
<td>4</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>1 M HNO₃ 0-300 g/l U 0-50 g/l Pu</td>
<td>14</td>
<td>-3.495/(x+8.600)-0.2036</td>
<td>1.280x+0.3471x+0.0316x²</td>
<td>4</td>
<td>20.9</td>
</tr>
<tr>
<td></td>
<td>4 M HNO₃ 0-300 g/l U 0-100 g/l Pu</td>
<td>14</td>
<td>0.6135/(x+2.381)-0.1369</td>
<td>-0.0199x+0.8076x+0.0732x²</td>
<td>4</td>
<td>21.7</td>
</tr>
<tr>
<td>Pu(NO₃)₂</td>
<td>0-0.5 M HNO₃ 0-5 g/l Pu+4 0-60 g/l Pu+3</td>
<td>13</td>
<td>0.04392/(x+0.2366)+0.0323</td>
<td>1.0066/(x+0.2257)+0.0533</td>
<td>3</td>
<td>20.5</td>
</tr>
<tr>
<td>Zr(NO₃)₆</td>
<td>1-4 M HNO₃</td>
<td>21</td>
<td>0.0366-0.0316x+0.0038x²</td>
<td>2.159x+0.1276x+0.0251x²</td>
<td>4</td>
<td>8.8</td>
</tr>
<tr>
<td>Ru(NO)₂(NO₃)₂</td>
<td>0.25-1.5 M HNO₃</td>
<td>16</td>
<td>1.114/(x+0.06494)-0.06302</td>
<td>4.294-2.590x+1.161x²</td>
<td>2</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>1.75-3.5 M HNO₃</td>
<td>16</td>
<td>0.04277/(x+1.432)-0.01510</td>
<td>7.190-3.620x+0.7466x²</td>
<td>2</td>
<td>16.9</td>
</tr>
<tr>
<td>Ru(NO)₃(NO₃)₃</td>
<td>0.25-1.5 M HNO₃</td>
<td>16</td>
<td>337.9/(x+0.2073)-253.9</td>
<td>3.816x+2.400x+1.400x²</td>
<td>3</td>
<td>26.1</td>
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<tr>
<td></td>
<td>1.75-4 M HNO₃</td>
<td>16</td>
<td>1.0308/(x+1.654)-0.3340</td>
<td>13.27x-8.174x+1.545x²</td>
<td>3</td>
<td>25.0</td>
</tr>
<tr>
<td>Y(NO₃)₃</td>
<td>0-6 M HNO₃ (TBP 15)</td>
<td>17</td>
<td>1.0399-0.0579x+0.0083x²</td>
<td>3.125-0.0927x+0.0096x²</td>
<td>3</td>
<td>29.2</td>
</tr>
<tr>
<td></td>
<td>0-5 M HNO₃ (TBP 485)</td>
<td>17</td>
<td>0.0216-0.0143x+0.0025x²</td>
<td>3.084/(x+0.0288)+1.528</td>
<td>3</td>
<td>21.0</td>
</tr>
<tr>
<td>Ge(NO₃)₃</td>
<td>0-5.5 M HNO₃ (TBP 485)</td>
<td>17</td>
<td>0.0598-0.0386x+0.0063x²</td>
<td>27.3/(x+3.39)+0.3644</td>
<td>3</td>
<td>24.0</td>
</tr>
<tr>
<td>Eu(NO₃)₃</td>
<td>0-5 M HNO₃ (TBP 485)</td>
<td>17</td>
<td>0.0904-0.0472x+0.0062x²</td>
<td>-0.34x+0.82x+0.9x²</td>
<td>3</td>
<td>28.5</td>
</tr>
<tr>
<td>Ga(NO₃)₃</td>
<td>0-5 M HNO₃ (TBP 100X)</td>
<td>13</td>
<td>0.0249-0.0143x+0.0021x²</td>
<td>1.749+0.314x+0.0083x²</td>
<td>3</td>
<td>43.5</td>
</tr>
</tbody>
</table>

Tab. 1 - K = K(x(NO₃)²), q = q(x(NO₃)²), (x = x(NO₃)²)
Fig. 2. Distribution coefficients vs HNO₃ molarity in aqueous phase.
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EXTRACTION OF COPPER WITH KELEX 100

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ABSTRACT

The influence of: pH, initial concentration of copper in the aqueous phase, concentration of reagent, temperature and stirring speed on the extraction equilibrium and kinetics of copper extraction with KELEX 100 was investigated. The calculated values of the distribution coefficients, rate constant of extraction and energies of activation enable the determination of the mechanism of the process. The diffusivity of copper in the aqueous phase was also calculated.

INTRODUCTION

In the last decade liquid-liquid extraction with chemical reaction is commonly used in the chemical industry in recovering metals from leach liquors. A number of publications has been devoted to the characteristics of different extractants (1-4). The biggest number by far of published papers is concerned with the study of the influence of: pH, phase ratio, initial concentration of the organic and aqueous phase, temperature and other parameters relevant for the equilibrium state. As earlier the extractors were designed according to the equilibrium states, kinetic effects tended to be ignored (5). On the other hand for the design of extraction equipments on a rational basis, the description of the extraction rate expressed by the relevant factors is necessary (6). Therefore in the last years much attention was payed to the study of the kinetics and mechanism as well as modeling of extraction processes.
In modeling of extraction processes several steps are involved such as: determination of equilibrium and kinetic data as a function of the relevant parameters, determination of the constants and coefficients in the kinetic equations and on the basis of such data formulation of the model equation and its solution.

For the extraction of copper from leach liquors many commercial chelating extractants are used as: LIX, KELEX, ACOARGA and other. In this paper will be reported some of the investigations of the influence of: pH, temperature, stirring speed, concentration of the solute and solvent on the kinetics of copper extraction with KELEX 100 from sulfuric acid solutions using SOLVESSO 150 as diluent.

According to the experimental results obtained the rate constant of extraction and coefficient of molecular diffusion were determined. The equation used for the determination of the diffusion coefficient represents an approximate model for the investigated extraction system.

EXPERIMENTAL AND DISCUSSION

The investigations were carried out in cylindrical cells 15 cm high and diameter 3,88 cm with four baffles of 3,0 cm high and 0,3 cm wide, with concave bottom. The experiments were performed with aqueous and organic phase 10 ml each. The kinetics was investigated by 125-1500 rpm of the stirrer. The concentration of the solution ranged 0,9-2,5 g dm$^{-3}$, while the concentration of the extractant KELEX ranged 1-5 Vol%. The investigated pH range was pH=0,9-4,5. The temperature range used was 20-50°C.

The influence of the initial pH on the extraction rate and equilibrium state is shown on the representative Fig. 1. From the data of this figure comes out that the initial pH has an influence on the time necessary for reaching equilibrium, but has no influence on the equilibrium state above pH=2,0. Therefore the further investigations we-
Carried out by pH = 4.05, which is in fact the pH of the solution without adding acid.

![Graph showing the percent of copper extracted as a function of time and pH.]

Some of the results showing the effect of the temperature on the kinetics, of a solution containing 0.9 g dm⁻³ Cu and 1 Vol% KELEX 100, by 1000 rpm, are given on Fig. 2. In the investigated temperature range 20-50°C the effect of the temperature is analogous to that of the pH. The increase of the temperature has influence on the rate of extraction but shows no effect on the equilibrium state.

Fig. 3 represents a plot of logK_p versus temperature for different copper and KELEX concentrations by 500 rpm. The data of this figure confirm this statement also in the case of other concentration. From these comes out that the temperature will appear as independent variable in the rate constant and in the diffusion coefficient.
FIG. 2. PERCENT OF COPPER EXTRACTED AS A FUNCTION OF THE TIME AND TEMPERATURE. [KELEX 100] = 1 vol %; $(C_{Cu})_0 = 0.9$ grdm$^{-3}$; $n = 500$ rpm.

FIG. 3. DISTRIBUTION OF COPPER AS A FUNCTION OF THE TEMPERATURE. $n = 500$ rpm.
The influence of the stirring speed on the kinetics is evident from the representative Fig. 4, which represents a plot of extracted copper versus time by extraction with 1 Vol% KELEX 100.

![Graph showing percent of copper extracted as a function of stirring speed and time.](image)

**Fig. 4. Percent of Copper Extracted as a Function of Stirring Speed and Time.** [KELEX 100] = 1 vol.%; \((C_{Cu})_0 = 12 \text{ grdm}^{-3}\); pH = 4.05; \(T = 293^\circ\text{K}\).

Two distinct regions are evident showing different influence of the hydrodinamic on the overall rate of copper extraction. The number of 700 rpm represents the upper limit where the rate of diffusion is a limiting step. For the investigated cases containing increased quantities of KELEX 100 this limit moves toward lower values of the stirring speed. Such data enable the determination of the necessary residence time for attaining equilibrium according to the stirring speed.

All the further investigations of the kinetics of extraction were carried out by 1000 rpm in the duration of two minutes. According to the obtained kinetic data the rate constant could be evaluated (7).
Presenting the experimental results of the kinetics in a semilogarithmic plot \( \ln (\frac{C_{Cu}^{t}}{C_{Cu}^{0}}) = f(t) \) where:

\( C_{Cu}^{t} \) - copper concentration in the aqueous phase in the time \( t \),

\( C_{Cu}^{0} \) - initial copper concentration in the aqueous phase,

for systems containing copper 0.9-2.5 gdm\(^{-3}\) and KELEX 100 1-5Vol% it comes out that this dependence can be adopted as linear for all investigated cases. On Fig. 5 are shown the obtained linear dependences for the case of extraction of solution containing 1.6 gdm\(^{-3}\)Cu, with 2Vol% KELEX 100 by different temperatures.

\[ \frac{C_{Cu}^{t}}{C_{Cu}^{0}} \]

* - \( T = 323^\circ K \)

* - \( T = 313^\circ K \)

* - \( T = 303^\circ K \)

* - \( T = 293^\circ K \)

**FIG. 5. TIME DEPENDENCE OF THE COPPER CONCENTRATION IN THE AQUEOUS PHASE BY DIFFERENT TEMPERATURES.**

\( n = 1000 \) rpm; \( C_{Cu}^{0} = 1.6 \) grdm\(^{-3}\); [KELEX 100] = 2 vol.%.

From the slope of the curves were calculated the values of the rate constant of extraction \( K \) for all the investigated cases. The temperature dependence of the so obtained rate constant could be derived from the plot \( \ln K = f(1/T) \). The results could be expressed as:
The values of the constant \( A \) depend on the combinations of the concentrations of copper and KELEX 100. The obtained values are in the range \( A = 89-148 \). The numerical value of the exponent of the equation (1) which includes the energy of activation and the constant \( R \) is the same for all the investigated cases. It comes out that the values of the energy of activation are independent of the investigated combinations. For all the investigated cases (by 1000 rpm) it was found this value to be 18.9 kJ/mol. The same value of the energy of activation for all the investigated cases confirms the fact that above 700 rpm the rate of mass transfer become independent of the stirring speed. On the other hand, the low values of the energy of activation point to diffusion control of the process followed by a very fast chemical reaction.

To measure the diffusion coefficient for copper sulphate a cell was used having a diameter of 3.88cm with flat bottom. The thickness of each stationary layer of both phases was 2.55cm. The investigations were carried out with solution containing 1.6 gdm\(^{-3}\) Cu and 1-3Vo1% of KELEX 100 in the temperature range 20-60\(^{0}\)C.

As the copper concentration in the aqueous phase changes with the time only along the thickness of the layer, for the given geometry of the cell, one dimensional mass transfer could be assumed, which could be described by the second Ficks law (8).

Assuming that: the chemical reaction is very fast (instantaneous in comparison with the rate of diffusion) and occurs on the interface, and all the thickness of the aqueous layer represents a diffusion layer, the diffusion coefficient could be calculated from the experimentally obtained kinetic data applying the solution of the second Ficks law with the appropriate boundary conditions. Since

\[
K = A \exp\left(-\frac{2274}{T}\right) \quad \text{(sec}^{-1}\text{)} \quad (1)
\]
the average concentration of the remaining copper in aqueous phase was measured, the solution for the average change of the concentration along the thickness of the layer was applied, which was obtained with the integration of the solution of the second Ficks law. From the values computed in this way the following expression for the temperature dependence of the diffusion coefficient was obtained:

\[ D = 1.46 \times 10^{-4} \exp(-481.5/T) \text{ (cm}^2\text{sec}^{-1}) \]  (2)

The diffusion coefficient (D) does not show dependence on the KULMEX 100 concentration.

Further work remains to be done on using the so obtained results for the solution of the expression (8, 9):

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - f(C) \]  (3)

The investigated two phase reaction system is kinetically considered as fast reaction system, and f(C) will be defined accordingly.

REFERENCES

Experiments were carried out in the continuously and countercurrently operating apparatus containing several fluidized beds of resin, separated from each other by a series of perforated plates.

The experimental results are in fair agreement with the predicted ones. The calculation was based on the theoretical model which takes into account different degree of the axial mixing of solid and liquid phases and the variation of the interdiffusion coefficients with the composition in the liquid film. Calculation procedure starts with the unsteady state mass balances which are solved step by step and which converge to the steady state solution. This procedure was found more practical than the solution of the system of nonlinear algebraic equations describing the steady state.

INTRODUCTION

Continuous ion exchange is of considerable interest in practical applications, although it is still in developing stage. Despite of many variations there are only two principal types of equipment and two modes of operation. In some cases the flow of resins and solution is continuous without interruptions (1,2,3). The fluidized bed is contained in an empty tall tube. The operation appears to be stable from the hydrodynamic point of view as well as from point of view of ion exchange itself.

If an empty column is used, the degree of axial mixing may become too high for an efficient separation when equilibrium is not favorable.
This was one of reasons for development of several contactors separated in stages (4-8). They operate cyclically. During a set time period both resin and liquid are fed continuously to the column. By interruption of the liquid flow a resin transfer is caused from one stage to the other. After the transfer, which normally takes only a short time, the liquid flow to the column is again established and new cycle is started.

One possibility to overcome intensive axial mixing of resins in deep fluidized beds is to use the built in internals. In a study of axial mixing of resins in fluidized beds it was found that the use of proper perforated plates limits particle mixing to the region between plates. It was also found that the flow of resins is possible and stable although somewhat constrained if the fractions of holes is properly chosen.

In the present work some experiments in continuously operated column with perforated plates are described. The experimental data are compared to the theoretical prediction, which is applicable also to the other types of continuous ion exchange operations.

EXPERIMENTAL

Experiments were carried out with the equipment described elsewhere (10). The essential part of it is a plexiglass column (5 cm I.D.), which is devided into 30 cm high stages by means of the perforated plates with evenly distributed holes (27 % blockage, d_h = 0.6 cm). Both the solution and resin are fed continuously to the column in a countercurrent flow. The feed of resin to the top of the column proceeds by dense phase flow, which is controlled by the rate at which water is pumped to the resin tank. Sampling points at each stage allow the withdrawal of the solution and determination of the axial concentration profile. Resin trap is provided for sampling of the outlet resin.

Before the run column was charged with the amount of resin sufficient to fill it as an expanded fluidized bed. The solution in the column at the beginning of
the experiments was deionised water. The chosen flow rates of solution and resin were set up. Samples of solution were taken in suitable time intervals. The steady state was achieved approximately within an hour. In this time interval both the compositions of the effluent solution and resin reached their final steady state values.

The reversible exchange of cations between dilute solutions of NaCl, CaCl₂ and mixtures of CaCl₂ and NaCl and resin, which was partially or fully converted to hydrogen form was studied. A strong acidic commercial resin Amberlite 200 C was used in all experiments. During the run the resin inventory in the column changed only slightly. The steady state value of the voidage was determined by the measurement of the resin holdup in a separate experiment.

CALCULATION OF THE EFFLUENTS

The same assumptions concerning the liquid and particle mixing, definition of diffusion fluxes as described in calculation of the semi-batch operation (11) are used in description of the countercurrent ion exchange. Also the same treatment of the equilibrium data in the ternary system Ca²⁺,H⁺,Na⁺ - Amberlite 200 C will be used as there. The procedure, which will be described is valid only for the ion exchange, which is controlled entirely by the mass transfer in the liquid phase, since it is assumed that the equilibrium concentration in solution is function of the average particle concentrations.

Mass balances

The schematic presentation of the ion exchange column in which countercurrent ion exchange is carried on is given in Fig.1. In each stage, which is separated from the others by perforated plate, particles are well mixed in axial and radial directions. The flow of liquid which approaches plug flow is simulated by series of mixing stages in the liquid phase. It is assumed that the flow rates and the composition of the inlet streams are known and that the effluent compositions of the liquid and solid phases must be calculated.
Fig.(2). Schematic presentation of stages in continuous countercurrent ion exchange

The steady state mass balances for liquid phase around the k-th sub-stage and for the solid phase in the stage I are:

\[ F C_T(x_i^{k-1} - x_i^k) = \sum_{j=1}^{p} \frac{k_{ij} a_p V_R C_T}{n} (x_j^k - x_j^{*k}) \]  \hspace{1cm} (1)

and

\[ S(y_i^1 - y_i^{1+1}) = \sum_{k=1}^{n} \sum_{j=1}^{p} \frac{k_{ij} a_p V_R C_T}{n} (x_j^k - x_j^{*k}) \]  \hspace{1cm} (2)
Mass balances, Eqs.(1) and (2), must be written for each solid mixing stage and for the two components in the ternary system. Together with the equilibrium relationships, with the equations for diffusivity and mass transfer coefficients one obtains a system of (2p+2(p-1))n+p/N equations, which must be solved simultaneously, since only the inlet compositions of solid and liquid streams are known. Even in the system with only three components the total number of equations becomes very large if the flow of liquid is close to the plug flow.

One possibility, to avoid the solution of the system of equations, which is suitable for binary systems, is to start the calculation by specification of the liquid feed and the composition of the outlet solids. Starting with the first stage, step by step calculation gives as the result the outlet composition of the liquid and the required composition of resin at inlet. This method however is not suitable in multi-component system.

In the preliminary study of dynamic behaviour of the continuous counter-current binary ion exchange we found that it was quite practical to solve the unsteady state mass balances step by step starting with suitable initial conditions. We applied this method also to the ternary system, since we found it more practical than the solution of the system of equations defined earlier. We have therefore solved Eqs.(3) and (4) instead of the Eqs.(1) and (2).

\[
\frac{C_T V_T}{n} \frac{dx_k^i}{dt} = FC_T (x_k^{i-1} - x_k^i) + \sum_{j=1}^{p} \sum_{j \neq i}^{n} k_{ij} a_p V_R C_T (x_j^k - x_j^k)
\] (3)

\[
Q_T V_R \frac{\Delta y_i^I}{dt} = \sum_{k=1}^{n} \sum_{j=1}^{p} k_{ij} a_p V_R C_T (x_j^k - x_j^k) (y_i^I - y_i^{I+1})
\] (4)

RESULTS AND DISCUSSION

A few experimental results are compared to the calculated data in Figs.2, 3 and 4. In Fig. 2 the distribution of the liquid concentration in the bed at the steady state conditions is plotted for an experiment with the binary system H\(^+\), Na\(^+\) - Amberlite 200 C. The ion
exchange column contained four stages completely filled up with fluidized resins. Although the flow rate was such that the liquid velocity in holes of the perforated plates considerably exceeded the terminal velocity of resins, the flow of solids was possible. Experimental data deviate from the calculated ones, however, the predicted distribution is in our opinion acceptable approximation. Approach to the steady state is illustrated in Fig.3, where the exit concentration of Ca$^{2+}$ ion from the first stage is plotted vs. time for an experiment in which the solution contained Ca$^{2+}$, H$^+$ and Na$^+$ ions. And finally the experimental and calculated concentration distributions are shown in Fig.4 for a ternary system Ca$^{2+}$, H$^+$, Na$^+$. Only two stages were used in this experiment.

In all three cases shown there is a certain disagreement between the experimental and calculated results. This is not unexpected, however, since considerable approximations had to be made in the model used in calculations. As imperfect as it may be, this model allows a rough prediction of the steady state ion exchange in ternary dilute solutions in without the aid of the experiment, provided the flow conditions are well known.

SYMBOLS

- $a_p$ - particle interfacial area per unit volume $\text{cm}^{-1}$
- $C_T$ - total ionic solution concentration $\text{meq cm}^{-3}$
- $F$ - flow rate $\text{cm}^3\text{s}^{-1}$
- $k_{ij}$ - multicomponent mass transfer coefficients $\text{cm s}^{-1}$
- $N$ - number of solid mixing stages
- $n$ - number of liquid mixing stages
- $Q_T$ - total exchange capacity of resin $\text{meq cm}^{-3}$
- $S$ - flow rate, of solids $\text{cm}^3\text{s}^{-1}$
- $X$ - equivalent fraction in liquid phase
- $Y$ - equivalent fraction in solid phase
- $V_{RL}$ - volumes of resin and liquid in solid in stage $\text{cm}^3$
SUPERSSCRIPTS

*  - equilibrium value
F  - value of variable in feed

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Fig. 2

\[ \text{Na}^+\text{H}^+ - \text{Amberlite 200 C} \]

- \( c_r = 10 \text{ meq/l} \)
- \( F = 195 \text{ cm}^3/\text{s} \)
- \( S = 0.23 \text{ cm}^3/\text{s} \)
- \( \frac{Q2}{N_r} = 10 \)
- \( \frac{Q2}{N_r} = 0.34 \)
- \( E = 0.75 \)

\[ \text{x} = \text{calculated} \]
\[ \text{△ experimental} \]

Stage number

Fig. 3

\[ \text{Ca}^{2+}/\text{H}^+/\text{Na}^- - \text{Amberlite 200 C} \]

- \( c_r = 10 \text{ meq/l} \)
- \( F = 195 \text{ cm}^3/\text{s} \)
- \( S = 0.21 \text{ cm}^3/\text{s} \)
- \( \frac{X_{CA}^C}{X_{CA}^C} = 0.8 \)
- \( \frac{V_{Ca}^C}{V_{Ca}^C} = 0.11 \)
- \( \frac{F_{Ca}^C}{F_{Ca}^C} = 0.75 \)
- \( E = 0.75 \)

\[ \text{时间, t (min)} \]

Fig. 4

\[ \text{Ca}^{2+}/\text{H}^+/\text{Na}^- - \text{Amberlite 200C} \]

- \( c_r = 10 \text{ meq/l} \)
- \( F = 195 \text{ cm}^3/\text{s} \)
- \( S = 0.71 \text{ cm}^3/\text{s} \)
- \( \frac{X_{CA}^C}{X_{CA}^C} = 0.60 \)
- \( \frac{V_{Ca}^C}{V_{Ca}^C} = 0.057 \)
- \( \frac{F_{Ca}^C}{F_{Ca}^C} = 0.19 \)
- \( E = 0.75 \)

\[ \text{时间, t (min)} \]

Stage number
Abstract: A review of mathematical models for description of the performance of extraction columns is presented and possible applications are shown on examples.

Introduction: In design and scaling up of extraction columns computer modelling may be used to improve the efficiency of the process. The following scheme is then applied:
- Find a reliable model, sufficiently realistic to reproduce the actual situation and yet so simple that its mathematical solution is possible in a reasonable time.
- Calculate or measure all necessary parameters for the model.
- Use the computer to derive the column performance from the available data and carry out parameter studies to find the best working regime of the future column.

For the above procedure experimental data are necessary, usually measured with the same system and the same column type, but they are used more efficiently than in a conventional design process. Some of the data may even originate from bench scale models and more can be obtained from them.
if the performance of the future column is properly simulated.

The following represents a review of some existing models applicable in liquid/liquid extraction and shows some examples of their use.

**Backmixing:** The flows inside a column are not ideal and the axial mixing causes deviations from the plug-flow pattern. A comprehensive backmixing theory was developed (1) and corresponding models were derived from it. They represent an improvement of the plug flow model but still involve considerable simplifications.

Two classical models are used: the differential (dispersion) and the stagewise. Both are closely related to each other and in most cases they can be interconverted exactly. The differential model has been developed analogously to molecular diffusion. It assumes an additional stream in the column flowing in the direction of negative concentration gradient of the solute. The governing differential equations written in dimensionless form contain five parameters for perfect description of the column performance: the extraction factor, number of transfer units, extraction grade and the Péclet numbers in both phases. Additionally, the dimensionless height is used. To demonstrate the importance of backmixing, Fig.1 shows the obtainable extraction grade in dependence on the number of transfer units for three different values of the

extraction factor. It can be seen that backmixing influences
the result most when the extraction factor is close to unity.
The case shown is that of equal backmixing in both phases,
when the deviations are the largest.

![Fig.1: Extraction grade for different conditions.](image)
Extraction factor: A-A: 0.2
B-B: 1.0 , C-C: 2.0.
Equal backmixing in both phases. In each group curves
for Pe=5, 10, 20, 50, 100 and 1000 are shown. (from bottom
to top).

An analytical solution of the model equations is easily
possible for steady state and constant parameters. In all
other cases numerical solutions may be used. A possible way
is to select a number of supporting points along the column
height, expand the differential equations in all of them
using Taylor's formula and solve the resulting set of algebraic
equations by some matrix method. Reasonable approximations
can usually be obtained with about 40 points. The more
backmixing occurs in the particular column the less points
are necessary. An example of concentration profiles obtained
using analytical solution with a linearised equilibrium curve
and a full scale numerical solution is shown in Fig.2 for
the toluene-acetone-water system. It can be seen that even in this simple case a considerable difference can arise so that linearisation should not be used where the equilibrium relation is curved.

In more complicated situations such as the presence of side streams, partially miscible solvents or variability of hydrodynamic parameters, it is easier to work with the stagewise models, even for differential columns. This model assumes that the column consists of a number of real or hypothetical stages with stepwise concentration changes among them. Backflows responsible for the backmixing are defined in directions opposite to the main flows of the respective phases. In this case the meaning of the intermediate concentrations is different and no diffusional mechanism is used for the backflow. However, the mathematical treatment is practically the same as in the previous case and the same programmes can be made to work for both models with only slight changes being necessary.
The possibility to use stagewise models for differential columns is demonstrated as an example in Fig. 3. For practical purposes even the shown coarse division to 15 stages would be sufficient for many applications.

Fig. 3: Examples of concentration profiles generated with different numbers of hypothetical stages (15 and 150).

The backmixing models are generally known and are slowly being accepted, even by practising engineers. No problems are involved in applying them to all possible extraction situations. We have written programs for steady and unsteady operations, immiscible and partially miscible solvents, stagewise and differential models, for simulation, evaluation and design, etc. Most of them run on a desk-top computer.

Forward movement of discrete drops: The backmixing models were derived from the theory of molecular diffusion and therefore assume continuity of both phases. This is justified in diffusion, which deals with molecules, but may fail in processes where drops are the smallest particles involved. To
improve the reliability of the models the diffusion concept was abandoned for the dispersed phase and several new models have recently been developed. Usually the concept of well mixed stages with backflow is maintained for the continuous phase, the behaviour of the dispersed phase being expressed using some new assumptions. The simplest possibility is to assume plug flow in the dispersed phase, which is justified with uniform and noncoalescing drops. The corresponding model works well with spray and perforated plate columns, providing the demands of uniformity and noncoalescence of drops are fulfilled. For drops of different sizes the rise velocities are not uniform and if marked drops are introduced for a short time interval this impulse is distorted as it travels inside the column. This was named forward mixing. (2) Representing the drop spectrum by a number of discrete classes a model can be derived for this situation. It is still easy to solve and has an advantage over backmixing in that it is possible the influence of drop size distribution on mass transfer and axial mixing of the dispersed phase. This is achieved by calculating the mass transfer rates individually for each drop class and averaging the results. An example of the possibilities of this model is shown in Fig.4 which shows the concentration profiles for a special case where all parameters except the broadness of drop size distribution were kept constant. (The larger the parameter delta, the more uniform the drops are). It can be seen that changing the drop size distribution causes

2) Rod V., Brit. Chem. Eng. 1966, 11, 483
changes in the number of transfer units by more than 100%.
It was found that the column performance is controlled by
the largest drops present and that a monodispersion therefore
yields the best mass transfer rates for the given mean dia-
Fig. 4: Example of influence
ter.
of drop size distribution on

achievable separation. Log-n
distribution with different
broadness (\$). Broken line -
monodispersion. Mean diameter
of drops is 2mm in all cases.

Coalescence and redistribution of drops: A simple way of ex-
pressing the fact that the drops can coalesce and be formed
again inside the column has been suggested by Misek and Rod
(3) who introduced a parameter called the coalescence height
which indicates the average distance the drops actually travel
in the column before being re-formed. The previous model can
be modified to allow for this parameter if special stages
are periodically inserted where all drops are mixed together
and formed again. Fig. 5 shows an example of profiles cal-
culated with otherwise constant parameters if the coalescence
height is being changed. The fact that the mass transfer
coefficient is time-dependent has been taken into consideration.

Fig. 5: Example of concentration profiles generated with different coalescence heights. Mass transfer coefficients from theoretical relations for rigid drops, medium width drop size distribution.

In the example shown the number of transfer units is increased nearly ten times between noncoalescing drops and drop coalescence and redistribution in each of the 50 column stages.

**Backflow of drops:** The models discussed up to now mainly predicted the separation ability of columns. A new possibility to predict loading, holdup profiles and flooding limits is given by the model derived by Jiricny et al. (4) The main ideas are as follows: there is a velocity profile in the continuous phase and the drops move in the direction and with a velocity given by the vector sum of their relative velocity and the local velocity of the continuous phase. Both coalescence and splitting are considered and expressed by rate equations. Using a few additional simplifications a workable program was written and tested for a series of special situations. One example out of many others is shown

in Fig. 6, where the hold up profiles can be seen for a special situation in dependence on flow rate of the continuous phase. The dispersed phase is introduced in the form of very large drops which are split and coalesced according to selected rules. In the case shown it takes about one third of the column height to reach steady state drop distribution which is then characterised by a more or less uniform value of the hold up. Eventually the hold up in one of the stages reached 100% and the column flooded.

Fig. 6: Example of axial hold up profiles in dependence on throughput of continuous phase. Broken line indicates breakdown caused by flooding in one of the stages.

Conclusions: There is a variety of computer models available for all possible situations. Backmixing theory is applicable without problems even to complicated cases. New models superseding this theory have emerged which improve the understanding of the fundamental processes and enable simulation of additional influences. All these models are easily programmable and can usually be used on desk-top calculators.
The Influence of a Disperse Phase on the Turbulence in a Fluid

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Summary

Based on the momentum- and mass-balances for two-phase flow, the vectorial time-averaged differential equations describing the continuous phase (fluid) and the particulate phase (disperse particles) are derived. The process of time-averaging results in four correlation-terms, containing the fluctuations of velocities and concentration. With the help of some simplifying models these terms are attributed to the terms of the main flow.

Introduction

The knowledge of the properties of turbulent flows is an essential task for modern engineering, but in spite of all research efforts, the randomness of the turbulent motion of a fluid remains a big unsolved problem. Homogeneously dispersed fine particles (solids, droplets, bubbles) added to a turbulent fluid cause still more problems, because depending on their size and concentration, they may increase or decrease the turbulence. Turbulent mixing processes of particles in fluids, turbulent particle-motions in classifiers and cyclons, pneumatic transport of solids in pipes, and the emission of pollutant particles in the atmosphere demonstrate that turbulent two-phase flows appear in very many technical and natural processes.

The usually applied mathematical tool to describe turbulence is the time-averaging operation of the mass-, momentum-, and energy balances. However, with this method new unknown correlation-terms are produced but the number of equations remains still the same. The loss of information, caused by the process of time-averaging has to be compensated by 'inventing' new equations for the non-vanishing fluctuation terms. This is obviously the central problem: the closure-up of the set of differential equations with the help of new equations which have to proof to be useful and to be able to support further calculations, and which are based either purely on experi-
mental data or on theoretical models or on combinations of both of them. For example Boussinesq [1] introduced the "eddy-viscosity" in order to relate the turbulent friction with the velocity-gradient of the main flow. Similar Prandtl [2] connected the fluctuation-term of the velocities with the velocity-gradient of the main flow by inventing the "mixing-length". More advanced models are based on equations of higher order; in these equations for example the mechanism of the energy transport can be demonstrated; the resulting k-ԑ-modell (k = kinetic energy of turbulence, ԑ = dissipation rate) and similar models [3] have been proofed to be very useful for many applications.

The relations become much more complicated if particles are dispersed in the turbulent fluid. There exists not only the response of the particles to the turbulent motion of the fluid, but also the re-action of the particle collective on the turbulence in the fluid; this effect will naturally increase with higher particle concentration. If the particles are small enough, so that their inertial response-time can be neglected, they will follow completely the fluid fluctuations, but the energy which they consume will cause a damping effect on the turbulence; on the other side if the particles are big enough they themselves will function like disturbing cells from which new turbulent vortices will be produced.

Tchen [4] has been one of the first scientists dealing with the response of particles to the fluid turbulence. His investigations have been confined to one particle in an infinite fluid. The most advanced studies have been published by Kuboi et al. [5], but also here the influence of the concentration is neglected. Neeße [6] has summarized the literature dealing with the re-action of the particulate phase on the fluid, but no generally valid equations could be derived. The aim is therefore to deduce the correlation-terms of the two-phase flow from the describing differential equations, and then to invent models for the relation between these terms and the main flow functions.
The Equations for Describing Turbulence in the Fluid-Particle-Flow

It is assumed that an incompressible fluid (density $\rho_f$) contains homogeneously distributed fine solid particles (density $\rho_s$) of spherical shape and same size (diameter $d_p$). Then the pressure $p$, the vectorial fluid velocity $\mathbf{v}$, the particle velocity $\mathbf{w}$, and the local porosity $\epsilon$ (ratio of fluid volume to total volume) are the unknown functions of the coordinates $(x,y,z)$ and the time $t$. From the mass-balances the following two equations are derived:

1. $\epsilon_t + \nabla \cdot (\epsilon \mathbf{v}) = 0$  
2. $(1-\epsilon) + \nabla \cdot [(1-\epsilon) \mathbf{w}] = 0$

The momentum-balances for each phase contain inertia, pressure $p$, field forces $\mathbf{K}$ (these three terms have to be multiplied with the volume fractions $\epsilon$ and $(1-\epsilon)$ respectively), and an interactional force. The latter one is approximately given by the product of particle-number (per volume) and Stokes' drag force acting on one particle. The equation for the fluid contains the newtonian friction force too:

3. $\rho f \epsilon_s \mathbf{v} + \epsilon_s \nabla \mathbf{v} \mathbf{T} \rho_f \mathbf{v} + \epsilon \nabla \mathbf{p} - \epsilon \eta_f \nabla \mathbf{v} - \epsilon \mathbf{K}_f + (\lambda \epsilon) (\mathbf{v} - \mathbf{w}) \eta_t / d_p^3 = 0$

Solid phase:

4. $(1-\epsilon) \rho_s \mathbf{w} + (1-\epsilon) \nabla \mathbf{w} \mathbf{T} (1-\epsilon) \mathbf{p} - (1-\epsilon) \mathbf{K}_s - (\lambda (1-\epsilon) (\mathbf{w} - \mathbf{w}) \eta_t / d_p^3 = 0$

The wall-friction of the fluid is considered by the friction-term (and boundary conditions); the wall-friction of the particles is neglected, its consideration would not change the principles of the following calculus. The set of equations (1) - (4) contains 4,6 or 8 scalar equations for 1,2 or 3-dimensional cases. The unknowns are $\epsilon$ and $p$ and additional 2,4 or 6 components of the velocities $\mathbf{v}$ and $\mathbf{w}$; i.e. the number of equations is always equal to the number of unknowns. These equations are not solvable analytically; it is assumed that they describe the laminar and the turbulent case as well. The velocities are made dimensionless by a velocity $v_0$, the lengths by the particle diameter $d_p$, the time by $d_p/v_0$, the pressure...
by $\rho_f v_0^2$, and the field forces by $\rho_f v_0^2/d_p$. If the unknowns are split into a time-mean value and a fluctuation-term:

$$\begin{align*}
\bar{\gamma} &= \bar{\gamma} + \gamma' \\
\bar{\omega} &= \bar{\omega} + \omega'
\end{align*}$$

then the eqs. (1) - (4) yield:

$$\begin{align*}
\bar{\varepsilon}_t + \nabla^T (\bar{\varepsilon} \bar{\gamma}) + \nabla^T (\bar{\varepsilon} \gamma') &= 0 \\
-\bar{\varepsilon}_t + \nabla^T [(\lambda - \bar{\varepsilon}) \bar{\omega}] - \nabla^T (\bar{\varepsilon} \bar{\omega}') &= 0 \\
\bar{\gamma}_t + (\nabla^T \bar{\omega}) \bar{\gamma} + (\nabla^T \gamma') \gamma' + \nabla \bar{\omega} - \nabla^2 \bar{\gamma} \bar{\omega}/\Re + \\
+ \lambda g \frac{\lambda - \bar{\varepsilon}}{\bar{\varepsilon}} \frac{\bar{\gamma} - \bar{\omega}}{\Re} - \frac{4g}{\varepsilon^2 \Re} (\bar{\gamma} \gamma' - \bar{\gamma} \gamma') - K_t &= 0 \\
\bar{\omega}_t + (\bar{\omega} \nabla^T) \bar{\omega} + (\bar{\omega} \nabla^T) \gamma' + \nabla \bar{\omega} - \\
- \lambda g \frac{\bar{\gamma} - \bar{\omega}}{\Re} - \bar{\gamma}' &= 0
\end{align*}$$

Four correlation-terms appear as new unknowns:

$$\begin{align*}
\bar{\varepsilon} \gamma', & \quad \bar{\varepsilon} \gamma', & \quad (\gamma' \nabla^T) \gamma', & \quad (\gamma' \nabla^T) \bar{\omega}'
\end{align*}$$

Modelling the Correlation-Terms

1) The term $(\gamma' \nabla^T) \gamma'$.

The following identity is valid:

$$\begin{align*}
(\gamma' \nabla^T) \gamma' & \equiv (\gamma' \nabla^T \gamma') \nabla - \gamma'(\nabla^T \gamma')
\end{align*}$$

The last term vanishes for a pure fluid; but in case of the presence of particles the continuity equation (1) does not allow that the divergence of the fluid-velocity vanishes if $\varepsilon = \text{constant}$.

The following model is made: a fluid volume-element is considered containing one particle. The divergence $(\nabla^T \gamma)$ is always equal zero; only if a particle crosses the border
of this element, the divergence is not vanishing, since a fluid-volume equal to the particle must cross the border too. Based on this idea a complicated calculation leads to the expression:

\[ \frac{\nabla}{\nabla} (\nabla T^\nabla) + \frac{\nabla}{\nabla} (\nabla T') = \]

\[ = -\left(\lambda - \varepsilon\right) \left[ T_{\nabla} + (\nabla T) \nabla + (\nabla T') \nabla - \nabla' (\nabla T') \right] \left[ \frac{2}{\varepsilon} \frac{3}{\varepsilon} \frac{3}{\varepsilon} \ln \left[ \frac{1 + \lambda \varepsilon}{\lambda - \varepsilon} \right] \right] \]

\[ \approx 2 \lambda \varepsilon \]

From eq. (11) the term \( \nabla (\nabla T') \) can be expressed as a function of \( (\nabla T') \nabla \) and terms of the main flow \( (\varepsilon, \nabla) \).

2) The term \( (\nabla T') \nabla \).

Here the main crux of fluid-particle flows appears: the particulate phase is sometimes (continuity-eq.) treated like a continuum; on the other hand (interactional force) it is considered as a sum of distinct particles. Therefore, the above explained model should not be applied here vice-versa, but for a first approximation, it is assumed that in eq. (11) the letter \( v \) can be substituted by \( w \) and \( e \) by \( (1-e) \).

3) The term \( \nabla (\nabla T') \).

If the continuity equation (1) is written out fully with all the fluctuation terms, then certain terms can be neglected due to their obviously small contribution and the following approximation can be stated:

\[ \frac{\nabla}{\nabla} = -\frac{\varepsilon}{\nabla (\nabla T') \nabla} \nabla (\nabla T') - \frac{\nabla (\nabla T') \nabla}{\nabla (\nabla T') \nabla} \]

\[ \text{Together with eq. (11) } \varepsilon' (\nabla T') \text{ can be recondicted to } (\nabla T') \nabla. \]

4) The term \( \nabla (\nabla T') \).

Similar to above, the following equation is valid:

\[ \frac{\nabla}{\nabla} = \left(\lambda - \varepsilon\right) \left[ \frac{\nabla (\nabla T') \nabla}{\nabla (\nabla T') \nabla} + \frac{\nabla (\nabla T')}{\nabla (\nabla T') \nabla} \right] \]

Conclusions

It is possible to attribute the four correlation-terms to the
functions of the main flow (time-averaged) and the two terms $\overline{v'v'}$ and $\overline{w'w'}$. The modelling of these terms can be carried out by (for example) mixing-length hypothesis or by two "eddy-viscosities" (for particles and fluid). This paper should contribute a first step to the closure-up procedure of the differential-equations with special consideration of the influence of the concentration.

Acknowledgment

The author wishes to thank the "Deutsche Forschungsgemeinschaft (DFG)" for the financial support of this research.

Literature


Backmixing and concentration Profile in a Pulsed Sieve Plate Extractor (PSE) *

K.-H. Reissinger **

The backmixing effects of both phases, the continuous and the dispersed phase resp., must be known for the exact design of extraction columns, because these effects reduce the driving concentration force and therewith the mass transfer between the phases. The general influence of backmixing on the concentration profile is shown in Fig. 1 schematically. The real concentration profile can be calculated with the well known backmixing models /6-8/, if the following parameters are known:

- Bodenstein numbers of both phases \( \text{Bo}_c, \text{Bo}_d \)
- hold up of dispersed phase \( d \)
- mass transfer area \( a \)
- total mass transfer coefficient \( k \)

At present time these parameters must be investigated experimentally, because the existing correlations are not exact enough for a sufficient prediction /11/.

The experiments were carried out in a pulsed sieve plate extractor with 150 mm in diameter and 3.97 m active length, as shown in Fig. 2. The residence time distribution of both phases was investigated by the transient tracer method.

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The evaluation of the measured curves and the calculation of the Bodenstein numbers were executed by the dispersion model /8,9/. The hold up was measured by shutting the feed and the outlet streams rapidly. For the investigation of the drop size distribution which is important for the calculation of the mass transfer area, a photo electric method was used /14/. The total mass transfer coefficients were calculated from the measured concentration profiles. In this way mass transfer coefficients were received without a backmixing influence.

Fig. 3 and 4 show typical curves of residence time distribution measurement for the continuous and the dispersed phase. While the conformity between measurement and calculation for the continuous phase is fine, there are partly great differences for the dispersed phase. The dispersion model is not able to describe the backmixing behaviour of this phase sufficiently because the model assumptions like monodispersion are not exactly fulfilled.

The Boₐ-numbers and the hold up are plotted in Fig. 5 as a function of load and pulse velocity A*F. The curves show an U-shaped character with a minimum between the mixer-settler and the dispersion operation region, as it was found elsewhere /16/. The increase of Boₐ-number in the dispersion region with increasing pulse velocity is caused by a decrease of dispersed phase velocity because of an increasing hold up and therefore less backflow in the drag of the droplets.

Fig. 6 contains the Boₐ-numbers and data of drop size distribution in dependence of load and pulse velocity as well. In this case the distribution curves have nearly the same U-shaped character with a minimum as mentioned above. The Boₐ-numbers are much higher than the Boₐ-values, that means less backmixing. The increase in Boₐ-numbers with increa-
sing A*F-product can be explained by a more stabilised flow behaviour because of an increase in hold up and therefore a decrease in the eddy formation as can be observed. The Sauter mean diameter depends only a little bit on pulse velocity; the width of drop size distribution is larger at low and high A*F-products than in the middle region.

The measurements of the concentration profiles lead to results as demonstrated in Fig. 7. Therefrom the total mass transfer coefficient was optimized. If all values were used for this purpose the recalculated profile is good; however using the outlet concentration only, this will give a deviation in the middle part of the column. The k-values for all experiments calculated in this way are plotted in Fig. 8. Likewise there is shown the product k*a as an index of efficiency. It can be derived from this figure that the PSE is working best on high pulse velocities. Moreover backmixing is low under these conditions. This recommendation can be made for all systems with high interfacial tension as water - toluene; for other systems it must be investigated.

The influence of Bo-number on the outlet concentration is presented in Fig. 9. For Bo> 20 no essential influence can be noted; that means on the other hand that deviations in Bo-numbers are without any important effect on the concentration profile in this range. For Bo< 20 a greater accuracy in calculation the backmixing parameters is necessary and possible. This figure also shows that a determination of Bo-numbers from concentration profiles is not recommended because the results are inaccurate.
Fig. 10 shows the dependence of total mass transfer coefficient on the outlet concentration. Variations in $k$-value are transmitted to outlet concentration in nearly the same size. Therefore it is very convenient to get the right $k$-value resp. the right $k^*a$-product.

At least the influence of backmixing on the concentration profile is directly presented in Fig. 11. It can be stated that the dispersion model is suitable for the calculation of concentration profiles in PSE. The next step must be to investigate larger column diameters in the same way to find out the correct scale up factors.
### Symbols used

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>m²/m³</td>
<td>specific mass transfer area</td>
</tr>
<tr>
<td>A</td>
<td>mm</td>
<td>amplitude of pulsation in the column</td>
</tr>
<tr>
<td>Bo</td>
<td></td>
<td>Bodenstein - number</td>
</tr>
<tr>
<td>c</td>
<td>kg/kg</td>
<td>concentration</td>
</tr>
<tr>
<td>c*</td>
<td>kg/kg</td>
<td>equilibrium concentration</td>
</tr>
<tr>
<td>d</td>
<td>m</td>
<td>drop diameter</td>
</tr>
<tr>
<td>D</td>
<td>m</td>
<td>column diameter</td>
</tr>
<tr>
<td>Dₓₐₓ</td>
<td>m²/s</td>
<td>axial dispersion coefficient</td>
</tr>
<tr>
<td>D</td>
<td>m²/s</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>extraction factor</td>
</tr>
<tr>
<td>F</td>
<td>min⁻¹</td>
<td>pulse frequency</td>
</tr>
<tr>
<td>h</td>
<td>m</td>
<td>height</td>
</tr>
<tr>
<td>H</td>
<td>m</td>
<td>column height</td>
</tr>
<tr>
<td>k</td>
<td>m/s</td>
<td>total mass transfer coefficient</td>
</tr>
<tr>
<td>m</td>
<td></td>
<td>distribution coefficient</td>
</tr>
<tr>
<td>Re</td>
<td></td>
<td>Reynolds number</td>
</tr>
<tr>
<td>Sc</td>
<td></td>
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</tr>
<tr>
<td>Sh</td>
<td></td>
<td>Sherwood number</td>
</tr>
<tr>
<td>t</td>
<td>s</td>
<td>time</td>
</tr>
<tr>
<td>u</td>
<td>m/s</td>
<td>relative velocity</td>
</tr>
<tr>
<td>v</td>
<td>m/s</td>
<td>superficial velocity</td>
</tr>
<tr>
<td>β</td>
<td>m/s</td>
<td>mass transfer coefficient</td>
</tr>
<tr>
<td>ε</td>
<td></td>
<td>hold up</td>
</tr>
<tr>
<td>η</td>
<td>Ps</td>
<td>viscosity</td>
</tr>
<tr>
<td>s</td>
<td>kg/m³</td>
<td>density</td>
</tr>
<tr>
<td>s</td>
<td></td>
<td>phase ratio (vol.)</td>
</tr>
</tbody>
</table>

### Subscripts

- c: continuous
- d: dispersed
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Flow behaviour in column extractors

**Fig. 1**

Ideal behaviour vs. real behaviour

**Fig. 2**

Experimental arrangement

- Water phase
- Organ phase
- Column dimensions:
  - Diameter: 150 mm
  - Number of trays: total 37, between 33 and 28
  - Plate spacing: 100 mm
  - Hole diameter: 2 mm
  - Free hole area: 23%
  - Distance between trays: 3330 mm, 2820 mm
  - Active height: 3970 mm
  - Total height: 5000 mm

Tracer feed, dropsize distribution, conductivity, fluorescence
Fig. 3

Residencetime distribution of continuous phase

Fig. 4

Residencetime distribution of dispersed phase
Influence of pulsvelocity AF on Bo2-number and hold up

Dependence of Bo2-number and dropsize distribution on pulsvelocity AF
Concentration profile

Fig. 7

Mass transfer conditions as a function of pulsvelocity AF

Fig. 8
Influence of backmixing on outlet concentration

**Fig. 9**

- Influence of backmixing on outlet concentration
  - Continuous phase
  - Calculated with $B_0\gamma/H$:
    - 15 m$^{-1}$
    - 30 m$^{-1}$
    - 60 m$^{-1}$
  - Dispersed phase
  - Calculated with $B_0\gamma/H$:
    - 7 m$^{-1}$
    - 14 m$^{-1}$

Influence of $k$-value on outlet concentration

**Fig. 10**

- Influence of $k$-value on outlet concentration
  - Organic phase
  - Water phase
  - Relative deviation of outlet concentration [%]
  - Relative deviation of $k$ [%]

<table>
<thead>
<tr>
<th>$B_0\gamma/H$ [m$^{-1}$]</th>
<th>$B_0\gamma/H$ [m$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>28</td>
<td>60</td>
</tr>
</tbody>
</table>
Influence of backmixing on concentration profile

![Graph showing the influence of backmixing on concentration profile. The graph plots column height against aceton concentration with two sets of data points. The table shows the conditions for two different cases:

<table>
<thead>
<tr>
<th>Bo/H [m⁻¹]</th>
<th>Bo/H [m⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>30</td>
</tr>
<tr>
<td>2.8</td>
<td>6.0</td>
</tr>
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</table>
AGITATED LIQUID-LIQUID EXTRACTION COLUMN WITH EC-PLATES

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Summary A newly developed extraction column with coalescence enhancing plates is presented. Experiments and their results in laboratory and pilot plant scale are discussed including a comparison to other equipment.

Introduction In the EC-(Enhanced Coalescence, Fig.1) column agitated mixing stages are separated by grids of vertically directed plates on which the dispersed phase coalesces after leaving each stage before being redispersed by the following mixer. Part of the cross-section remains free for the countercurrent flow of the continuous phase, the actual area depending on the phase ratio.

Selection of internals The configuration of the internal elements had to be determined first in a three-stage laboratory column with the test system toluene-acetone-water concerning the parameters

- construction of the coalescence enhancing plates
- characteristic dimension of the plate's openings
- type of impellers
- height of stage $H_s$ and height of the plate $H_p$. 
Here it was decided to prefer high phase velocities to high separation efficiencies. The resulting construction consists of 20mm high plates of corrugated steel coated with PTFE which is strongly wetted by toluene and therefore provides reliable coalescence of the dispersed phase. With plate's openings of 9mm hydraulic diameter a free cross-section of 91% is obtained. Impellers with four concave blades were selected for the mixing cell of 40mm height, best combining radial transport of the liquid and low cross-section in the stage. An additional examination of varied impeller diameters where drop-size, radial velocity and power consumption were measured led to the design rule that the impeller diameter should be 1/3 of the column diameter.

Pilot plant column Consequently an installation on pilot plant scale was constructed. With 75mm column diameter and 2m length it contains 32 stages.

A special design was chosen for the bottom section of the column. According to the literature (e.g. [1]) and for observation purpose fine drops which are usually formed at any height of the column are carried downstream with the continuous phase corresponding to their drop size and the velocity of the continuous phase. As the column's cross-section widens at the bottom these small drops accumulate there because they coalesce at a lower rate than larger drops thus causing flooding at high throughputs after some time. This effect is particularly observed in columns with mechanical
agitation due to the wide drop size distribution produced.

To prevent this a funnel was inserted at the bottom of the extraction zone (Fig.2) in which the continuous phase is accelerated and immediately released into the widened cross-section where the fine drops can coalesce and finally ascend into the column with the main stream of the dispersed phase. An element of Sulzer packing below the funnel reliably prevents the fine drops from leaving the column and also distributes the dispersed phase main stream rising from below.

The column is equipped with probes to draw samples of inlet and outlet streams as well as of the separated phases at seven points along the effective zone (Fig.3). Furthermore the dispersed phase holdup in a mixing cell can be measured by drawing a certain volume of the dispersion out of four stages. At the same points capillaries are inserted into the column through which a dispersion sample flows, passing a sight-glass so as to be photographed for the subsequent evaluation of the drop size distribution.

Backmixing of the continuous phase is determined by conductivity measurement of a KCl-pulse at two points along the column. For backmixing measurements of the dispersed phase a pulse of coloured toluene is evaluated by two newly developed light detecting probes. These are designed to be placed inside the mixing cell, to separate toluene from the water phase, to determine the light passing from an LED to a photocell through a very small sample volume and to lead the
measured liquid out of the column.

**Mass transfer measurements**  After initial determination of the solute concentrations with density measurement irregularities in these results led to the following test: A glass cylinder was filled with a certain volume of toluene through which deionized water continuously flowed and then was stirred to obtain a large interface. At certain time intervals toluene samples were taken and evaluated by both density and gaschromatographic measurements (Fig.4).

According to the GC results the acetone present at the beginning rapidly vanished. The density results however showed an imaginary acetone concentration which grew slowly until the end of the first day when the experiment was interrupted. On the following days the density behaved analogously, with the value measured at the beginning lying each day above the starting value of the previous day.

The growing slope of the DM-curve can be explained with the toluene volume in the cylinder diminishing with the removal of samples. No reason was found however for the continuous decrease of the density, as especially a possible dispersion of water in toluene would result in a contrary effect. In any case from then on concentrations were measured by GC-analysis. For acetone concentrations in water however, the density measurement can be considered to be correct.

The mass transfer experiments were carried out at various
loads and rotor speeds (Fig. 5) up to the flooding point. An optimum rotor speed results for each load coinciding with the maximum rotor speed at higher loads where flooding limits further operating points.

The highest separation efficiency is obtained with the relatively low throughput of 20 resp. 30 \( \frac{m^3}{m^2h} \) which correspond to stage efficiencies of 46 resp. 37% (Fig. 6). Above and below these maxima the efficiency is reduced through the effect of backmixing expressed by lower Péclet numbers. Furthermore the mass transfer from toluene to water allows significantly higher loads than the opposite direction.

Changing the phase ratio in favour of the toluene phase leads to a considerably wider load characteristic of the column limited only by the capacity of the experimental installation (Fig. 7). The increase of the water portion instead results in a smaller operating range tending to a constant minimum.

The described results are compared with those measured on other extraction equipment in Fig. 8. Here the EC column shows an efficiency well comparable to the other types. However, its operating range not only covers the frame of all conventional equipment but also substantially exceeds it. Due to its evident flexibility the EC conception is therefore expected to be suited for many applications in extraction practice.
Outlook  The present state of development and the results obtained permit propositions for the further use of the EC conception. While versions with the small diameter of 75mm would be feasible in the described way or with ceramic plates where the water phase is to be dispersed, development should be advanced with a column of larger diameter, possibly starting with a three-stage specimen to examine the effects of the larger cross-section.

[Fig.8] Stichlmair J., Chem.-Ing.-Tech. 52, 1980, Nr.3

Fig. 1  EC laboratory column
Fig. 2  Bottom section
Fig. 4. Comparison of acetone concentration measurements in toluene with gas chromatography and density measurement.

Parameter Load (m³/m²h):
- □ - 10
- △ - 30
- × - 50
- ▼ - 20
- ○ - 40
- + - 60

m.t. direction: water-toluene
vol. phase ratio: W:T = 1:1.5

Fig. 5. Mass transfer results at various rotor speeds.
Fig. 6 Typical mass transfer results of the pilot column

Fig. 7 Load characteristic of the pilot column at various phase ratio without mass transfer

Fig. 8 Comparison of extraction columns (source: Stichlmair)
Starting point of this industrial research work was the development of an extraction apparatus that, in comparison to conventional extractors should accomplish much higher specific throughput. The ulterior motives were economic considerations such as saving costs for the investigation and the solvent demand.

Beside the hydrodynamic analysis and the optimization of the installations, the main attention was paid to the operating behavior in case of hydrodynamic overload.

The result of the theoretical considerations was an apparatus consisting of dispersion cells and fixed installations for the phase-guiding. Experiments showed, that closed paddle wheels (Fig.3) for dispersion and concentric cones as fixed installations were suitable constructions /1/ (fig.1).

Fig.1: INSTALLATIONS OF THE SHE

To develope scale-up guidelines, columns of 100, 200 and 400 mm in diameter were investigated.

Mode of action (Fig.2):

The fixed installations force the phases to pass defined canals between the dispersion cells.

In canals "II" of these installations the dispersed phase drops are forced to coalesce and the coalesced dispersed phase then leaves these canals with the velocity "$v_2$".

By this demand the narrowing of the canals that causes
a dam-up of the drops, is fixed. The technological advantage of the coalescence and redespersion of the dispersed phase compared with common countercurrent extraction columns (RDC) is the similarity in the mass transfer behavior to mixer-settler plants.

The continuous phase is forced to pass the canals "I". The high velocity \( v_1 \) of the continuous phase at the outlet opening hinders the drops with the rising velocity \( v_3 \) to enter the canals "I" in countercurrent flow.

**Fig. 2: PRINCIPLE MODE OF ACTION OF THE FIXED INSTALLATIONS OF THE SHE**

The selfstabilizing effect of this column can be explained by the following mode of action.

In case of hydrodynamic overload the dam-up of the dispersed phase in canals "II" reaches the inlet opening of the installations. On account of the wave movement in the boundary layer a periodic overflow of the dispersed phase forms a strand flow in the canals "I". By this strand flow the symptoms of flooding, phase inversion, disappear. Phase inversion occurs then, when the dam-up reaches the inlet opening, because then the hold-up in the dispersion cells reaches a level that causes the dispersion of the continuous phase in the dispersed phase drops.

This selfstabilizing effect gives the great advantage that periodic flooding can be stopped by lowering the flow rate of the phases or by lowering the number of revolutions of the agitator. In case of flooding, emptying of the column is not necessary anymore!

**Fig. 3 shows the design of the fixed installations for industrial columns, consisting of octagonal pyramids. The agitator shown in Fig. 3 is the same as used in our laboratory columns, but for industrial plants other possibilities, like packings, should be considered.**

**Fig. 3: SHE - EXTRACTOR**
Results:

Operating limits (Fig. 4):
The determination of the operating limits shows the high
specific throughput - up to 100 m$^3$/m$^2$h based on the system
water - toluene - and selfstabilizing behavior over the
whole operating range.
The operating limit was reached when the dam-up in canals
"II" grew up to the inlet opening. This was observed by
scattered indication of the phase inversion.

Fig. 4: OPERATING LIMITS

The dependence on the number of revolutions for this type
of column is similar to other constructions /2/. The maximum
specific throughput is reached at the lower limit of the
number of revolutions. This limit is the operating point
at which an incontestable function of the extraction process
is still guaranteed.

On account of the excellent stability, the approximation to
the optimal operating point near the operating limit is
much easier.

The geometric relations of the fixed installations were held
constant for all experiments. For the treatment of systems
of different physical properties or in case of extreme phase
rates, it is possible to vary the geometry. For example this
might be done by an adaptation of the outlet openings of the
canals.

Entrainment of the dispersed phase at the bottom of the
column was only observed in case of extreme overload.

Using the "dispersion model" /3/ developed at our institute,
countercurrent extraction columns are calculated as
demonstrated /3/ /4/.

Height of the column = height necessary for theoretical mass
transfer
+ height for axial mixing of both phases
For the calculation of the extent of dispersion it is necessary, to know the axial mixing parameters ($B_0$ and $D_{ax}$) which are also calculated by the dispersion model /5/.

Fig. 5 shows the results of the experiments leading to the parameters of the axial mixing of the continuous phase. The correlation for $\frac{1}{B_0}$ results from experiments realized in columns of 100 and 200 mm diameter.

**Fig. 5: AXIAL MIXING OF THE CONTINUOUS PHASE**

In the range of low load the axial mixing is higher than in comparison to that of an RDC. That results from the fact, that there are low frequency currents in the continuous phase at low load, which increase the axial mixing. From about 60 $m^3/m^2h$ total throughput, the axial mixing is lower than in an RDC, beside the fact that at this high load the RDC cannot be used anymore.

Fig. 6 shows the axial mixing of the dispersed phase, according to the results of the columns of 100 and 200 mm diameter.

**Fig. 6: AXIAL MIXING OF THE DISPERSED PHASE**

In this column the axial mixing of the dispersed phase depends on the following effects:

1. In case of low load there are low frequency currents in the continuous phase which transfer to the dispersed phase.

2. Small drops are dragged off with continuous phase in areas of high specific velocity of the continuous phase.


4. Different rising velocities of the drops resulting from different diameters cannot extend over the whole length of the column as the drops are forced to coalesce between the stirring cells.
Fig. 7 shows the superposition of the results shown in Fig. 5 and Fig. 6. This leads to a dependence similar to that of the RDC with the difference, that the SHE reaches the value

\[
\frac{Bo_d}{Bo_c} = 1
\]

at lower numbers of \(Bo_c\) and might become less than one. The RDC reaches this value at \(Bo_c = 20\). In comparison to that, the SHE reaches \(Bo_d/Bo_c = 1\) at \(Bo_c = 5\). That gives a great advantage for the calculation of the SHE as for this column the axial mixing of both phases is constant over a wide operating range and the determination of the axial mixing parameter of the continuous phase even for industrial columns is much easier than that of the dispersed phase.

**Fig. 7: COMPARISON OF THE AXIAL MIXING OF BOTH PHASES**

**Conclusion:**

Summarizing the results of the hydrodynamic analysis, the SHE is an extraction column that gives the following advantages to

1. High specific throughput
2. Selfstabilizing effect in case of overload
3. Incontestable working conditions near to the loading limit
4. Influence on the residence time distribution by variation of the fixed installations
5. In connection to the results of mass transfer experiments, similarity to the principles of the "mixer-settler" extractor is given

In addition to these investigations a method for the calculation of extraction columns, including the turbulent flow conditions in the stirring cells will be developed. The result will be published.
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>SI Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>l</td>
<td>characteristic length</td>
<td>[m]</td>
</tr>
<tr>
<td>n</td>
<td>number of revolutions</td>
<td>[s⁻¹]</td>
</tr>
<tr>
<td>( \bar{v} )</td>
<td>average velocity</td>
<td>[m/s]</td>
</tr>
<tr>
<td>( \bar{V} )</td>
<td>specific phase rate</td>
<td>[m³/m² h]</td>
</tr>
<tr>
<td>v</td>
<td>velocity</td>
<td>[m/s]</td>
</tr>
</tbody>
</table>

\[
\text{Bo} = \frac{\bar{v} \cdot l}{D_{ax}} \quad \text{Bodenstein number}
\]

\[
D_{ax} \quad \text{axial dispersion coefficient [m²/s]}
\]

### Indices

- ax: axial
- c: continuous
- d: dispersed
- R: agitator

### References

1. Österr. Patentschrift A 4568/80 "Zweiphasengegenstromapparat"
Table of Figures:

Fig. 1: INSTALLATIONS OF THE SHE
Fig. 2: PRINCIPLE MODE OF ACTION OF THE FIXED INSTALLATIONS OF THE SHE
Fig. 3: SHE - EXTRACTOR
Fig. 4: OPERATING LIMITS
Fig. 5: AXIAL MIXING OF THE CONTINUOUS PHASE
Fig. 6: AXIAL MIXING OF THE DISPERSED PHASE
Fig. 7: COMPARISON OF THE AXIAL MIXING OF BOTH PHASES
INSTALLATION

CONSTRUCTION WITH
CONCENTRIC CONES

PRINCIPLE MODE OF ACTION
SHE extractor
OPERATING LIMITS

System: Water - Toluene
Water - Butylacetat

SHE 200
AXIAL MIXING OF THE CONTINUOUS PHASE
System: Water - Toluene

\[
\frac{1}{B_{oc}} = 0.0055 \frac{nDR}{V_C} + 0.079
\]

+ SHE 200
* SHE 100
AXIAL MIXING OF THE DISPERSED PHASE
System: Water - Toluene

\[ \frac{1}{B_{o_d}} = 0.0016 \frac{1}{v_d} + 0.08 \]

+ SHE 200
* SHE 100
COMPARISON OF AXIAL MIXING OF BOTH PHASES

System: Water - Toluene

\[
\frac{\text{Bo}_d}{\text{Bo}_C} \quad + \text{ SHE 200} \\
\ast \text{ SHE 100}
\]
SECONDARY DISPERSION SEPARATION ON FIBROUS BEDS

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Abstract: The article deals with separation of secondary liquid-liquid dispersions on closely packed glass fiber beds. The efficiency of the coalescer was measured using the concept of breakthrough velocity, and correlated by means of modified Spielman-Goren equation for filtration coefficient. Wide range of parameters affecting the coalescer performance have been studied: physical properties of liquids, operating variables and some geometric characteristics of glass fibers. Contrary to our previous work, oil-in-water type of dispersion was studied. General conclusion can be made that this type of dispersion is more difficult to be separated than the reverse one. Optimal pH of the continuous phase must be provided for satisfactory separation efficiency.

Introduction

Forced coalescence of secondary dispersions on various porous materials is an important method for final separation of liquid phases. Fibrous mats composed of closely packed glass fibers represent the most simple, however very effective way to achieve this task.

A considerable amount of work on the field have appeared during decades.1-8 Some of them are fundamental from the view point of possible mechanisms, some other more experimental in nature. Relatively
little success have been noted in sense of a sound design equations of the fiber coalescers. However, considerable progress in understanding the processes going on in fibrous beds has been achieved. Considering separation efficiency, most of the authors used filter coefficient:

\[ \lambda = \frac{-\ln \frac{n_L}{n_0}}{L} \]  

i.e. the logarithmic ratio of number of particles, of a given size coming in and out from the coalescer of bed depth L. The alternative way is application of breakthrough velocity \( V_b \). The present work tries to bring together these two concepts on the basis of critical analysis of the relevant literature and practical experience.

The most important semitheoretical correlation was proposed by Spielman and Goren. They related the dimensionless filter coefficient to the so-called adhesion group:

\[ \frac{\lambda d_T^3}{d_p^2} = c \left( \frac{A d_T^2}{n_c U d_p^4} \right) \]  

where \( A \) represents the Hamaker constant, allowing for the effect of surface forces. \( c \) and a are constants.

The filter coefficient defined by Equation (1) is suitable for dispersion having uniform drop size which is impractical. From these reasons Eq. (2) was modified using filter coefficient defined in terms of volume ratio \( \frac{x_L}{x_0} \) instead of the number ratio \( \frac{n_L}{n_0} \). Consequently for a required coalescer performance (e.g. separation of 99% of the dispersed phase) the modified filter coefficient may be expressed as:

\[ \lambda^* = \frac{\ln \frac{x_L}{x_0}}{L} = \frac{k}{L} \]
The corresponding superficial flow velocity is called the critical velocity and enters into adhesion group. The Hamaker constant can be for two phase liquid systems being separated on a solid phase of given composition (e.g. glass fibers) substituted with the product of interfacial tension $\gamma$ and the square of characteristic drop size $d_p^2$. The Sauter mean diameter $d_{ps}$ can be readily applied in the modified form of the correlation (2):

$$\frac{d_f^3}{L d_{ps}^2} = K \left( \frac{\gamma d_f^2}{\eta_c U_{cr} d_{ps}^2} \right)^b$$

(4)

The constants $K$ and $b$ must be for a given geometry obtained from experimental data. This type of equation is suitable for design purposes since it contains only factors that are normally well known, so that the maximum permitted flow rate for any bed depth can be calculated.

Experimental

The experiments were carried out on the apparatus shown in Figure 1. With minor alterations it was the same as used in our previous work. Liquids used in the experiments were mutually saturated distilled water and various organic liquids as the dispersed phase. Limited number of tests were made with aqueous solutions of surface active agents. Physical properties of the systems are presented in Table 1.

Glass fibers are provided of nominal diameter 12 $\mu$m. They are chopped into bundles 15 mm long, carefully stretched in width, presoaked and inserted by hand into the coalescer in form of parallel layers. There were no problems regarding homogeneity of the fibrous bed although it was not specially controlled.

Inlet and outlet concentration of the dispersed phase (i.e. organic phase) in the continuous one were measured by means of total carbon
analyser. Special technique was developed for sampling and analysing the heterogeneous mixtures.

Preliminary tests revealed that for the case of organic-in-water type of dispersion there is no difference between glass fibrous bed presoaked with the dispersed or with the continuous phase. From practical reasons the fibers in this study were presoaked with the aqueous phase. Volumetric flow ratio of the liquids entering the mixing tank was constant 1:100 at stirer speed 25 s⁻¹.

Samples of the dispersion leaving the coalescer at various flow rate were left 5 minutes and then analysed on total organic content. The flow rate of dispersion was gradually increased, until positive breakthrough was established visually and analytically.

Results and Discussion

Numerous experiments were carried out in order to obtain relation between the outlet concentration of dispersed phase and the total flow rate (or superficial velocity of the dispersion). Preliminary tests showed strong influence of pH on separation efficiency. Therefore, the dependence between outlet concentration and flow rate was measured for several liquid-liquid systems, all aqueous continuous, at various pH values and different bed depths. Typical results are presented in Figure 2 for the system ethyl acetate-water. The highest value of pH represents systems without addition of sulfuric acid (i.e. inherent pH). There is obviously an optimal value of pH for which the critical separation velocity is maximal at a given bed depth. This is more clearly shown in Figure 3. A family of similar curves was determined for each system, all having the extremes at pH about 4. The same value was reported by Takahashi et al. who used bubble column for dispersion separation.

When the critical separation velocities for various systems at optimal pH were correlated using Equation (4), better agreement was
found when the dispersed phase viscosity was used instead of the continuous phase in the modified adhesion group. Quality of the correlation is satisfactory however more liquid systems have to be examined before any definite conclusions will be drawn.

List of symbols

A Hamaker constant
d_f fiber diameter
d_p particle (drop) diameter
d_ps Sauter mean drop diameter
n number of drops
U superficial velocity
U_cr critical superficial velocity
x volume fraction of dispersed phase
\gamma interfacial tension
\eta_c continuous phase viscosity
\lambda filtration coefficient

Literature


Table 1. Properties of liquids used in studies of coalescence, at 20°C

<table>
<thead>
<tr>
<th>Liquid system</th>
<th>γ (mN/m)</th>
<th>n_d (mPa.s)</th>
<th>ρ_d (kg/m³)</th>
<th>solubility in water (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kerosene-water</td>
<td>41.47</td>
<td>1.54</td>
<td>778.0</td>
<td>0.05</td>
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<tr>
<td>butylacetate-water</td>
<td>11.28</td>
<td>0.741</td>
<td>882.4</td>
<td>7.0</td>
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<td>ethylacetate-water</td>
<td>6.47</td>
<td>0.464</td>
<td>901.3</td>
<td>85.8</td>
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<tr>
<td>MIBK-water</td>
<td>9.71</td>
<td>0.590</td>
<td>801.0</td>
<td>28.8</td>
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<tr>
<td>paraffin oil-water</td>
<td>43.7</td>
<td>29.3</td>
<td>840.0</td>
<td>0.05</td>
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<tr>
<td>paraffin oil+kerosene (3+1) - water</td>
<td>34.6</td>
<td>13.1</td>
<td>825.3</td>
<td>0.05</td>
</tr>
<tr>
<td>paraffin oil+kerosene (1+1)-water</td>
<td>32.3</td>
<td>6.5</td>
<td>809.7</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Figure 4: Experimental apparatus

Legend

1 - mixing tank
2 - turbine stirrer
3 - motor
4 - coalescer
5 - settler
6 - cooling coil
7 - separator
8 - peristaltic pump
9 - drainage of the settler
10 - centrifugal pump
11 - main drainage
12 - rotameter
13 - valve
14 - fibrous bed
15 - perforated plates
16 - screw
17 - sampling tube
18 - air drainage
19 - sealings
Figure 2: Outlet dispersed phase concentration as a function of superficial velocity and pH for system ethyl acetate in water.

Figure 3: Critical separation velocity as a function of pH and bed depth for ethyl acetate-water.
SESSION C:
REACTION ENGINEERING
TEXTILFASERN AUS LENZING
sind veredelte Natur aus pflanzlichem Rohstoff
Über 100.000 Tonnen jährlich
davon 25.000 Tonnen Lenzing-MODAL
aus Europas größtem Viskosefaserwerk
Unsere neuen Produkte
Maschinen
Meßgeräte
Chemikalien
Verpackungen
Verfahrenstechnik
erobern neue Märkte

CHEMIEFASE LENZING AKTIENGESELLSCHAFT
A-4860 LENZING - AUSTRIA - TELEFON: 07672/2511 - TELEX: 026-606 lenfa a
Chemical Reaction Engineering

Plenary Lecture

3rd Austrian-Italian-Yugoslav Chemical Engineering Conference

Graz 1982

by

J. C. R. Turner
University of Exeter
England
Introduction

When I was asked to chair the Reaction Engineering session at the 3rd CEC, I was also asked to provide an introductory review paper. This posed a problem: how to speak usefully about a subject which has grown vastly in the last twenty years and which has also rather lost its original coherence. I have decided to divide my talk into three sections:

i) A history of the development of the subject.

ii) An assessment of the present position of the subject.

iii) A brief discussion of the papers to be presented later at this conference.

I must first apologise to my audience for referring rather a lot to publications in the English language. You will doubtless have expected that from an Englishman, and I would not like to disappoint your expectations, but there are two rather more solid reasons for this. Firstly English - or at least a passable imitation of the language - is sometimes the only common means of communication (e.g. at this Conference?). The other day I interviewed a prospective graduate student, who must be one of the few Irans who speak English with a Welsh accent.
Secondly, the United States, which has 130 University Departments of Chemical Engineering accredited to the AIChE has provided the centre of gravity of the subject, and the members of those faculties have provided a lot of publications!

The Historical Development of Chemical Reaction Engineering

The rapid growth of chemical engineering can be said to have started in the United States in the 1930's, and in 1935 MacMullin and Weber (1) presented a paper on CSTR's to the AIChE. In the discussion, A.P. Colburn's comments were somewhat cool. At that time reactor design was based on analogies with batch, or bench, chemistry - which we now know are often incorrect.

A decade later Denbigh (2) pointed out the effects which a change from batch to continuous operation could have, particularly on polymerisation reactions. In these cases the nature of the product (e.g. molecular weight distribution) is markedly changed.

I might mention here that when teaching chemical reaction engineering in the United States, I have noticed the weaker background in chemical kinetics possessed by students - weaker than would be found elsewhere. It is perhaps for this reason that American textbooks on chemical reaction engineering devote so much space to chemical kinetics. Elsewhere it would be expected that our students would have been taught that material in their chemistry courses.

However, this assumption may prove to be wrong in the future, since chemistry (like physics) discards subjects which it no longer finds interesting. Since I was a physical chemist, the increasing concentration on molecular behaviour (spectroscopy, chemical physics) has led to less interest in the behaviour of material. I have been assured by those who should know that many catalytic chemists, skilled in the theory and experiments of single-crystal metal faces, have only a sketchy knowledge of mass-transfer effects. Thiele's paper in 1939 (3) would have been more accessible to physical chemists then than now.

The divergence between chemists and chemical engineers is well exemplified by Levenspiel's comment (4) that not 1 in 50 new PhD's in chemistry could calculate the exit composition from a plug-flow reactor in which \( A + 2B \), even assuming constant \( T, P \) and (naturally) first-order kinetics. Of course any BSc
chemical engineers could do it and would claim no
prizes for that.

But to revert to my historical development, an
early landmark was Danckwerts' paper (5) on residence
times. There had been earlier work, e.g. by Gilliland
and Mason (6), but this paper laid the foundations for
what turned out to be a rapid building programme. For
some years it seemed that every issue of every Journal
contained a residence-time paper. Happy days - long
since gone! Many of the conclusions, interesting in
their derivation, were unimportant, but have led to
considerations of mixing in reactors, selectivity and
so forth, which are important.

In the last quarter-century the growth of chemi-
cal reaction engineering has mirrored that of science
as a whole. It is now virtually impossible for any
one person to feel competent to deal with the whole
subject; even to have a feel for what the subject is
about is now difficult. This poses problems for those
who have, like myself, to teach successive generations
of students, to give them a basis, an orientation, in
the subject.

There are also difficulties for those in indus-
try to assess the value of what is being published.
As early as 1964, van Heerden, (7), in his opening
address to the 3rd European Symposium on Chemical
Reaction Engineering drew attention to doubts about
the value (to industry) of much of what was being done in the subject, and stressed that in his opinion the "lack of kinetic data will be chronic". We will in general neither know the kinetics precisely enough, nor, if we did, be able to control the temperature precisely enough to be able to use them.

Parts of chemical reaction engineering have split away from the main subject like religious sects, and the high priests have developed their own language and ceremonies. As an example I choose fluidisation, where a considerable academic effort has been applied. I quote Grace (8), a skilled practitioner of the art, who looked at the heavy reliance on certain well-known models, "one might reasonably conclude that these approaches have been supported by at least the majority of experimental evidence. Nothing could be further from the truth."

These pessimistic thoughts can be counterbalanced by the knowledge that practical chemical reaction engineering has developed greatly since 1950. Though we still can't design a catalyst, we can measure and understand catalytic behaviour better than we could. Work on fluidisation, on bubble reactors - to mention but two areas - has been helpful, even if no firm would yet design such reactors on academic principles alone.

So to sum up, we have a subject, chemical
reaction engineering, which has grown immensely, and has become compartmentalized. Much of what is published is ingeniously mathematical, but it often rests on a frail basis, or none, of experiment. It often cannot realistically be tested, and may not, even if so tested, be applicable in practice. Provided that everyone is clear about this situation, and delusions of grandeur are avoided, there is, I suppose, little damage in allowing academics to follow their inclinations.

Some Comments on the Present Position in Chemical Reaction Engineering

If we look at chemical reaction engineering today, we see a subject which has divided into areas, in each of which much detailed work is going on. The series of International Symposia, held every four years in Europe, provide valuable information on the development of chemical reaction engineering, and it is helpful to look at the most recent one, held in Nice in 1980, to see where we are now (9, 10).

At this Symposium there were 66 papers + 9 plenary lectures. One fact stands out: although many academics in this field have consulting contacts in industry, industry provided only some 15% of the papers. This has always been the situation; although industry is where chemical reaction engi-
neering finds its outlet, it has always proved difficult to persuade industry to tell the profession what has been done. There are obvious reasons, such as industrial secrecy, to prevent the most recent developments being presented at conferences. But I think that there is a defensiveness, an unwillingness to appear foolish before all those clever academics, which prevents all but the most self-confident companies from describing their undoubted advances. It is true that some academics (though none here, I am sure) are arrogant and off-putting, but most of us would like to hear of applications of theory. Industrialists do attend these symposia, they even go to (some) of the lectures, and take part in discussions. I wish they did present their views more often.

But enough of that; I wish to look at some areas of chemical reaction engineering:

1) **Flow systems**

The early work, on plug-flow reactors and stirred-tank reactors, provided a coherent base for the initial development of chemical reaction engineering, and this is now firmly entrenched in all undergraduate curricula. More recently the existence of multiple steady states has excited academic interest (more of this later). Another related area is the non-steady operation of reactors, which may lead to improved performance. I don't think industry has seen much advantage
from this work yet, but it is interesting. Fortuin et al. (9, p.439) gives an example of a CSTR showing multiple steady states and limit cycles, while Hudgins et al. (9, p.273) describe operating a catalytic reactor under feed cycling. Pismen (10, p. 1950) gives a general review.

2) Residence-times, segregation etc.

Danckwerts' paper (5) originated a large number of publications in this field. It was already known that the equation

$$\bar{c} = \int_0^\infty c(t)E(t)dt,$$

for the exit composition from a reactor, $\bar{c}$, was only exact in general for a first-order reaction. Plug-flow reactors, and perfectly mixed reactors could be dealt with (the latter case giving two answers in general, for minimum and maximum mixedness). For other distributions, $E(t)$, the bounds within which the yield could lie were described by Zwietering (11), while Danckwerts also discussed in later work the concepts of segregation and micromixing. Interest now in this field concerns the effects of micromixing in reactors with more than one reagent, usually fed to the reactor in separate streams (e.g. Lintz and Weber, 9, p. 203). Where there are successive reactions (substitution or polymerisation) and these are "fast" in comparison with mixing-times in the
reactor, then it is not just the overall reaction rate which may be affected, but also the product distribution. This effect of mixing on selectivity is of importance; a reactor which produces the wrong material is more of a problem than one which produces rather less of the right material than expected. One can mention work by Villermaux and co-workers, at Nancy, and by Bourne, Rys and others at ETH, Zurich.

3) Catalytic reactors

Here we have a field ranging from the chemical physics of surfaces to the behaviour of porous catalyst particles in the unsteady state. The subject is vast and detailed. There are virtually unlimited numbers of different chemical systems for the physical chemist to examine, and to try to understand the molecular kinetics. The formulation of any effective catalytic surface into a porous pellet introduces the topics of mass and heat transfer, which come into the picture again when these pellets are used in a packed-bed reactor. As a textbook for graduate students one can mention Carberry's work (12), which repays careful reading. In recent years this field has proved fertile for applied mathematicians, particularly in the United States. In his two-volume work on the mathematics of diffusion, Aris (13) refers to the "pedestrian part of the subject" being "copious without order", whereas the topics of the second volume (uniqueness, stability etc.)
are "energetick without rules".

For someone such as myself, listening to the accounts of bifurcation, orthogonal collocation and so forth, the feeling is rather of having wandered into a High Mass in Latin, with a very inadequate command of the language. Perhaps this analogy is already dated, given the modern trend in the Catholic Church.

With all this activity going on, one is not surprised to find at least a dozen papers in this field in reference 9, and the approaches now used 'spill over' into other fields, too. One wonders how much attention industry pays to all this, and one notes Paspek and Varma's comment (9, p. 33) that "the comparison of theoretical models with actual experimental results has unfortunately not been pursued in any great detail." Again, Emig et al. (9, p. 249) say "it has been shown that multiple steady states are very unlikely to occur under technical operating conditions of catalytic fixed bed reactors."

But such multiple steady states, limit cycles, and oscillations are accessible, to laboratory reactors at least. They are undoubtedly of interest to academics, and - given the variety of behaviour - one can expect much further work in this field.

Emig et al. (9, p.249) and Hlavacek et al. (9, p.258) do consider runaway, and parametric sensitivity. These are of obvious importance to any industrialist
trying to operate a process. My own experience, in connection with ICI's Nylon works, showed the great difficulty of controlling an exothermic packed-bed reactor, given inevitable slight fluctuations in the feed temperature.

Another area of practical concern is the deactivation of catalysts, by the (one hopes, slow) accumulation of poisons, or of coke, or by a transformation of, e.g., metal crystallites. There are several papers in Ref. 9 on this topic. The process, or processes, leading to the loss of catalytic activity may be varied, and difficult to determine. Their effect on the overall behaviour of a catalytic reactor is a further complication. One can see that in industry fairly rough-and-ready models of reactor deactivation may have to be used to try and optimise economic performance.

So, to sum up, one can see work continuing in this field. Much of this will be detailed, and mathematical, and not easily accessible to non-specialists. Good review articles will continue to be needed.

4) Gas-liquid reactors

Chemical reaction engineering and gas-absorption technology come together with the subject of gas absorption with chemical reaction. This is another field in which Danckwerts has made a leading contribution. His textbook (14), is a fundamental reference,
and one must also mention the work of Sharma at Bombay. It may in some cases be possible to treat the "physical" mass-transfer processes and the "chemical" reactions separately, but in many cases this cannot be done. Heterogeneous catalysis may also be involved, as in many trickle-bed reactors. At first sight, a stirred tank of liquid, through which a reagent gas is bubbled, might seem comparatively simple (how many treatments of this type of reactor start off with the confident assertion of 'well-mixed liquid and plug-flow gas'). But it is not long before complications become impossible to ignore. What is the effective liquid-gas surface area, how is this affected by surface-active components, are there gross circulation patterns in the reactor, what happens if the impeller design is changed? The list seems endless, and the literature is vast. The underlying reason is that we don't understand two-phase flow very well, let alone the interaction between two-phase flow and chemical reaction. As a result, it is not too surprising to hear of major disappointments when experimental rigs have been scaled up to the production scale. There are several papers in Ref. 9 on this topic, and we can expect much further work. I wonder whether it will be feasible to establish a reasonably-simple framework for a phenomenon involving so many possible variables. I remember an attempt to 'model' bubble reactors with as many as 17 variables, but I myself received little physical enlightenment from such a model.
It might have been better - at least for interpolation - to look for a purely empirical statistical fit to a small number of variables.

5) Gas-solid reactors

The models which have been championed by, among others, Levenspiel in the United States and Kunii in Japan, such as the "shell-progressive" model, are now established in teaching curricula. Where the particles are small enough to be fluidised, the technology and the terminology change. The growth of fluidisation as a research area, with its own symposia, etc., has been quite remarkable - particularly since so much of the work has been divorced from practical reality, however interesting to the academics. I have already quoted Grace (8); Levenspiel, who is not attracted by deep mathematics, and who does like to have a realistic physical grasp of a process, can be similarly quoted. In his paper with Park and Fitzgerald (9, p. 295) he discusses large-scale fluidised-bed combustors (fluidised combustion has recently given a practical boost to fluidisation). They say "no bubble and cloud and emulsion regimes, no two-phase models. Because models 1 through 10 (of 11 considered) all assume a gas flow pattern in which the bubbles rise faster than the interstitial gas, none of them can be used to predict, even qualitatively, the flow of gas in a utility scale AFBC." So there! I cannot pretend that everyone else
agrees with them, but it has always seemed to me that industrial fluidised-beds, in which a churning sand-storm may be raging, will not be adequately described by the application of the Davies-Taylor theory of rise of spherical-cap bubbles.

6) Biochemical Reaction Engineering

The recent emergence of bio-technology has provoked a fashionable interest in the field. There is a slightly uneasy feeling that the subject is about to 'take off', and that the world will not be the same place when genetic engineering gets going. Biochemical reaction engineering has, of course, been around for some time in, for example, the production of antibiotics, the fermentation processes, and in waste-water treatment. There are some difficulties in bringing together the techniques of biology and of chemical engineering. It is rare to find anybody competent in both fields; biologists often have a weak grasp of engineering mathematics, and engineers know very little about living systems. In the development of their Deep Shaft process for the production of single-cell protein, ICI found many problems in the successful fusion of biology with engineering. This process, by the way, can also be adapted to sewage treatment (with the completely-changed objectives of minimum cell growth and maximum CO₂ production).

At Nice there was a session devoted to biochemical
reaction engineering (9, pp. 99-141, 10, p. 1854).

7) Electrochemical engineering

Lastly, I wish to mention electrochemical engineering, on which there were also some papers at Nice. This subject brings together physical chemists and chemical engineers, but so far electrochemistry has not made a very great impact on chemical engineering - if one excepts NaOH/Cl₂ production, and aluminium manufacture. Of course, all engineers make use of the product of the electroplating industry, and should know about corrosion. But the application of electrochemical oxidation or reduction in the production of chemicals - organic syntheses, for example - has not so far matched the enthusiasm of its supporters.

The applications of ion-exchange can also be regarded as chemical reaction engineering. I have had an interest in this field myself. The major use of ion exchange is, of course, in the production of a vital chemical, in vast quantity, at superlative levels of purity, and ridiculously low cost - water. Modern power generation would also be impossible without ion-exchange. But this is not the occasion to 'sell' ion-exchange!
Chemical Reaction Engineering at the 3rd CEC

As well as reviewing chemical reaction engineering, I would like, as Chairman of the session on chemical reaction engineering, to introduce the papers being presented here at the 3rd CEC. I shall try to place them in the context of what I have already said.

Conti, Sicardi and Baldi describe the different hydrodynamic regimes in stirred gas-liquid contactors. They present results of their own, using a "Rushton" stirred tank, and also attempt to bring together the techniques, and terminology, of several other workers. We see in their paper some of the difficulties involved in considering gas-liquid reactors.

Marton, Havas-Dencs and Szokonya present a paper on the furfural reactor. I shall see in the discussion whether their treatment of 'time' in a semi-continuous reactor is correct; this point of course lies behind the early work of Denbigh (2), and is often the cause of confusion for chemists. It may be of interest to some of us, as we eat our breakfast cereal, to know that the first industrial production of furfural was by the Quaker Oats Company in 1922.

Oliveri Del Castillo and Rivolta try to fit a model to a gas-liquid reactor for the production of acetic acid from acetaldehyde - another gas-liquid reaction problem. The familiar assumptions of plug-flow in the gas and well-mixed liquid are made.
Trotta and Del Giudice treat the problem of reaction between a solid and the liquid flowing over it. I must confess to being defeated by the mathematics here - I hope to get some understanding of the physics from their presentation.

Catalyst deactivation is the subject of the paper by Zrnčević and Gomzi. They have deliberately poisoned a supported nickel catalyst, used for benzene hydrogenation, by dosing the feed with thiophene. Their results deserve study.

Kurtanjek discusses the effect on a heterogeneous reaction of changes in the catalyst surface. Multiple steady states, oscillations and "chaotic behaviour" are mentioned, while from the lush mathematical growth bifurcation rears its head.

Pavko and Levec present work with a rotating basket reactor. This technique is commonly employed in differential reactors for fluid-solid reactions. The extension to 3-phase reactions can give rise to problems, such as imperfect wetting, for example.

The paper by Petrus, de Roo, Stamhuis and Joosten on the use of ion-exchange catalysis for the hydration of butene, was of particular interest to me. This was not only because it involves ion-exchange, but because it brought back memories of a Shell refinery and of sitting on top of a tank of 'black acid' measuring the feed rate to a vacuum filter by swinging a pendulum to find the liquid surface. "Health and Safety" would
probably not permit this now, but I have survived over 25 years since the experience. The aim of the filter was to remove fine carbon particles formed by butene decomposition in the strong sulphuric acid, which carbon both caused SO₂ evolution in the subsequent concentration step, and also led to enhanced butene loss. Clearly Joosten and his co-workers have a much better process.

I must again admit defeat by Kiprijanova-Radovanović and Markovska, in their mathematical modelling of a copolymerization. Perhaps they will show us some of their computer simulations.

Lastly we have a paper by Rizzuti and Yue on a photocatalytic reactor. The use of solar energy for chemical reactions (perhaps as a store for such energy, if not for chemical production) has excited interest around the world.

There was a paper in this area at Nice (9, p. 413), and it is interesting to see one here.

Finally, may I congratulate those authors for whom English is not their native language. It must have involved a great deal of effort to present their papers in English; I know that I could not approach their performance in any of the languages of the host nations of this conference.
References


HYDRODYNAMIC REGIMES IN GAS-LIQUID STIRRED VESSELS

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Introduction
In gas-liquid stirred vessels some hydrodynamic regimes, connected with the gas circulation in the vessel, must be considered (1-3); each regime is characterized by peculiar gas-liquid interactions which affect the mechanisms of momentum, mass and heat transfer.

In previous works it was observed that the gas hold-up (4-6), the gas liquid mass transfer (7), the solid suspension (8) and the solid liquid mass transfer (8) followed different mechanisms depending on the regime involved, but the definition and the determination of the various regimes were not in a complete agreement.

For this reason in this report the various regimes are carefully defined and some maps are tentatively drawn to define their regions of existence.

Besides correlations proposed in literature for gassed power number and gas hold-up in connection with the hydrodynamic regimes are discussed.

Experimental
Tests have been carried out with pure liquids and aqueous solutions in a vessel with Rushton geometry. The tested systems are listed in Table I. For each experimental run the velocity of the stirrer, the shaft torque and the gas hold-up were measured. The technique used to evaluate the gas hold-up is described elsewhere (9).

Hydrodynamic regimes
As pointed out by Smith (10) it is necessary to consider separately the hydrodynamics of the gas-liquid system in the immediate vicinity of the stirrer zone and in the whole vessel. Under a practical point of view, the considerations on the whole system behaviour are more immediate: for this reason this description has been preferred in this work.

Three main regimes can be observed; namely:

a) by-pass: the gas flows up in a cylindrical zone around the shaft, having crossed the stirrer zone without being dispersed in the vessel;
b) loading: the gas is dispersed by the stirrer only in the upper part of the vessel;
c) total aeration: the gas is dispersed also in the part of the vessel below the stirrer.

There is a lack of homogeneity in the literature about the definition of these hydrodynamic situations; other definitions are listed and compared in Table II.
Transition from a hydrodynamic regime to another

In Table III are listed the various methods used by different Authors to define the regime transitions. The transition a-b is visually clearly defined because by increasing the stirrer velocity $N$, at a constant gas flow rate, it is easy to see the value of $N$ at which the gas bubbles are spread out from the stirrer zone. As observed by other Authors (10), this transition is affected by a not negligible hysteresis effect; this means that, even if the transition is easy to see, it is possible to get different stirrer critical speeds by increasing or lowering the stirrer velocity. Averaged values have been therefore considered in this work. Fig. 1 shows our experimental values of gas hold-up vs. $N$ at constant superficial gas velocity $v_8$; the transitions defined by visual observation are shown too.

According to the method III (Table III) proposed by other Authors (5), the a-b transition will occur when the hold-up is no longer constant and begins to increase with $N$; for these Authors and in disagreement with our visual findings the values of $N$ at which the transition occurs should not depend on the gas flow rate.

The b-c transition, instead, is not easy to see; generally it is assumed that it occurs when the gas bubbles begin to enter also the part of the vessel beneath the level of the stirrer. This transition was determined by Roustan (6) by observing variation in the slope of the gas hold-up curves; on the contrary Fig. 1 shows that no sensible change of the curve slope occurs in correspondence with the b-c transition. Nienow et al. (1) define the b-c transition by considering the minimum of the curve of the gassed power number $N_p$ vs. the aeration number $N_A$ (method II in Table III). Fig. 2 shows $N_p/N_p^0$ vs. $N$ for the system air-buthanol: the b-c transition defined by visual observation (method I) practically coincides with the minimum of the curves.

Regime maps
a) Pure liquids

As usually made for other multiphase apparatuses (horizontal and vertical pipes with two phase flow, trickle bed reactors etc.) an immediate and useful representation of the various hydrodynamic regimes might be made by means of maps which show the range of the influential parameters at which a certain hydrodynamic situation occurs.

Unfortunately the individuation of the various regimes for the aerated stirred vessels was made by various Authors with different techniques (see Table III) giving rise to very different correlations which often involve different dimensionless numbers: a unique map which considers all the various proposals is hence very difficult to do (as shown by Wiedman et al. (11).

The very poor agreement between the various correlations proposed in the literature is shown in Fig. 3 where, as an example for the a-b transition, the stirrer tip velocity $N_D$ is plotted vs. the aeration
number according to the Nienow's proposal (1).
Moreover some correlations consider that the fluid properties may play a role in the regime transitions whilst in others this effect is completely neglected.
Our results obtained with three different pure liquids seem to show that the influence of the physical properties of the liquids is negligible on the a-b transition: in fact all the values for this transition are well correlated in the plot of $ND$ vs. $N_A$ (see Fig. 4b): this means that in this case only the tip stirrer velocity $ND$ and the gas superficial velocity $v_g$ are relevant parameters.
The same correlation is not satisfactory, instead, for the b-c transition; in fact this transition is probably affected by the size of the bubbles and hence by the properties of the liquid: as shown in Fig. 4a a better correlation for this transition may be obtained by considering the dimensionless number $X$.

b) Liquid solutions
For liquid solutions the effect of the physical properties is surely not negligible but also not very clear; as shown in Fig. 5, by varying the concentration of the solution (at constant gas flow rate) the value of $N$ changes with a not monotonic trend. This effect is more relevant for the b-c transition.

Power consumption
As shown in Fig. 2, the a-b transition corresponds to a sharp decrease of the power number; this occurs because in this hydrodynamic situation large bubbles form behind the blades of the turbine and the form drag of the stirrer diminishes. The minimum of the ratio $N_p/N_g$ should probably correspond to the presence of 6 stable large cavities around the blades (12) and coincides practically with the transition b-c as obtained by visual observation.

By increasing the $N$ value the large cavities are transformed in clinging and then in vortex cavities and the power number increases. The minimum is less pronounced at high gas flow rates, but the trend is very similar for all the liquid examined.

The correlation proposed by Michel and Miller (13):

$$P_g = C \left( \frac{P_g}{C^2 ND G - 0.56} \right)^m = C N^m$$

is shown in Figs. 6a (for pure liquids) and 7 (for aqueous solutions); the best lines corresponding to regime c are also plotted. The figures confirm that the correlation /1/ is valid only in the regime c. Moreover it can be noted that the correlation valid for pure liquids is very similar to that valid for the aqueous solutions (compare the best lines of Figs. 6a and 7.

Fig. 6b confirms that a unique correlation cannot interpret satisfactorily all the experimental curves: the lines calculated by using the correlation of Michel and Miller (13) show that this correlation is valid only for the regime c.
Gas hold-up

Fig. 8a shows the experimental data for a pure liquid; the correlation is in the form:

\[
\frac{H}{1-H} = A \gamma_a \alpha \beta
\]

as previously suggested by other Authors for pure liquids (2). In the figure is plotted the line which best fits the data in the regime c; the data points which refer to the regime a are not well interpreted by this correlating line.

It is also interesting to observe that the correlation /2/ is not able to interpret satisfactorily all the data which refer to liquids with very different physical properties; in fact the best fit lines for water and pure glycol give very different \( \alpha \) and \( \beta \) values (9).

Fig. 8b shows, as an example, the same correlation /2/ applied to a sugar solution (60% of sugar in water). Again the hold-up values in the regime a scatter with respect to the values in the regimes b and c. As observed for pure liquids, the correlation /2/ gives good results for a well defined liquid system, but shows a large scatter when used for different liquids because the values of \( \alpha \) and \( \beta \) are strongly affected by the solution properties.

References
6. Roustan M., private communication
### TABLE I

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Conc. (%)</th>
<th>Density (kg/m³)</th>
<th>Viscosity (cp)</th>
<th>Surf. tens. (dynes/cm)</th>
<th>Symbols</th>
<th>Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol (in water)</td>
<td>100</td>
<td>1109</td>
<td>25.2</td>
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<td>a</td>
<td>abc</td>
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<tr>
<td></td>
<td>80</td>
<td>1095</td>
<td>11.44</td>
<td>52</td>
<td>△</td>
<td>△</td>
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<tr>
<td></td>
<td>60</td>
<td>1082</td>
<td>7.34</td>
<td>55</td>
<td>▽ ▽ ▽</td>
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<tr>
<td></td>
<td>40</td>
<td>1049</td>
<td>3.47</td>
<td>60</td>
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<tr>
<td></td>
<td>20</td>
<td>1025</td>
<td>1.8</td>
<td>64</td>
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<td>▽ ▽ ▽</td>
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<td>60</td>
<td>1280</td>
<td>63</td>
<td>68</td>
<td>▽ ▽ ▽</td>
<td>▽ ▽ ▽</td>
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<tr>
<td>(in water)</td>
<td>54</td>
<td>1254</td>
<td>30</td>
<td>65</td>
<td>▽ ▽ ▽</td>
<td>▽ ▽ ▽</td>
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<tr>
<td>(in water)</td>
<td>32</td>
<td>1136</td>
<td>3.9</td>
<td>67</td>
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<td>2.15</td>
<td>68</td>
<td>▽ ▽ ▽</td>
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<tr>
<td>Butyl alcohol</td>
<td>100</td>
<td>810</td>
<td>3.4</td>
<td>25</td>
<td>▽ ▽ ▽</td>
<td>▽ ▽ ▽</td>
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<tr>
<td>Water</td>
<td>100</td>
<td>1000</td>
<td>1</td>
<td>72</td>
<td>▽ ▽ ▽</td>
<td>▽ ▽ ▽</td>
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### TABLE II

<table>
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<tr>
<th>Regime</th>
<th>Definition of the regime</th>
<th>Authors</th>
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<tbody>
<tr>
<td>a</td>
<td>by-pass</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>by-pass</td>
<td>Loiseau et al. (14)</td>
</tr>
<tr>
<td></td>
<td>flooding of the stirrer</td>
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<td></td>
<td>slightly aerated liquid</td>
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<td></td>
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<td>no gas dispersion</td>
<td>Westerterp et al. (17)</td>
</tr>
<tr>
<td></td>
<td>no gas dispersion</td>
<td>Van Dierendonck et al. (5)</td>
</tr>
<tr>
<td>b</td>
<td>loading</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>loading</td>
<td>Loiseau et al. (14)</td>
</tr>
<tr>
<td></td>
<td>flooding of the vessel</td>
<td>Nienow et al. (1)</td>
</tr>
<tr>
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<td>Rushton and Bimbinet (16)</td>
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<td></td>
<td>aerated liquid</td>
<td>Wiedman et al. (11)</td>
</tr>
<tr>
<td>c</td>
<td>total aeration</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>total gas circulation and secondary circulation loops</td>
<td>Nienow et al. (1)</td>
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<td></td>
<td>flooding</td>
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### TABLE III

<table>
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<tr>
<td></td>
<td>flooding of the impeller</td>
<td>III</td>
<td>(6)</td>
</tr>
<tr>
<td></td>
<td>flooding point</td>
<td>IV</td>
<td>(11)</td>
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<td></td>
<td>engorgement</td>
<td>I</td>
<td>(15)</td>
</tr>
<tr>
<td></td>
<td>minimum agitation rate</td>
<td>V</td>
<td>(17)</td>
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<td></td>
<td>minimum agitation rate</td>
<td>III</td>
<td>(5)</td>
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<tr>
<td>b-c</td>
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<td>this work</td>
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<td></td>
<td>onset of flooding</td>
<td>II</td>
<td>(1)</td>
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<td></td>
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<td>III</td>
<td>(16)</td>
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<tr>
<td></td>
<td>loading point</td>
<td>III</td>
<td>(6)</td>
</tr>
<tr>
<td></td>
<td>desengorgement or loading</td>
<td>I</td>
<td>(15)</td>
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</table>

I = visual observation
II = minimum of Npg curves vs. N
III = variation of the slope of hold-up curves vs. N
IV = variation of the slope of the torque curves vs. N
V = variation of the slope of kgsa curves vs. N
FIG. 1

FIG. 2

FIG. 3

Westerterp (with different σ)

Van Dierendonck et al.

Brujin et al.

Bruxelmans

this work

+ water

X butyl alcohol

o glycol

H - 100

Np/Np

N
rpm

N
rpm

N
rpm

V = 1.18 mm/s

V = 2.36 mm/s

V = 3.4 mm/s

V = 4.7 mm/s

N
A

100

m/s

0.9

0.6

0.4

0.2

3

5

10

20

N
A

100

m/s

0.9

0.6

0.4

0.2

3

5

10

20
\[ X = \frac{N D}{(69.0.25)} \]

**FIG. 4a**

- $N$: rpm
- $D$: m/s

**FIG. 4b**

- + water
- $x$: butyl alcohol
- $o$: glycol

**FIG. 5**

- b-c transition
- a-b transition

**FIG. 6b**

- Power dissipated by the stirrer: $P_g$ with gas, $P_0$ without gas

**FIG. 8a**

\[ M = \frac{P_g^2 ND^3}{Q^{0.56}} \]
FIG. 7

$M = \frac{D^2 N D^3}{Q^{0.56}}$

FIG. 8a

Power dissipated by the stirrer per unit volume

butyl alcohol

FIG. 8b

saccharose 60%
KINETICAL STUDIES OF A STRIPPING-OUT FURFURAL REACTOR

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Furfural, a potential plant component, is generally found in polysaccharide (pentosans) form. Because there polysaccharides are hydrolized at a much faster rate than the cellulose matrix, different furfural production methods utilize that fact excluding the decomposition of cellulose itself [1]. The main operation unit of the pentosane-containing materials or pentose solution based furfural production process is the two-stage reactor. Here the furfural produced in the chemical reaction is extracted or stripped out. This paper presents the process-model of a laboratory scale, atmospheric, non-steady-state reactor after some selectivity investigation. The model and its data set is based on experiments carried out in an isotherm (108 °C) tank reactor. The formation, decomposition and stripping out steps were tested in 35 mass percent sulphuric acid solution containing initially 5-380 g/l d-xylose and 4.2-75 g/l furfural respectively. A relatively simple model structure was found adequately for processes (at 0.5< M <18).
1. FURFURAL PRODUCTION STEPS

Hydrolysing polysaccharides with strong mineral acids at elevated temperatures, simple water soluble sugars are obtained. As a following step, furfural as well as methoxy-furfural are formed from the decomposition products, pentoses, uronic acids, and hexoses, respectively. Furfural is essentially formed in two steps:

a) the first step is the water uptake, i.e. pentosane is hydrolysed to pentose

b) the second step is the water loss, i.e. releasing one mole water, pentose becomes furfural, which to prevent further decomposition, is either extracted or stripped out of the system.

In general, industry-scale furfural production methods are similar, except that the a) and b) steps are performed in one or two units and that of extraction or stripping out is used to recover the furfural produced [2, 3].

There is a considerable amount of literature on the hydrolysation process of pentosane containing materials (corn-cob, rice-straw, deciduous tree, and bagasse etc.) [5].

2. FORMATION AND DECOMPOSITION KINETICS OF FURFURAL

The reaction scheme of the homogeneous phase reaction in acidic medium can be written as follows [2, 3, 4] [6]:

...
d-xylose $\xrightarrow{r_1}$ fufural $\xrightarrow{r_2}$ decomposition product

A number of explanations appeared in the literature relating to decomposition of fufural. Omitting their analysis, the kinetic model proposed by SCHÖNEMANN [7] and DUNLOP [1] was accepted and revised. Under given $H^+$ concentration and isotherm conditions the kinetics scheme is originally:

$$d$-xylose $\xrightarrow{k_1}$ intermediate $\xrightarrow{k_i^f}$ fufural $\xrightarrow{k_3^f}$ acids + resin

Thus the kinetic equation set is written as:

$$\frac{dx}{dt} = -k_1 x$$ \hspace{1cm} (1)

$$\frac{di}{dt} = k_1 x - k_i^f i - k_i^f f_1$$ \hspace{1cm} (2)

$$\frac{df}{dt} = k_i^f i - k_2^f f_1 - k_3^f$$ \hspace{1cm} (3)

$$\frac{db}{dt} = k_2^f f_1 + k_3^f$$ \hspace{1cm} (4)

However, the kinetic studies failed to identify the intermediate. It was also SCHÖNEMANN, who introduced the simplifying assumption, $\frac{di}{dt} = 0$ and making use of the relations resulting from assumption, namely $k_i^f \gg k_1$ and $k_i^f \gg k_2^f$, the intermediate $i$ can indeed be eliminated and the necessary kinetic equations become:
3. THE MODEL OF THE STRIPPING PROCESS

The flowchart of the semicontinuous furfural producing stripping system is shown in Figure 1.

Assumptions:

a) Both phases are ideally mixed.

b) The \( \alpha \) phase is the stagnant liquid, the \( \beta \) phase is the steam phase bubbling through the \( \alpha \) liquid \((V^\alpha \gg V^\beta)\).

c) Only furfural takes part in the mass transfer between the phases.

d) The \( \alpha \) and \( \beta \) phases are in thermal equilibrium.

e) Due to the slow reaction, the quasi-equilibrium distribution of the furfural between the two phases can accounted for with a constant \( K \).

f) The transfer mechanism is adequately represented by the two-film theory, i.e. chemical reaction is assumed to take part in the bulk of the liquid phase.

\[
\frac{dx}{dt} = -kx
\]

\[
\frac{df}{dt} = k_1x - k_2x f - k_3f \quad (3.a)
\]

\[
\frac{db}{dt} = k_2x f + k_3f \quad (4.a)
\]
Starting from Equations 1.3.a, and 4.a, taking part in the \(\alpha\)-phase can be applied the SCHUNEMANN'S idea:

\[
\begin{align*}
    \frac{dx^\alpha}{dt} &= -k_1 x^\alpha \\
    \frac{df^\alpha}{dt} &= k_1 x^\alpha - k_2 \frac{x^\alpha \cdot f^\alpha}{w} - k_3 \frac{f^\alpha}{w}
\end{align*}
\]

Where

\(F = \) calculated concentration of yield-furfural from difference of formed and decomposed furfural

\(W = \) a mass ratio of furfural in liquid + vapor phase and furfural in liquid phase.

The selectivity of the important product:

\[
S = \frac{\frac{df^\alpha}{dx^\alpha}}{\frac{dx^\alpha}{dx^\alpha}} = \frac{k_1 x^\alpha - \frac{k_2 x^\alpha f^\alpha}{w} - \frac{k_3 f^\alpha}{w}}{k_1 x^\alpha}
\]

It can be seen that \(w \rightarrow \infty\) (practically \(w > 10\))

\[
\lim_{w \to \infty} S = 1
\]

If the \(x_0 < 75 \text{ g/l}\) it may be a good assumption [8].

However authors measured the \(S = \frac{df^\alpha}{dx^\alpha}\) data set when \(9.2 < w < 38\), but \(S\) was smaller than one in all case if \(x^\alpha > 75 \text{ g/l}\). The best correlation may be as follows:

\[
\lim_{w \to \infty} S = \frac{k_1 x^\alpha}{(k_1 + k_2 x^\alpha)(k_1 + k_2 x^\alpha)^2}
\]

so the kinetics-scheme are proposed by authors:
The model of stripping-out system as well as is presented:

In $\alpha$-phase:

$$\frac{dx}{dt} = -(k_1 + k_2)x^x - k_2x^x$$  \hspace{1cm} (7)

$$\frac{df}{dt} = k_1x^x - k_2x^x f^x - k_D(Kf^x - f^A) - k_3f^x$$  \hspace{1cm} (8)

$$\frac{dp}{dt} = k_3f^x + k_2x^x f^x$$  \hspace{1cm} (9)

$$\frac{dp}{dt} = k_D(Kf^x - f^A)$$  \hspace{1cm} (10)

The $p^x$ is in fact a quantity proportional to the yield of the stripped furfural.

In $\beta$-phase

$$(Bf) - (B_0, f_0) = V^x k_D(Kf^x - f^A) + V^A \frac{df^x}{dt}$$  \hspace{1cm} (11)

Because $f_0 = 0$, and let us see that moment, when

$$V^A \frac{df^x}{dt} = 0$$

Then:

$$\frac{f^x}{f^A} = \frac{1}{K} + \frac{B^A}{V^x K k_D} = \frac{1}{K} + \frac{M}{K k_D}$$  \hspace{1cm} (12)

In technological terms $M$ is called the stripping out-model. If $K$ and $k_D$ do not depend on each other and
on M, then Equation 12 is reduced to a linear relationship.

4. ADEQUACY OF STRIPPING-OUT MODEL

Kinetic measurements were made in d-xylose solutions. The equation system containing Equation 6, 7, 8, 9, 10 and 12, characterising the kinetic model was generated on a MEDA 81-T type analogue computer. Kinetical constants were calculated by well-known identificational method.

In summary, we can concluded that the model structure presented makes use of an easily measurable or identifiable parameter set, satisfying the usual design requirements.

SYMBOLS USED

\( b \) concentration of the byproduct in the liquid phase (g/l)
\( B \) volumetric flow rate of the vapour phase (l/h)
\( f \) concentration of furfural in the liquid phase (g/l)
\( \bar{f} = \frac{f}{x_0} \text{ dimensionless furfural concentration (–)} \)
\( i \) concentration of the intermediate in liquid phase (g/l)
\( k_1, k_2, k'_1, k'_2, k'_3, k^*_2, k^*_3 \text{ reaction rate constants} \)
\( k_0 \) compounded mass transfer coefficient (l/h)
\( K \) apparent equilibrium distribution coefficient
\( M \) stripping out module (by definition \( M = \frac{B}{V_M} \))
\( p \) concentration of furfural in the condensate (g/l)
\( u \) control-variable (defined in Equation 6) (l/h)
$\times$ concentration of d-xylose in the liquid phase (g/l)

$V$ volume of the reaction liquid mixture (l)

Indexes

$\alpha$ equilibrium value

$\alpha_l$ liquid phase

$\alpha_v$ vapour phase

$\circ$ initial value

REFERENCES

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A semitheoretical model to describe the behaviour of a gas liquid reactor for the oxidation of acetaldehyde to acetic acid.

G. Oliveri Del Castillo, L. Rivolta
Montedipe Spa, Montedison Group Milan, Italy

Summary
A research work both in pilot and industrial scale was performed to improve the exercise of commercial reactors. A semitheoretical model has been developed in sufficient agreement with experimental results suitable for extrapolation. This work is presented as a typical example of the process development activity of the chemical engineers engaged with gas-liquid reactors in the case, unfortunately very frequent, of insufficient chemical and mass-transfer data. The model is extended to the by-products; new experimental data are presented.

1. Introduction
In the design of a new gas-liquid reactor, knowledges of kinetics, mass-transfer, fluodynamics are involved, a lot of information rarely available, whose determination requires long time in laboratory tests, is expensive and the result uncertain. In addition the side reactions are more unknown, their behaviour is necessary for any calculation. The same difficulty for the investigation of an existing commercial reactor; in this case the situation is more favorable due to the possibility of test runs. The process engineers engaged on such equipment are often alone with their experience, capability and stimulus to pursue the activity also in an uncertain or unknown field; research people offer obviously any support and have an incentive to their work.

2. The theoretical support
Figure 1 shows a simplified picture of commercial reaction
section: in Table 1 some operating typical conditions are reported. Liquid phase is considered as fully homogeneous.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Some operating conditions of Montedipe reactors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>0.5±1 kg/cm² g</td>
</tr>
<tr>
<td>Temperature</td>
<td>45±65 °C</td>
</tr>
<tr>
<td>Aldehyde selectivity</td>
<td>&gt;95 %</td>
</tr>
<tr>
<td>Conversion 1st reactor</td>
<td>~70 %</td>
</tr>
<tr>
<td>Conversion 1st + 2nd reactors</td>
<td>~92 %</td>
</tr>
<tr>
<td>Aldehyde concentration in liquid</td>
<td>~0.01–0.04 mol fr.</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Mn acetate</td>
</tr>
</tbody>
</table>

Due to the large recycle flow rate and isothermal, the oxygen concentration profile in gas phase is tubular. The liquid flow regime seems to be bubbling in both reactors according to the generalized diagram of figure 2.[1] The main reaction

\[ CH_3CHO + \frac{1}{2}O_2 \rightarrow CH_3COOH \] (1)

\[ G_t \text{ Kg/m}^2 \text{ sec.} \]

may be considered as very fast and happening in the liquid.
film layer at the interface; the slowest step is the oxygen mass-transfer depending on available gas-liquid contacting area. The reaction (1) occurs in many intermediate steps; the kinetics is given by the following general expression

$$R = k[A]^n[B]^m[H_2]^p$$

(2)

The oxygen mass-transfer in an elementary surface is

$$-dN_{ox} = k_1 P \cdot y \cdot dS$$

(3)

The enhancement factor $$\lambda$$ is

$$\lambda = \left( \frac{m}{m+1} \right) k D_A [A]^m [B]^n [H_2]^p \cdot \frac{5}{k_1} C$$

(4)

Exponent $$m$$ may be considered as $$1$$, $$n$$ is reported in the literature to be $$0.5$$ to $$1.5$$ /3//4/. $$p$$ is more complicated and uncertain /5/. This field had to be explored by our work. By easy substitutions and integrations, the final basic equation is obtained

$$I_p/2 = \left( \frac{k_1}{k} \right) I_{Q_0} \int \left[ \frac{p}{P + (1-\xi)z/20} \right]^{\frac{p}{2}}$$

(5)

where

$$I_p = \frac{2}{z} \frac{D}{T} \frac{H}{e} \frac{\sigma}{d} \frac{\beta}{\gamma} \frac{\xi}{\beta} \frac{c}{d}$$

(6)

$$I = \int \frac{c+b}{d}$$

(7)

This expression is valid for 1st reactor; a similar for 2nd stage. $$J_p$$ is the same for both. It is interesting to observe that in eq. (6) are grouped all properties or parameters unknown or only largely approximated; for our purposes it is not necessary to know them separately but it is sufficient to evaluate the group $$J_p$$. A first test on the commercial plant has been able to assign a tentative value to $$I_p$$, used later to forecast other possible answers in different conditions (but at constant selectivity). Subsequent tests in the same plant confirmed this value and the opinion of factory people of a non-dependance of reactor behaviour from catalyst concentration. See figure 3 for exponent $$n = 1$$. The same calculations have been done for $$n = 0.5$$ and $$1.5$$; the results are reported in table 2. The former value $$n = 1$$ gives the best
dispersion and a practical correspondence of the middle values separately calculated for both reactors.

![Figure 3](image)

**Table 2** Middle values for different exponent n in eq. (5)

<table>
<thead>
<tr>
<th>n</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>n=1</td>
<td>0.00445</td>
<td>0.001942</td>
<td>0.000847</td>
</tr>
<tr>
<td>n=2</td>
<td>0.006336</td>
<td>0.00207</td>
<td>0.000682</td>
</tr>
<tr>
<td>n=3</td>
<td>0.00545</td>
<td>0.00201</td>
<td>0.000759</td>
</tr>
</tbody>
</table>

% difference between middle 1st reactor and general middle

<table>
<thead>
<tr>
<th>Standard deviation</th>
<th>1st reactor</th>
<th>2nd reactor</th>
<th>1st + 2nd reactors</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.46</td>
<td>14.7</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>15.2</td>
<td>15.0</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>22.3</td>
<td>14.9</td>
<td>22.6</td>
<td></td>
</tr>
</tbody>
</table>

Together with material balances, vapour-liquid equilibria and eq.(5), all tests have been recalculated and compared with experimental results: as example figure 4 shows the residual oxygen.
3. The pilot plant research
In the commercial plant it was not possible to test a few parameter; for this purpose a glass pilot reactor has been built up. The water content in liquid phase has shown a remarkable effect on conversion and selectivity; it has been explained by a dependence of $[\text{Mn}]$ from water concentration. Taking account of the selectivity variation and of this effect on reaction rate, eq. (5) has been rewritten as follows:

$$\frac{[\text{H}_3\text{O}]_I}{e^{(I-E^p)}10^2} \cdot \phi_{\text{CAT}}$$

(7)

$\phi_{\text{CAT}}$ is found to be expressed by

$$\phi_{\text{CAT}} = ( \frac{[\text{Mn}]}{0.066} )^{-0.2916 + 4.05[H_2O]}$$

(8)

Figure 5 shows the obtained points from the pilot runs.

The correction factor (8) represents the selectivity multiplied by $[\text{Mn}]^{p/2}$. From the analysis of by-products it has been possible to evaluate separately this two effects and to recognize the expression of exponent $p$ as function of water concentration, resulting positive or negative respectively at low and high $[H_2O]$. The value $\phi_{\text{CAT}} = 1$ is obtained for an intermediate water concentration, corresponding to the level of the commercial reactors ($[H_2O] = 0.07$) and in agreement with the results of commercial plant as exposed in para. 2.

4. The by-products analysis
Table 3 is referred to some side reactions taking place where oxygen is present, i.e., in the liquid film layer at
the interface. In addition there are other side-reactions, i.e. esterifications, not shown in table 3, which occur in the liquid bulk.

**Table 3** Some side-reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \frac{K_i}{K} )</th>
<th>( \beta_1 - p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{CHO} + 0.5 \text{O}_2 \rightarrow \text{CH}_4 + \text{CO}_2 )</td>
<td>0.0042</td>
<td>-1.0</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CHO} + \text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{CO}_2 )</td>
<td>0.022</td>
<td>-0.60</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CHO} + 3/2 \text{O}_2 \rightarrow \text{HCHO} + \text{CO}_2 + \text{H}_2\text{O} )</td>
<td>0.0071</td>
<td>-0.528</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CHO} + 3/2 \text{O}_2 \rightarrow \text{HCOOH} + \text{CO}_2 + \text{H}_2\text{O} )</td>
<td>0.0029</td>
<td>-0.342</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CHO} + 5/2 \text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} )</td>
<td>0.033</td>
<td>-0.67</td>
</tr>
</tbody>
</table>

An easy rearrangement of the general expressions for the reactions rates has allowed to find following equation

\[
\text{by-product }_1 = \frac{K_i}{K} \cdot [\text{Mn}]^{\beta_1 - p}.
\]

The kinetic constants \( K_1 \) are in such a way calculated in reference to that for the main reaction \( K \). Table 3 shows the obtained values for the ratio \( K_i/K \) and for exponent \( \beta_1 - p \) at 55°C. Figures 6 and 7 shown as examples the dependancies of \( \text{CO}_2 \) and methanol formation from \([\text{Mn}]\) and water concentration.

![Fig. 6](image-url)
The same for other by-products; the selectivity may be calculated from these figures, exponent $p$ from eq. (8) and from table 3. Figure 8 shows a comparison for experimental and calculated outlet oxygen.

5. Conclusions
A lot of information on the chemistry, kinetics and products not published in the former literature is derived from our work especially oriented for engineering purposes. A semitheoretical model sufficiently tested has been developed, suitable for scaling-up and of much more possibilities than a traditional empiric model, described by a few polynomial equations. This later may be built-up with a more exact interpolation of the experimental data from a mathematical point of view, but specific of equipment and operating test conditions and to be used with caution in extrapolation.
The summarized theory is presented in ref. [6/7/7] related to commercial plant and in a new manuscript to be published describing the more complete work in pilot plant. This later is available on request.

References


Symbols used

[A][A*] oxygen mol fraction in the liquid and at the interface

[b, c] numerical constant

[B] acetaldehyde mol fraction in the liquid

[C] total concentration in the liquid, kmol/cm³ liq.

[dₐ] middle bubble diameter at the inlet, m

[dₜ] tubes diameter, m

[D] oxygen diffusivity in the liquid, sqm/h

[Dₙ] gas-liquid specific flowrate, kg/sqm sec

[H] parameter

[Kₜ] Henry constant for oxygen, kg/sqcm

[Hₜ] water mol fraction in the liquid

[I] integral

[K] kinetics constant for acetic acid

[K₉] ib. for by-product i

[K₆] oxygen mass-transfer coeff. in the liquid, kmol/sqm h atm

[Lₘₙₚ] catal. concentration, g/l

[m, n, p] exponent

[N] oxygen flowrate in the gas phase, kmol/h

[N₉] reaction tubes number

[P] pressure at the outlet, kg/sqcm

[Q₉] dry air flowrate, kmol/h

[R] acetic acid reaction rate, kmol/h cum liq.

[S] gas-liquid interface, sqm

[X] Lockhart-Martinelli parameter

[αₜ] exponent

[ε] gas hold-up

[λ] reaction enhancement factor

[φ] CAT correction factor due to catalyst concentration

[ξ] 1-oxygen conversion
A FINITE ELEMENT SOLUTION OF BOUNDARY LAYER PROBLEMS WITH SURFACE REACTION

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ABSTRACT

Mass transfer in a laminar boundary layer with non isothermal surface reaction was simulated by a newly developed finite element model which uses the Galerkin criterion. The numerical method is reliable and general. Comparisons with exact and approximate solutions were made for the case of irreversible catalytic reactions taking place along a flat plate. Results were obtained for configurations wherein the solid boundary is characterized by discontinuous variations of the catalytic efficiency.

INTRODUCTION

Heat and mass transfer coefficients between particles and fluid are one of the basic information needed for unit operations where a dense phase of fine particles is utilized. Especially for the purpose of rational design of catalytic reactors, absorption towers, and other fixed or fluidized bed equipment, it has been recognized that the prediction of particle to fluid heat or mass transfer coefficients is important in the course of the estimation of local or overall conversions. To improve the accuracy of current methods it is desirable to inquire into basic mechanism of the local transport with the aid of a proper mathematical model.
Among the works most frequently cited in the literature are those of Acrivos and Chambrè \((^1\)) and Lindbergh and Schmitz \((^2\)). Some recent studies by Mihail \((^3\)) and Mihail and Teodorescu \((^4\)) are also relevant to the solution of the problem.
In this paper a two-dimensional finite element solution scheme is developed which permits to find the reactant concentration and temperature on the external catalytic surface of arbitrary shape. The examples chosen to illustrate the interaction of boundary flow with chemical reaction is limited to the flat plate. Further investigations undertaken to see the effects of more hydrodynamically complex situations will be presented in a future work.

**DESCRIPTION OF THE PROBLEM**

The model being considered is a two-dimensional system in which an inert fluid containing a single reactant flows past a solid surface of arbitrary shape. A boundary layer of constant physical properties develops over the solid. An exothermic reaction occurs on the whole surface or part of it (Fig. 1).
It is assumed that the hydrodynamic problem has been first solved, so that the component velocities are known. It is worth noting that the longitudinal dispersion is accounted for.

![Fig. 1 - Domains of definitions and related boundaries.](image-url)
MATHEMATICAL FORMULATION

The governing boundary layer eqns are a well known set of coupled non linear partial differential eqns that describe the conservation of mass, energy and momentum. In the case of surface chemical reactions, these governing eqns are identical to those valid for inert boundary layers. The chemical reaction effects on these eqns enter through their boundary conditions.

Let we distinguish between fluid and solid phase:

**fluid phase (subdomain $\Omega_1$)**

\[\begin{align*}
\frac{\partial}{\partial x}(k_x \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y}(k_y \frac{\partial T}{\partial y}) + \rho c_p \left( \frac{\partial}{\partial x}(u \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y}(v \frac{\partial T}{\partial y}) \right) &= 0 \\
\frac{\partial}{\partial x}(\rho c \frac{\partial C}{\partial x}) + \frac{\partial}{\partial y}(\rho c \frac{\partial C}{\partial y}) - (u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y}) &= 0
\end{align*}\]

(1) (2)

The following mixed boundary conditions were considered:

\[T = T_m, \quad C = C_m \quad \text{on the part } \Gamma^1 \quad \text{of boundary } \Gamma; \quad (3)\]

\[\frac{\partial T}{\partial n} = \frac{\partial C}{\partial n} = 0 \quad \text{on } \Gamma^2 \quad (\Gamma^1 \cup \Gamma^2 = \Gamma) \quad (4)\]

Here $n$ denotes the outward normal direction to $\Gamma$ and $T_m$ and $C_m$ denote undisturbed flow conditions.

On $\Sigma$ we have

\[\begin{align*}
k_x \frac{\partial T}{\partial x} \ell_x + k_y \frac{\partial T}{\partial y} \ell_y + q_1 &= 0 \\
\frac{\partial}{\partial x}(\rho c \frac{\partial C}{\partial x}) \ell_x + \frac{\partial}{\partial y}(\rho c \frac{\partial C}{\partial y}) \ell_y + j_1 &= 0
\end{align*}\]

(5) (6)

where $\ell_x$ and $\ell_y$ represent the direction cosines of the outward normal to the interface $\Sigma$, which is arbitrarily considered as the positive side of the fluid subdomain $\Omega_1$. In addition $q_1$ and $j_1$ are respectively the specific heat and mass fluxes which may be treated as piecewise functions of the position on $\Sigma$.

**solid phase (subdomain $\Omega_2$)**

\[\begin{align*}
\frac{\partial}{\partial x}(k_x \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y}(k_y \frac{\partial T}{\partial y}) &= 0 \\
\frac{\partial}{\partial x}(\rho c \frac{\partial C}{\partial x}) + \frac{\partial}{\partial y}(\rho c \frac{\partial C}{\partial y}) &= 0
\end{align*}\]

(7) (8)

Of course eqn(8) is only valid for an homogeneous model.
Boundary conditions

\[ T = T_\infty, \quad C = C_\infty \quad \text{on} \quad \Gamma_i \]
\[ \frac{dT}{dn} = \frac{\partial C}{dn} = 0 \quad \text{on} \quad \Gamma_i \quad (\Gamma_1 \cup \Gamma_2 = \Gamma) \]
\[ k_x \frac{dT}{dx} \xi_x + k_y \frac{dT}{dy} \xi_y - q_2 = 0 \quad \text{on} \quad \Sigma \]
\[ \frac{\partial C}{\partial x} \xi_x + \frac{\partial C}{\partial y} \xi_y - j_2 = 0 \]

where \( \xi_x \) and \( \xi_y \) are the direction cosines defined in (5) and (6).

Clearly in any particular problem the portions \( \Omega_1, \Gamma_1 \) and \( \Omega_2, \Gamma_2 \) will be such that \( \Omega_1 \cup \Omega_2 = \Omega \) and \( \Gamma_1 \cup \Gamma_2 = \Gamma \).

Matching conditions at the phase interface are

\[ q_1 + q_2 = \left\{ (\alpha H) \mathcal{R}(C_r, T_r) \right\} \quad (13) \]
\[ j_1 + j_2 = \mathcal{R}(C_r, T_r) \quad (14) \]

where \( \mathcal{R} \) is the rate at which the reactant is consumed by the reaction and \( \alpha \) denotes surface conditions.

FINITE ELEMENT FORMULATION

Spatial discretization of the governing eqns and prescribed boundary conditions follows the standard finite element procedure \((5, 6)\) with the temperature and concentration variations being specified in terms of the nodal values \( T_\xi \) and \( C_\xi \), according to

\[ \bar{T} = \sum_{i=1}^{m} N^\xi_i T_\xi; \quad \bar{C} = \sum_{i=1}^{m} N^\xi_i C_\xi \quad (15) \]

in which \( m \) is the total number of nodes and \( N^\xi_i \) are the element shape functions.

Applying the Galerkin weighted residual procedure to the errors involved in the approximate satisfaction of the eqns \((1-14)\), leads to the following discrete equation system:

**Fluid phase** (subdomain \( \Omega_1, 2 \) \( m_1 \) eqns being \( m_1 \) the total number of element in \( \Omega_1 \))

\[ \int_{\Omega_1} \frac{S}{k} \left( \bar{T} \right) \, d\Omega + \int_{\partial \Omega_1} \mathcal{W}(\bar{T}) \, d\Sigma + \int_{\text{in}} \frac{N}{k} \, q_1 \, d\Sigma = 0 \quad (n=1,m_1) \quad (16) \]

where \( \frac{S}{k} \) and \( \mathcal{W} \) are differential operators defined by
\[ L_k = b_k \frac{\partial N_k}{\partial x} \frac{\partial x}{\partial x} + b_y \frac{\partial N_k}{\partial y} \frac{\partial y}{\partial y} \]  
\[ \varphi = N_k \left( u \frac{\partial x}{\partial x} + v \frac{\partial y}{\partial y} \right) \]  
\[ \int_{\Omega_1} L_k \, d\Omega + \int_{V} \varphi \, dV + \int_{\Omega_2} N_k \, d\Omega = 0 \]  
\[ r = 1, m \]

The solid phase (subdomain \( \Omega_2 \), \( 2m \) eqns being \( m \) the total number of elements in \( \Omega_1 \))

\[ \int_{\Omega_2} L_k \, d\Omega + \int_{\Omega_2} N_k \, d\Omega = 0 \]  
\[ r = 1, m \]

If we add term by term eqns (16, 19) and (20, 21), using eqns (13, 14) to eliminate the heat and mass fluxes, we obtain a total of \( m = m_1 + m_2 - m_\Sigma \) eqns, being \( m_\Sigma \) the number of nodes of both \( \Omega_1 \) and \( \Omega_2 \) lying inside \( \Sigma \):

\[ \int_{\Omega} L_k \, d\Omega + \int_{V} \varphi \, dV - \int_{\Omega_1} N_k \, \Delta H \, \mathcal{R}(T, C) \, d\Omega = 0 \]  
\[ r = 1, m \]

Eqns (22) and (23) can be rewritten as a single eqn in the form

\[ \mathbf{H} \mathbf{\Phi} = 0 \]  
(24) where \( \mathbf{\Phi} = \{ T, C \} \) and \( \mathbf{H} = \begin{bmatrix} H^T & K^T \\ 0 & H^C + K^C \end{bmatrix} \)

The elements of the matrices appearing here are defined as

\[ H_{ij} = \int_{\Omega} \left[ b_k \frac{\partial N_k}{\partial x} \frac{\partial x}{\partial x} + b_y \frac{\partial N_k}{\partial y} \frac{\partial y}{\partial y} \right] \, d\Omega + \int_{V} \varphi \, dV \]  
\[ K_{ij} = \int_{\Omega} \left[ \varphi \frac{\partial N_k}{\partial x} \frac{\partial x}{\partial x} + \varphi \frac{\partial N_k}{\partial y} \frac{\partial y}{\partial y} \right] \, d\Omega \]  
\[ H^C_{ij} = \int_{\Omega} \left[ \varphi \frac{\partial N_k}{\partial x} \frac{\partial x}{\partial x} + \varphi \frac{\partial N_k}{\partial y} \frac{\partial y}{\partial y} \right] \, d\Omega + \int_{\Omega} \left[ u \frac{\partial N_k}{\partial x} \frac{\partial x}{\partial x} + v \frac{\partial N_k}{\partial y} \frac{\partial y}{\partial y} \right] \, d\Omega \]  
and for a \( n \)-order irreversible chemical reaction

\[ k_{n_k} = \int_{\Omega} N_k \, d\Sigma \]  
\[ k^T_{n_k} = -\{ \Delta H \} k^C_{n_k} \]
Solution of the system (24) has been performed by a banded non-symmetrical solver. Since the equations are non-linear, it is apparent that an iterative technique must be employed where the updated variables are used to evaluate at successive iterations. It must be observed that in the isoparametric formulation all integrations are carried out by the use of Gauss quadrature formulae.

Effectiveness factor

The effect of mass transfer through the boundary layer is qualitatively described by the effectiveness factor $\eta$. In the special case of first order surface reaction the values of $\eta$ can be readily obtained from the simple formula

$$\eta = \frac{k^c}{\mu} \frac{\bar{C} \left( \frac{c}{C_{\infty}} \right)}{\left( \frac{c}{C_{\infty}} \right)}$$

APPLICATION AND RESULTS

In order to compare the results with those known from other solutions the discussion will be limited to flows past flat plates. Of course more complicated geometries do not offer any additional difficulties.

Isothermal catalytic reaction

Uniform velocity profile - The availability of the analytical solution (7) advised the choice of this example. A mesh of 40 quadrilateral parabolic elements was used to represent the domain discretization. The results of Fig.2 are self-explaining. For $Re < 1$ it is apparent that a more dense mesh should be used.

![Fig.2- Reactant concentration distribution along a catalytic flat plate in the asymptotic case $Sc \to 0$. Nodal values compared to the analytical solutions (solid lines).](image-url)
Laminar boundary layer flow - Solutions for problems of this kind are given in \(^1\) and \(^7, 8\). The results obtained with the proposed model are compared with those of Rosner in Fig. 3: the accuracy is very good when taking into account that the numerical values obtained by this author using an approximate solution are, for \(n = 1\), some percent less than those obtained analytically by Chambré and Acrivos \(^3, 8\).

Fig. 3 - Surface distribution of reactant over a catalytic flat plate for several reaction orders. Solid lines refer to the approximate values reported by Rosner \(^7\).

Non isothermal catalytic reaction

Constant catalytic efficiency

The problem is identical to that considered in \(^4\) and solved using a superposition integral. Fig. 4 represents some results of the computation employing the data reported in Table 1. The results obtained can be compared only qualitatively with those published by Mihail.

Fig. 4 - Dependency of the surface temperature and concentration on plate length (\(Re_L = 500; k_0 = 10^9 \, h^{-1}; \beta = 0.1\))
and Teodorescu. Their longitudinal profiles are very similar in shape to those of Fig. 4. A quantitative comparison is not possible because these authors do not report the exact values of the parameters used.

Table 1 - Data employed in computation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>°k</td>
<td>0.0021 m²/h</td>
</tr>
<tr>
<td>kX</td>
<td>0.074 W/m K</td>
</tr>
<tr>
<td>ρ</td>
<td>0.75 kg/m³</td>
</tr>
<tr>
<td>c_p</td>
<td>0.245 kJ/kg K</td>
</tr>
<tr>
<td>T∞</td>
<td>460 K</td>
</tr>
<tr>
<td>c_p</td>
<td>0.003 kmol/m³</td>
</tr>
<tr>
<td>(-ΔH)</td>
<td>590000 kJ/kmol</td>
</tr>
</tbody>
</table>

A mesh of 50 elements was used for all the tests; however the longitudinal grid size was varied in order to provide a higher density of grid points where the temperature gradient is steeper.

Discontinuity of surface catalyticity

In this example it is assumed that the surface is made of different materials so that the catalytic efficiency will have discontinuous variations (9, 10). For this complex problem a mesh of 90 elements was used. Fig. 5 shows the temperature and concentration profiles computed by using the data itemized in Tab. 1 and assuming k_y = k_x and °x = °y. From the results obtained it may be observed that

Fig. 5 - Surface distributions of temperature and concentration over a flat plate with discontinuous variations of the catalytic efficiency (γ = 23.5, β = 0.1).
the general behavior of a catalytic surface with multiple active regions is not the same as that of a uniform one. This is due to two effects: on the upstream non-catalytic surface the reactant accumulates and as soon as it reaches the catalytic surface, the reaction proceeds at a much greater rate than that which develops on a uniform catalytic surface. In contrast to this phenomenon, there is the reduction of the surface temperature due to axial heat dispersion. However, this aspect of the problem, which is quite complex, will be the object of a future investigation.

ACKNOWLEDGEMENT
The authors acknowledge the financial support of the "Ministero della Pubblica Istruzione".

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>C</td>
<td>reactant concentration</td>
</tr>
<tr>
<td>$c_p$</td>
<td>specific heat</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate constant</td>
</tr>
<tr>
<td>$k_o$</td>
<td>frequency factor</td>
</tr>
<tr>
<td>$L$</td>
<td>characteristic dimension</td>
</tr>
<tr>
<td>$\rho$</td>
<td>fluid density</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>activation energy parameter</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>dimensionless adiabatic temperature rise</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Schmidt number</td>
</tr>
<tr>
<td>$\text{Re}$</td>
<td>Reynolds number</td>
</tr>
</tbody>
</table>

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CATALYST POISONING ON THE BENZENE HYDROGENATION

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ABSTRACT

The deactivation of a commercial Ni-SiO₂-Al₂O₃ catalyst was studied in an isothermal differential reactor using the hydrogenation of benzene to cyclohexane as a model reaction. The reaction was studied in kinetic and diffusion rate-controlling regimes at the temperature between 382-477 K and atmospheric total pressure.

The results indicate that the rate of catalyst poisoning in kinetic rate-controlling regime is relatively slow in comparison with the rate of diffusion in the bulk of the catalyst, which means that the catalytic active centers are poisoned uniformly with time (homogeneous poisoning).

During catalyst poisoning in the diffusion rate-controlling regime was observed that the catalyst with smaller particle diameter are poisoned faster than particles with larger diameter, while in the same time the catalyst effectiveness decreases with increase of the particle diameter and vice versa.
I N T R O D U C T I O N
Within recent years considerable effort has been expended on studies of diffusional limitation of rates in heterogeneous catalytic reactions. A number of experimental investigations have advanced the understanding of diffusion effect on catalytic reactions, but studies of poisoning reactions have been almost entirely restricted to theoretical considerations\textsuperscript{1-7}, and few experimental studies\textsuperscript{8-11}. It is generally recognized that a substantial amount of additional experimental work will be necessary to test the many theoretical conclusions which have been presented.

From this reason here will be reported the experimental values on the deactivation of catalyst in kinetic and diffusion rate-controlling regimes using the hydrogenation of benzene to cyclohexane as a model reaction.

E X P E R I M E N T A L  S E C T I O N
The catalyst used in this study was commercial nickel on silica-alumina catalyst (code R1-10 supplied by BASF) containing 21% Ni. The catalyst was reduced "in situ" by heating in H\textsubscript{2} at 743 K for 10 hr. Benzene and thiophene was Merck-rein grade and hydrogen was electrolytic grade.

A p p a r a t u s (Fig.1.) The kinetics of benzene hydrogenation and of the poisoning reaction was measured in a small differential isothermal reactor.
Fig.1. Schematic of the Flow Reactor System.

1,7 - generator of hydrogen 14 - reactor
2,4,8 - needle valve 15 - gas sampling
3,9,13 - saturator 16 - gas chromatograph
17 - integrator valve

The reactor consisted of a stainless steel tube with a porous glass disk on which the catalyst was loaded. Reaction temperature was measured with an uncovered iron constantan thermocouple, which was not catalytically active.

The reaction system consisting of a parallel connected benzene and thiophene saturators (6,10) with reactor (14) (to permit switching from thiophene-free and thiophene-containing feed), and GLC sampling valve (15). The reactor effluent was analyzed chromatographically (PYE UNICAM chromatograph with Carbowax column, flame ionisation detector, PYE UNICAM DP 88 computing integrator). Reaction conditions: hydrogen pressure, 9,91
Reaction rates were determined from:

\[
\text{rate} = \frac{F}{W} \cdot \text{conversion}
\]

where \( F \) is the feed rate in moles per minute and \( W \) is the weight of catalyst in gram.

**RESULTS AND DISCUSSION**

Deactivation function in this work is expressed in terms of the thiophene content of the catalyst, not in terms of time, because time is not always the true variable for the deactivation\(^1\). The difference between the amount of thiophene entering and leaving the reactor represents the amount of poison adsorbed on the catalyst. Figure 2 shows the transient thiophene concentration profile in the reactor effluent during in situ poisoning catalyst.

Initially all thiophene feed to the reactor was adsorbed on the catalyst. As thiophene coverage of catalyst surface increased, thiophene concentration in the exit stream increased, eventually approaching the same level as that in the feed stream. The fraction of thiophene adsorbed relative to the total thiophene adsorbed is obtained by graphically integration of hatched area.

The behavior shown in Fig. 2 represents only typical results, similar transient response was obtained for all runs.
Figure 2. Transient thiophene concentration profile in reactor effluent in situ poisoning of Ni-catalyst. \(W=0, \text{olo} \ g, \text{p}_T = 0,12 \ \text{kPa}, \text{T}=426 \ \text{K}\)

Figure 3 shows the activity of catalyst as a function of poison content on the catalyst. The activity of the catalyst falls linearly with increasing poison content and then follows by an inflection in the graph, after which the activity falls far less steeply with a further increase in the poison content. The effect of the poison up to region of inflection is represented by an expression

\[
a = 1 - \zeta \mathcal{C}_T
\]

(2)

in which the poisoning coefficient, \(\zeta\), is used to compare the toxic action of different substances. The results indicate that the rate of catalyst poisoning
in kinetic rate-controlling regime is relatively slow in comparison with the rate of diffusion in the bulk of the catalyst, which means that the catalytic active centers are poisoned uniformly with time (homogeneous poisoning).  

![Graph showing catalyst activity as a function of poison content.](image)

**Fig. 3.** The activity of the catalyst as a function of poison content of the catalyst ($W=0.010 \, g$, $p_T=0.12 \, kPa$, $d = 0.07-0.081 \, mm$).

The analysis of deactivation rates was carried out based on a "separable" form of rate equation, linear in concentration of poison (see Fig. 3.) and availability of active site. Thus the rate of deactivation in
terms of normalized activity is
\[-\frac{da}{dt} = k_d C_{T} a\] (3)

by assuming that catalytic activity was proportional to the number of remaining sites. According to this relationship a plot of \( \ln a \) vs. \( t \) should result in a straight line with slope \( C_T k_d \), which enables calculation of deactivation rate constants.

The values determined for \( k_d \) and \( E_d \) are given in Table 1.

**Table 1. Parameters for thiophene poisoning kinetics.**

<table>
<thead>
<tr>
<th>( T, K )</th>
<th>( 10^3 k_d, \text{ Pa}^{-1}\text{min}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>390</td>
<td>0.39</td>
</tr>
<tr>
<td>403</td>
<td>0.61</td>
</tr>
<tr>
<td>427</td>
<td>1.02</td>
</tr>
<tr>
<td>440</td>
<td>1.71</td>
</tr>
<tr>
<td>450</td>
<td>1.74</td>
</tr>
</tbody>
</table>

\( E_d = 5.32 \text{ kJ mol}^{-1} \)

Figure 4 shows the activity of three various size of catalyst particles as a function of poison content on the catalyst. The shape of catalyst poisoning curves (two lower curves) demonstrated that a nonlinear relationship between catalyst activity and fraction of surface poisoned can be effectively mimicked by intrapellet diffusion resistences.

The overall effectiveness of the catalyst pellet during its active life can be characterized with an effectiveness factor, defined as the ratio of the actually observed reaction rate to the reaction rate which would pre-
vail if all remaining catalytic surface could be exposed to the bulk reactant concentration, i.e. if all external and internal mass transfer resistances were eliminated.

**Fig. 4.** The activity of the catalyst as a function of poison content of the catalyst ($p_T=0.12$ kPa, $T=427$ K).

Figure 5 displays the change of $\eta$ with dimensionless time for a variety of combinations of internal mass transfer control in catalyst pellets. The results indicate that the catalyst wore the poisoning process is hindered by an greater internal mass transfer process, generally have a longer lifetime than those with a purely kinetically controlled poisoning reaction. In the case of impurity poisoning, increasing the mass transfer resistances for the poison usually increases the mass transfer resistences for the reactants, thus reducing the effectiveness factor for the main reaction quite significantly.
CONCLUSIONS

The rate of catalyst poisoning in the kinetic rate-controlling regime is relatively slow in comparison with the rate of diffusion in the bulk of the catalyst, which means that the catalytic active centers are poisoned uniformly with time. Internal mass transfer resistances tend to increase the lifetime of poisoned porous catalyst particles but, simultaneously decreases the effectiveness factor.

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Some Effects of Phase Change of Catalyst Surface on Heterogeneous Reactions

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A model for heterogeneous catalytic reaction with catalyst surface transformation is considered. Transformation between two phases is modeled by Avrami's theory of nucleation and phase growth. It is assumed that new phase is nucleated from chemisorbed species of one of reactants. Considered are two general cases: new phase is inactive, and new phase provides active sites for the reaction. Expressions for the reaction rates are developed. Determined are regions of multiple solutions and a condition for bifurcation to an oscillatory state.

A number of intriguing features have been observed in many heterogeneous catalytic reactions, such as: slow drifts in activity, multiple steady states, flickering of reaction rate, autonomous oscillations, and chaotic behaviour. Aside from possible practical utilization of this phenomena, they attract interest of chemical engineers because in explaining them they hope to broaden knowledge of fundamental processes in catalytic systems. Works of M. Sheintuch, R.A. Schmits (1), K.F. Jensen et al. (2), and N. Slinko et al. (3) are comprehensive reviews of experimental findings and current theories.

This work is based on observations in experimental work of Z. Kurvanjek et al. (4, 5) with the contact potential difference measurements during the oscillatory oxidation of hydrogen on nickel. It is believed
that the oscillations are due to the process of successive oxidation and reduction of the catalyst surface. The LEED experiments of P.H. Holloway and J.B. Hudson (6, 7), J.W. May et al. (9), and recently by Auger electron spectroscopy experiments of P.K. de Bohx et al. (8) with the same reaction revealed that process of oxidation occurs through mechanism of nucleation and growth of nickel oxide patches. Avrami (10, 11, 12) theory of kinetics of phase change transformation is applicable in mathematical modeling of such process.

The catalyst surface is viewed as being covered with patches (islands) of the new phase of different sizes, some of them isolated and others overlapped (Figure 1.). Three general cases are considered. First we treat the problem when the new phase nucleates from chemisorbed species of one of reactants, say A, and further development of the new phase depends on $\Theta_A$. The new phase is consumed (destroyed) through the interaction of chemisorbed species of the second reactant, B. The untransformed fraction of the surface is catalytically active, while the new phase is inactive. In the second case we consider the situation in which liberated heat (or side product, or created surface defects) during the surface reaction between $\Theta_A$ and $\Theta_B$ provides activation energy for nucleation of the new phase. The new phase is inert and is consumed by the second reactant. In the third case is treated the problem in which the new phase provides active sides for the reaction. The three cases are presented on the Figure 1. Transformation of the new phase starts around nucleus created from interaction of chemisorbed species with metal. For example in oxidation reactions, nucleus of oxide are created through the exchange mechanism with metal atoms. First positive metal ion on the surface is the nucleus which facilitates further transport of chemisorbed oxygen and metal, so the oxidation pro-
ceeds. Dynamics of appearance of nucleus on the surface can be described by simple power law kinetics

\[ d \mathcal{N}(t) = k_m \mathcal{N}^m \, dt \quad (1) \]

where \( \mathcal{N}(t) \) is the total number of nucleus created up to time \( t \).

\[ \mathcal{N}(t) = \int_0^t k_m \mathcal{N}^m(t) \, dt \quad (2) \]

Nucleus are centers around which the new phase grows. If we consider the growth being nonpreferential, then the patches are flat symmetrical discs. In a simple case we consider the growth of the radius proportional to the surface coverage of \( \mathcal{N} \).

\[ dr(t) = \lambda_{\mathcal{N}} \mathcal{N}(t) \, dt \quad (3) \]

The increment of the surface area at time \( t \) for the disc which grows around the nucleus created at time \( \tau \) is

\[ d \sigma(t-\tau) = 2\pi r(t-\tau) \, dr \quad (4) \]

The total nonoverlapped contribution of individual discs is the sum of all surfaces that started to grow from nucleus created at \( t = 0 \) up to \( t = t \)

\[ d \sigma(t) = \int_0^t k_m \mathcal{N}^m(\tau) \, d\sigma(t-\tau) \, d\tau \quad (5) \]

It remains to relate these quantities to the corresponding properties of the actual overlapped surface. Assuming that the nucleus are randomly distributed so that overlapping is uniformly random. So on the average, the change in the new phase is only a fraction of the change of the nonoverlapped surface. The following relation is due to Avrami (11)
though it was originally derived in a slightly different context. 

\( \theta_t \) is the fractional coverage of the transformed overlapped surface. The analogue relationship holds for the case when the new phase is destroyed by the chemisorbed species \( \theta_B \). The dynamics of the surface transformation is tight together with dynamics of adsorption/desorption and chemical reaction. Considering the first case (Figure 1.), the balance equations are

\[
\frac{d\theta_A}{dt} = k_a^A (1-\theta_A-\theta_B) \theta_A - k_a^A \theta_A^2 - \gamma_A(\theta_A, \theta_B)
\]

\[
\frac{d\theta_B}{dt} = k_a^B (1-\theta_A-\theta_B) \theta_B - k_a^B \theta_B^2 - \gamma_B(\theta_A, \theta_B)
\]

\[
\frac{d\theta_t}{dt} = k_t (1-\theta_t) \theta_A \int_0^t \theta_A \, dt \, dz - k_t^2 \theta_A \int_0^t \theta_B \, dt \, dz
\]

For the reaction rate

\[
\gamma_A = 2 \gamma_B(\theta_A, \theta_B) = k \theta_A \theta_B
\]

the steady state solution is

\[
\gamma_A = \frac{k A \theta_A \sqrt{k_B P_B}}{(4 + \sqrt{k_A P_A} + \sqrt{k_B P_B} )^2} (1-\theta_t)^3
\]

where the fraction of the new phase is

\[
\theta_t = \frac{1}{1 + k_m (k_B P_B / k_A P_A)^{2/3} + 1}
\]
In the derivation of (10) it is assumed that the order of nucleation of the new and the old phase is the same, i.e. \( n_A = n_B = n \), and \( K_q \) is the equilibrium constant between the two phases

\[
k_m = \frac{k^4}{k^4}
\]

(11)

In general it can be shown that the equation of the type (7) have steady state solution in the form

\[
\sigma_\alpha^r (p_A, p_B) = \sigma_\alpha (p_A, p_B) \cdot F(\theta_t)
\]

(12)

In other words, the reaction rate over the transformed surface is separable in the reaction rate \( r_o \), as if the transformed phase were not present, times the function \( F \) of the coverage \( \theta_t \) of the transformed surface.

In the Figure 2 is shown the graphical solution of (9) and (10) as a function of partial pressure of A at constant pressure of B. The rates are plotted for different values of equilibrium constant \( K_q \). The rates have maximum with long tails approaching zero. It is interesting to note that since the rates have maximum they could lead to the falsification of reaction mechanism, if proper interpretation of phase transformation were not taken.

When the orders of transformation are different, \( n_A \neq n_B \), the steady state has multiple solutions. The solutions are the roots of the equation

\[
\theta^m - \theta^{m-1} + C(p_A, p_B) = 0
\]

(13)

\[
n = m_B - m_A
\]

\[
\theta_t = \lambda - \theta_t
\]
Figure 1. Schematic diagram of the phase transformation of catalyst surface.

Figure 2. Reaction rate curves for different values of the equilibrium constant between the two phases.
The C function depends on partial pressures, adsorption/desorption and phase transformation equilibrium constants

\[ C = k_n \left( 1 + \frac{1}{k_n p_a} + \frac{1}{k_n p_b} \right)^m \frac{(k_n p_a)^{n \phi} (k_n p_b)^{n \phi + 1}}{(k_n p_a)^{n \phi + 1}} \]  

(15)

One solution of (13) is \( t \to 1 \). In the Figure 3. is shown the reaction rate for the case \( n_a = 0 \), \( n_b = 2 \), so that the equation (13) has three solutions in the range where the condition \( G > 4 \) is satisfied. A special case can be considered when the phase transformation is dynamically limited by the kinetics of nucleation, while growth of new phase is instantaneous and finite in size. These assumptions lead to a set of autonomous equations, i.e. the change of catalyst surface state is only determined by the present state, rather than the total history of the surface. The kinetics of an individual patch of transformed surface is given by the equation

\[ \dot{\theta}(t - \tau) = k_n \theta_n(t) H(t - \tau) \]  

(16)

where the \( H \) is the Heaviside function. Stability analysis of linearized system can be utilized to derive the following condition for bifurcation of a steady state solution to an oscillatory state.

\[ \tau = \frac{B}{J} < 0 \]

\[ \omega^* > 0 \]

\[ |J| = \omega \cdot t \]  

(17)
Figure 3. Multiplicity of the steady state reaction curves.

Literature

PARTICLE WETTING IN A LABORATORY ROTATING BASKET REACTOR FOR GAS-LIQUID-SOLID KINETIC MEASUREMENTS

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SUMMARY: Dissolution of benzoic acid particles was used to study solid-liquid mass transfer and particle wetting in a laboratory rotating basket reactor. Reaction kinetics studies in gas-liquid-solid system are often carried out in this type of reactor. Assuming that the reactor performance depends on particle layer thickness, the effect of basket thickness to particle diameter ratio was investigated. Runs were done in the presence and absence of gas, assuming that the ratio of the coefficients obtained at the same rotating speed is equal to the wetting efficiency. When the power input per unit mass of liquid is more than $5 \times 10^6 \text{cm}^2 \text{s}^{-3}$ and basket thickness to particle diameter ratio is less than 1.5, external mass transfer resistance can be neglected and in addition particle wetting, which can disturb kinetic measurements, can be avoided.

INTRODUCTION

When reactants are present in the gas and liquid phases and a chemical reaction takes place on a solid catalyst, kinetic measurements can be carried out in stirred tank reactors, preserving a gas-liquid-solid system. Komyama and Smith (1) carried out such experiments in a slurry
reactor. The same authors (2) also used a mixing reactor, where catalyst particles were held in stationary baskets. For the same purpose, Suzuki and Kawazoe (3) placed catalyst particles in rotating baskets. They all reported that external resistances can be neglected. The fact that the gas bubbles disturb kinetic measurements was not mentioned. Njiribako et al (4), who used rotating baskets in their experiments concluded, that catalyst particles were only partially wetted. Pavko and Levec (5) also reported that kinetic parameters obtained from a rotating basket reactor were in error owing to incompletely wetted catalyst, while external mass transfer resistances were not significant. That catalyst wetting was only partial and was due to the thick and bubble flow resistant bed of particles (basket thickness to particle diameter ratio was more than five).

The purpose of this work was to find the basket design and power input, such that external mass transfer resistances and partial wetting can be avoided when carrying out kinetic measurements.

EXPERIMENTAL

Dissolution of benzoic acid particles in the presence and absence of N₂ was used to study liquid-solid mass transfer and wetting efficiency. Experiments were carried out in a small plexiglass reactor of 12 cm tank diameter, held in a thermostat bath at 25°C. To examine the effect of particle bed thickness on the reactor performance, three pieces of four blade basket impellers of 10 cm diameter were made of 4.5 cm, 8.5 cm and 14.5 cm plexiglass plate, so that three different thicknesses were achieved. At the tip of each blade (4 cm wide), 2 x 3 cm piece was
simply cut out and a polyethylene screen of 20 mesh size was stretched over both sides. As a result the baskets obtained were covered with one, cross-shaped, lid. The reactor is schematically shown in Figure 1.

To obtain benzoic acid particles of a certain diameter, 0.8 x 0.8 cm cylinders of pulverized benzoic acid were made first on a piston press at constant pressure. After that, cylinders were broken and sieved through standard sieves of 2.50 - 3.15 mm openings.

The experiment started by loading baskets with a certain
amount of benzoic particles of 0.28 cm average particle diameter and then setting them into the reactor. After fixing four baffles and the reactor lid, a batch of distilled and preheated water was poured through the sampling hole. Then, a timing mechanism and a motor driving the basket impeller at a certain speed were turned on simultaneously. When experiments in the three phase system were carried out, gas feeding through the sparger ring, located below the basket impeller, also started. During the run, sampling with 2 ml pipettes was carried out every 10 - 30 seconds. Analysis was made using a Total Organic Carbon Analyser.

Power consumption was measured separately on a Model ELB (Bench Scale Equipment Co.) experimental agitator.

Particle to liquid mass transfer coefficients were calculated from the following expression:

\[ k_s = \frac{V_1}{m \Delta t a_t} \sum_{i=1}^{m} \ln \frac{C_i - C_1}{C_i - C_2} \]  

(1)

where \( C_1 \) and \( C_2 \) are the concentrations at the beginning and the end of the time interval \( \Delta t \) while \( C' \) is the equilibrium concentration. \( V_1 \) is the liquid volume, \( a_t \) is the particle surface area and \( m \) is the number of time intervals, respectively.

The ratio of mass transfer coefficients thus calculated obtained in the runs with and without gas at the same rotating speed was assumed to be equal to the wetting efficiency.

Particle properties and operating conditions are listed in Table 1.
TABLE 1. Properties of benzoic acid particles and operating conditions at $10^5 \text{Pa}$ and $25^\circ \text{C}$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_p$, cm</td>
<td>0.283</td>
</tr>
<tr>
<td>$\rho_p$, g/cm$^3$</td>
<td>1.55</td>
</tr>
<tr>
<td>$E_3$</td>
<td>0.50</td>
</tr>
<tr>
<td>$S$, cm$^2$/g</td>
<td>15.7</td>
</tr>
<tr>
<td>Mass of catalyst, g</td>
<td>7.5 - 27.0</td>
</tr>
<tr>
<td>Volume of liquid, cm$^3$</td>
<td>1360 (gas), 1710 (no gas)</td>
</tr>
<tr>
<td>Superficial gas flowrate, cm/s</td>
<td>0.2</td>
</tr>
<tr>
<td>Speed, s$^{-1}$</td>
<td>1.7, 3.3, 5.0, 6.7</td>
</tr>
<tr>
<td>Basket thickness, cm</td>
<td>0.45, 0.85, 1.40</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

In order to investigate rotating basket reactor performance, the runs with three rotating baskets of different thicknesses were carried out in the presence and absence of gas. The resulting mass transfer coefficients presented in Fig. 2 increase in a linear fashion with rotating speed $n$. Since Suzuki and Kawazoe (3) reported that $k_a$ is proportional to $n^{0.67}$, this deviation in exponent value could be due to the rotating basket construction. It can be further concluded that mass transfer coefficients and average linear flow velocity through the bed increase at a constant rotating speed when basket thickness is reduced, according to the lowering flow resistance through the bed. From the correlation of Hirose et al (6) it was roughly estimated that average linear velocity through a 1.4 cm thick bed of 0.28 cm
particles is about 10 cm/s. With a thickened particle layer (0.45 cm), the linear velocity increases to approximately 20 cm/s, when in both cases power input per unit mass $\varepsilon = 7 \times 10^4\text{ cm}^2\text{s}^{-3}(n = 6, 7\text{ s}^{-1})$ is attained (there is no sense to use higher power input). On the other hand, if only $\varepsilon = 3 \times 10^5\text{ cm}^2\text{s}^{-3}$ is introduced, linear velocities decrease to approximately 4 cm/s and 2 cm/s, respectively. Thus, if kinetic measurements are carried out at about $\varepsilon = 5 \times 10^4\text{ cm}^2\text{s}^{-3}$, and basket thickness to particle ratio is designed to be at most 1.5, external mass transfer resistances can be neglected according to the type of reaction: if a first order
reaction is assumed for example and a slow chemical reaction takes place \((k = 10^{-3}s^{-1})\), surface concentration is practically equal to the bulk concentration. However, in a presence of very fast chemical reaction \((k = 10^{-1}s^{-1})\) surface concentration is reduced to only 50% of bulk concentration.

In this work wetting efficiency was also investigated. It was assumed, that the ratio of mass transfer coefficients obtained from the runs done in the presence and absence of gas is equal to the wetting efficiency. Resulting values are shown in Table 2.

**TABLE 2. Wetting efficiency in rotating basket impellers.**

<table>
<thead>
<tr>
<th>(n(s^{-1}))</th>
<th>(\times 10^{-4}(cm^2s^{-3}))</th>
<th>Wetting efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(z/d_p) = 5.0</td>
<td>(z/d_p) = 3.0</td>
</tr>
<tr>
<td>1.7</td>
<td>0.35</td>
<td>0.91</td>
</tr>
<tr>
<td>3.3</td>
<td>1.48</td>
<td>0.74</td>
</tr>
<tr>
<td>5.0</td>
<td>3.53</td>
<td>0.57</td>
</tr>
<tr>
<td>6.7</td>
<td>7.28</td>
<td>0.60</td>
</tr>
</tbody>
</table>

\(z/d_p\) - basket thickness to particle diameter ratio

It was expected that wetting efficiency increases slightly with rising rotating speed in all three baskets according to the higher bubble velocities through the bed. In our previous work (5) the very low wetting efficiency \((0.36 - 0.47)\) in 1.4 cm thick bed was reported. This surprising data, obtained from kinetic measurements in rotating basket and liquid full reactor, was attributed to the gas bubbles trapped inside the catalyst batch. The results of this work also confirm our previous supposition. It is seen further that thickening of the particle layer essentially improves wetting (practically total wetting is attained at \(z/d_p\) equal to 1.6), due to the lowering flow resistance through the bed.
Thus, the following conclusions can finally be made:
when the power input per unit mass of liquid is more than
$5 \times 10^4 \text{cm}^2 \text{s}^{-3}$ and basket thickness to particle diameter
ratio is less than 1.5, external mass transfer resistance
can be neglected and particle wetting can also be avoided.

NOMENCLATURE

- $a_t$: particle mass transfer area, cm$^2$/cm$^3$
- $C$: concentration, mol/cm$^3$
- $d_p$: diameter of particles, cm
- $k$: apparent reaction rate constant, s$^{-1}$
- $k_s$: liquid-particle mass transfer coefficient, cm/s
- $m$: number of time intervals
- $n$: rotating speed
- $S$: mass transfer area per unit mass, cm$^2$/g
- $\Delta t$: time interval, s
- $V_l$: volume of liquid, cm$^3$
- $z$: basket thickness, cm
- $C_B$: power input per unit mass of liquid, cm$^2$/s$^3$
- $\phi_p$: bed porosity
- $\rho_p$: density of particles, g/cm$^3$

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   9(1976) 220.
DIRECT HYDRATION OF LINEAR BUTENES TO 2-BUTANOL CATALYZED BY STRONG ACID ION EXCHANGERS

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Summary

2-Butanol (sec-butylalcohol) may be produced in a one step process by the hydration of linear butenes catalyzed by strong acid ion exchangers. A very attractive feature of this process compared to the conventional one is that it has no sulfuric acid reconcentration step. The reaction proceeds in the presence of liquid water. Simultaneously with the formation of the alcohol isomerization of the butenes takes place. It is found that a reaction scheme in which all reactions proceed via an intermediate carbonium ion describes the kinetics well. The values of the kinetic and equilibrium constants of these reactions have been determined.

Some consequences for the design and operation of a commercial reactor are indicated. It seems most attractive to use as reactor type a bubble column packed with ion exchange resin and to remove the produced alcohol from the reactor with the butene-rich phase.

1. Introduction

2-Butanol (sec-butylalcohol) is produced at a large scale. It is mainly used as a solvent and as starting material in the production of methyl-ethylketone (MEK). Commercially the most important route is a two step process. The first step involves the absorption of butenes from a feed, usually containing all linear butene isomers and some saturated C4-compounds, in concentrated sulfuric acid. This leads to the formation of the acid sulfate of the butenes. In the second step this sulfate is hydrolyzed in a large excess of water, yielding 2-butanol and dilute sulfuric acid. This acid has to be concentrated, which is an energy consuming process, proceeding under very corrosive conditions. The prevention of SOx emission also requires an appreciable investment in the plant.

Using a strong acid ion exchange resin as a catalyst, 2-butanol can be produced in a one-step process circumventing most of these disadvantages. In this process a butene stream and liquid water are fed to a reactor containing the resin. The exit stream contains the product. The ion exchange resin behaves as immobilized acid catalyzing the hydration. An ion exchanger-catalyzed process for the production of 2-propanol is operated commercially by Deutsche Texaco [1]. To our knowledge no such process is in operation for 2-butanol, although some patents have been granted concerning this process [2].
In the literature very few data are available on the reaction kinetics of this potentially interesting process to produce 2-butanol. Douglas [3] presents some experimental results but from these no numerical data on the rate constants of the reactions can be obtained. The present contribution gives the results of experiments on the kinetics and chemical equilibrium positions of the reactions involved and some consequences for the design of an industrial scale reactor for the strong acid ion exchanger catalyzed process.

2. Reactions

The acid catalyzed formation of 2-butanol from butenes probably proceeds by an A-S,2 mechanism [4] via a carbonium ion as an intermediate. Besides reacting to the alcohol the intermediate carbonium ion may be converted to the three isomeric butenes. Hence the hydration and isomerization reactions proceed simultaneously. The reaction scheme is

\[
\begin{align*}
1\text{-butene} & : C_4H_8 + H^+ \rightarrow -H_2O \\
cis-2\text{-butene} & : C_4H_8 + H^+ \rightleftharpoons C_4H_9^+ \rightleftharpoons C_4H_{10}^0 + H^+ 2\text{-butanol} (1) \\
trans-2\text{-butene} & : C_4H_8 + H^+ \rightleftharpoons C_4H_{10}^0 + H^+ 2\text{-butanol}
\end{align*}
\]

This scheme clearly shows the catalytic role of the proton present in the resin. At relatively high concentrations of the alcohol produced, the carbonium ion may also combine with the alcohol, leading to the formation of 2-butoxy-2-butane (di-sec-butylether). In the experiments the ether never was found. It is therefore not included in the reaction scheme.

3. Kinetics

The rate of formation of the carbonium ion from the isomeric butenes and alcohol is expected to be proportional to the butene or alcohol and acid group concentration, both within the resin phase. The rate of formation of the alcohol is expected to be proportional to the carbonium ion and water concentration within the resin. The concentrations within the resin phase are awkward quantities to use in practice. To eliminate them, it is assumed that at physical equilibrium the concentration of each component in the resin phase is proportional to its concentration in the surrounding fluid, the proportionality constant (partition coefficient) being independent of the composition over the range of concentrations involved. It is further assumed that the concentration of the acid groups within the resin is constant for a given ion exchanger. In practice the mol fraction of water in the fluid surrounding the ion exchanger approaches 1. Therefore it is assumed that the water concentration in the resin is constant. Using these assumptions and eliminating the carbonium ion concentration by assuming its net rate of formation to be zero (steady state assumption) the following expressions for the rate of production \( r \) in terms of concentrations in the fluid surrounding the ion exchanger are obtained.

\[
r_A = k_a ([D]_L - [A]_L) \text{ mol m}^{-3} \text{ s}^{-1}
\]
Here \( A, B, C, \) and \( T \) represent 2-butanol, 1-butene, cis-2-butene and trans-2-butene respectively. The \( k_i \)'s are the pseudo-first order rate constants of the formation of the carbonium ion from component \( i \). They are proportional to the acid group concentration in the resin and the partition coefficient of component \( i \). The equilibrium constants \( K_i \) are defined as

\[
K_B = \frac{[A]_L}{[B]_L, eq.} \quad K_C = \frac{[A]_L}{[C]_L, eq.} \quad K_T = \frac{[T]_L}{[T]_L, eq.}
\]

The values of equilibrium and rate constants were determined experimentally.

4. Equipment and procedure

The experiments to determine the rate- and equilibrium constants were carried out in a tubular reactor with an internal diameter of 5 mm. The reactor was filled with spherical ion exchange resin particles of the type XE - 307 H (ex Rohm and Haas). A sieve fraction of 0.60 - 0.71 mm was used.

The feed, consisting of a solution of one of the isomeric butenes or of 2-butanol in water, was metered by a positive displacement pump through a preheater coil to the reactor. Preheater and reactor were both immersed in a thermostated oil bath. The stream leaving the reactor was cooled and passed through a bed of a strong base ion exchanger (Amberlite IR-401) of accurately known capacity. The bed served to remove any traces of sulfuric acid which might result from the desulfonation of the resin under certain conditions. Under normal operating conditions the rate of desulfonation is very low, however [5]. The solution passed through a filter and a back pressure regulator to maintain the system pressure at 6 MPa. The product stream was completely evaporated and analyzed in an online gas chromatograph. The composition of the feed and the pressure in the reactor were chosen such that always only one homogeneous liquid phase was present.

As the ratio of length of packed bed over particle diameter always exceeded 100, the reactor could be considered as a plug flow reactor. The measurements of the equilibrium constants were performed by feeding a 0.25 w% 2-butanol solution in water to the reactor at very low LHSV.
Decreasing the flow rate by 50% resulted in a product stream of the same composition, indicating that chemical equilibrium was reached in the reactor. The temperature range investigated was 80 - 150°C. From the concentrations in the product stream the equilibrium constants $K_i$ were calculated according to equation (4). To obtain the values of the rate constants $k_i$, the following procedure was used. Feeds consisting of 2-butanol or one of the butenes dissolved in water were pumped to the reactor at a relatively high LHSV so that chemical equilibrium was not reached in the catalyst bed. The product distribution in the liquid leaving the reactor was determined. The rate constants were found by minimizing the differences between these product compositions and calculated ones obtained by solving the set of differential equations describing the concentration of each species in a plug flow reactor, using the rate expressions (2).

5. Results and discussion

**Equilibrium constants**

In Figure 1 the experimentally determined values of the equilibrium constants $K_i$ are plotted vs. $1/T$ on a semi-logarithmic scale. In a practical situation, the value of the overall equilibrium constant $R$ is of interest.

$$R = \frac{[A]_L}{[B]_L + [C]_L + [D]_L} = [\Sigma K_i^{-1}]^{-1}$$ (5)

The value of $R$ is also given in Figure 1. From the slopes of the $\ln K$ vs $1/T$ lines the heats of formation of the alcohol from the butenes in the liquid phase are calculated. Table I gives the results.

Table I also shows heats of reaction in the gas phase as determined by Cope [6]. These tend to be slightly higher. No experimental data on the heats of reaction in the liquid phase were found in the literature.

**Table I: summary of equilibrium and kinetic constants**

<table>
<thead>
<tr>
<th>Reactant</th>
<th>$K_i$ 130°C</th>
<th>$-\Delta H_R$ 130°C kJ mol$^{-1}$</th>
<th>$-\Delta H_R$ 125°C kJ mol$^{-1}$</th>
<th>$k_i = k_{o,i} \exp(-E_{a,i}/RT)$</th>
<th>$k_{o,i}$ 135°C mL·mIE·s$^{-1}$</th>
<th>$E_{a,i}$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butene</td>
<td>167.3</td>
<td>48.5</td>
<td>50.6</td>
<td>$1.70 \times 10^{1}$</td>
<td>6.18 $\times 10^{10}$</td>
<td>99.6</td>
</tr>
<tr>
<td>cis-2-butene</td>
<td>36.6</td>
<td>36.5</td>
<td>43.1</td>
<td>$1.74 \times 10^{11}$</td>
<td>6.17 $\times 10^{14}$</td>
<td>101.0</td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>24.5</td>
<td>38.6</td>
<td>39.7</td>
<td>$1.74 \times 10^{11}$</td>
<td>6.17 $\times 10^{14}$</td>
<td>135.1</td>
</tr>
<tr>
<td>2-butanol</td>
<td>24.5</td>
<td>38.6</td>
<td>39.7</td>
<td>$1.74 \times 10^{11}$</td>
<td>6.17 $\times 10^{14}$</td>
<td>135.1</td>
</tr>
</tbody>
</table>

From the values in Table I the relative amounts of the various isomeric butenes at chemical equilibrium can be calculated. The values are hardly temperature dependent, typical values being 53 mol% trans-2-butene, 37 mol% cis-2-butene and 8 mol% 1-butene.
Reaction rate constants

Figure 2 shows an Arrhenius plot of the reaction rate constants. The mean relative error in the calculated product compositions using these rate constants is 9.7%.

Table I contains the pre-exponential factors and activation energies. The rate constants of the formation of the carbonium ion from the three butenes are all of similar magnitude, while that from the alcohol is considerably smaller. The activation energy of the latter is larger. From the equilibrium and rate constants the relative rates of formation of the three butenes and 2-butanol from the carbonium ion can be calculated. It is found that the carbonium ion reacts for approximately 60% to 2-butanol, a value which is hardly temperature dependent. Of the butenes cis- and trans-2-butene are formed in almost equal quantities (18%) while very little 1-butene is formed (4%). This kinetically determined isomer distribution deviates appreciably from the distribution at chemical equilibrium. No data on the isomerization of butenes in the water phase could be found in the literature.

In Figure 3 the relative amounts of the isomeric butenes in the liquid phase during the reaction are given starting with alcohol-free feeds of varying compositions. The actual reaction paths can be represented in a tetrahedron in which the top represents 2-butanol.
6. Some remarks on the design of an industrial reactor

On the basis of the data presented some remarks can be made on the design and operation of a commercial reactor. The practical range of reactor temperatures is rather narrow. To avoid very large reactor volumes (say < 100 m³ for a 50,000 t/a 2-butanol production) reaction temperatures over 120°C are required. The thermal stability of the ion exchange resins presently available becomes a limiting factor at temperatures over 145°C [5].

Two fluid phases will be present in the reactor, a water-rich and a butene-rich one. The produced alcohol will be present in both phases. The maximum 2-butanol content of the water-rich liquid phase can be calculated from the solubility of the butenes in that phase and the value of the overall equilibrium constant K. Using Brooks' and McKetta's [7] data for the butene solubility the calculated maximum 2-butanol content of the water-rich phase is approximately 0.8 mol % or 3.3 w% at 130°C and the saturation pressure of the butenes (about 3.5 MPa). The maximum 2-butanol content decreases with increasing temperatures. This implies that removal of the produced alcohol with the water-rich phase probably is unattractive in view of the high distillation costs.

Removal of 2-butanol from the reactor with the butene-rich phase seems to be more attractive. Preliminary experiments on the system 2-butanol-water-butene showed that the ratio of the mol fractions of 2-butanol in the butene-rich and the water-rich phase is about 25 in the temperature range 130-160°C. At 130°C the maximum 2-butanol content of the butene-
rich phase may even become 20 mol % or 25 w% at pressures of about 6 MPa.
The water content of this phase is rather low (about 3 mol %). There-
fore much less distillation energy will be required to obtain pure 2-bu-
tanol from this product stream. With increasing temperature the maximum
2-butanol content of the butene-rich phase and therefore also the maxi-
mal butene conversion per pass through the reactor, decreases. Uncon-
verted butenes can be separated and recycled. It is clear that a high
butene content of the feed is beneficial to the process.

The feed rate of water to the reactor can be limited to the amount that
reacts with the butenes and to make up for losses. As reactor type a
trickle bed seems not suitable as wetting of the catalyst by water will
present a problem. Therefore the reactor should be operated as a bubble
column packed with ion exchange particles, the water-rich phase being
the continuous one. The butenes are fed at the bottom.

Using the data of Oshima [8] it is estimated that mass transfer limita-
tions between the butene- and water-rich phase may reduce the overall
rate of reaction by more than 50% at temperatures over 130°C. This pro-
blem may be alleviated to some extent by recirculating the water-rich
phase over the reactor.

More detailed data on phase equilibria and mass transfer are required
before a detailed design of a reactor can be made. Work is in progress
in our laboratory on these subjects.

7. Literature cited

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MATHEMATICAL MODEL OF FLOW PROCESS VESSEL FOR CONTINUOUS COPOLYMERIZATION OF ACRYLONITRILE-VINYLACETATE

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ABSTRACT

To get the final product with wanted and uniform properties becomes today imperative and needs such operating of the process at which it could be obtained. For this reason the mathematical model should be contained all of the parameters which define the final product (1).

Mathematical model of the flow process vessel for continuous copolymerization of acrylonitrile-vinylacetate is developed at adopted fluid-dynamic model "plug-mixing", steady state and isothermal conditions.

On the base of the kinetic equations of binary copolymerization, generating functions \( g_1(s_1, s_2) \) and \( g_2(s_1, s_2) \) of the radical distribution \( c_1(1,1) \) and \( c_0(1,1) \), generating functions of dead and total copolymer \( g_0(s_1, s_2) \), \( G(s_1, s_2) \), are obtained.

To determine the polydispersity coefficient molecular weight distribution moments \( u^{(0)}, u^{(1)}, u^{(1)}, v^{(2)}, u^{(1)} \) are found as derivatives of the generating functions for the alive and total copolymer.

The model will be used for a computer simulation of this process, which is a subject of our further investigations.
MATHMATICAL DESCRIPTION OF THE FLOW PROCESS VESSEL

On the base of the kinetic equation of binary copolymerization(2), generating functions \( R_1(s_1,s_2) \) and \( R_2(s_1,s_2) \) of the radical distribution can be developed in the following manner:

Let

\[
\frac{dc_1(l_1,l_2)}{dt} = k_{11}M_1c_1(l_1^{-1},l_2) + k_{21}M_1c_2(l_1^{-1},l_2) -
(k_{11}^{M_1} + k_{21}^{M_2})c_1(l_1,l_2) - (k_{11}^{R_1} + k_{21}^{R_2})c_2(l_1,l_2) \quad (1)
\]

\( l_1 
eq 1, l_2 
eq 0 )

\[
\frac{dc_2(l_1,l_2)}{dt} = k_{12}M_2c_1(l_1,l_2^{-1}) + k_{22}M_2c_2(l_1,l_2^{-1}) -
(k_{21}^{M_1} + k_{22}^{M_2})c_2(l_1,l_2) - (k_{21}^{R_1} + k_{22}^{R_2})c_2(l_1,l_2) \quad (2)
\]

\( l_1 
eq 0, l_2 
eq 1 )

\[
\frac{dc_2(0,1)}{dt} = k_{21}^{M_1}c_1(0,1) - (k_{21}^{M_1} + k_{22}^{M_2} + k_{21}^{R_1} + k_{22}^{R_2})c_2(0,1)
\]

be multiplied by \( \frac{l_1}{s_1} \frac{l_2}{s_2} \) and upon application of

\[
g(s_1,s_2) = \sum_{l_1=1}^{\infty} \sum_{l_2=1}^{\infty} c(I) \frac{l_1}{s_1} \frac{l_2}{s_2} \quad (3)
\]

for binary copolymer, at zero initial conditions, the equations

\[
[k_{11}^{M_1}(1-s_1) + k_{12}^{M_2} + T_1]c_1 - k_{21}^{M_1}s_1c_2 = l_1s_1 \quad (4)
\]
\[-k_{12} M_2 s_2 e_1 + \left[k_{22} M_2 (1-s_2) + k_{21} M_1 + T_2 \right] e_2 = I_2 s_2 \quad (5)\]

where

\[T_1 = k_{11} R_1 + k_{12} R_2, \quad l_1 = \frac{I k_{11} M_1}{k_{11} M_1 + k_{12} M_2}, \quad I = 2 f k_{x} M\]

\[T_2 = k_{21} R_1 + k_{22} R_2, \quad l_2 = \frac{I k_{22} M_2}{k_{11} M_1 + k_{22} M_2}

are obtained.

Equations (4), (5) can be solved to give

\[e_1(s_1, s_2) = \frac{y_1 \left[(1-y_2) l_1 / k_{11} M_1 + dy_2 I_2 / k_{12} M_2 \right]}{(1-y_1)(1-y_2) - dy_1 y_2} \quad (6)\]

\[e_2(s_1, s_2) = \frac{y_2 \left[dy_1 I_1 / k_{21} M_1 + (1-y_1) I_2 / k_{22} M_2 \right]}{(1-y_1)(1-y_2) - dy_1 y_2} \quad (7)\]

where

\[y_1 = \omega_1 s_1, \quad y_2 = \omega_2 s_2, \quad d = k_{12} k_{21} / k_{11} k_{22}\]

\[\omega_1 = \frac{k_{11} M_1}{k_{11} M_1 + k_{12} M_2 + T_1}, \quad \omega_2 = \frac{k_{22} M_2}{k_{12} M_2 + k_{21} M_1 + T_2}\]

\[e_0(s_1, s_2) \text{ is obtained in a manner as it was already given.}\]

Thus

\[\frac{dc(I)}{dt} = \frac{1}{2} \sum \sum \left\{ k_{11} t c_1(I') c_1(I') + 2 k_{12} t c_1(I') c_2(I') + \right.\]
leads to

\[
\frac{dg_0(s_1,s_2)}{dt} = \frac{1}{2} \left( k_{11}^+ t_1^2 + 2 k_{12}^+ t_1 t_2 + k_{22}^+ t_2^2 + (k_{11}^+ R_1^+ + k_{12}^+ R_2^+) g_1 + (k_{21}^+ R_1^+ + k_{22}^+ R_2^+) g_2 \right)
\]

or

\[
g_0(s_1,s_2) = \frac{1}{2} \int_0^t \left[ (k_{11}^+ t_1^2 + 2 k_{12}^+ t_1 t_2 + k_{22}^+ t_2^2 + (k_{11}^+ R_1^+ + k_{12}^+ R_2^+) g_1 + (k_{21}^+ R_1^+ + k_{22}^+ R_2^+) g_2 \right] dt
\]

Generating function of total copolymer \( G(s_1,s_2) \) in relation to \( g_1(s_1,s_2) \), \( g_2(s_1,s_2) \) and \( g_0(s_1,s_2) \) is

\[
G(s_1,s_2) = \sum_{l_1=1}^{\infty} \sum_{l_2=1}^{\infty} s_1^{l_1} s_2^{l_2} c(I) + c_1(I) + c_2(I)
\]

With \( c_1(I) + c_2(I) \ll c(I) \) equation 11 results in

\[
G(s_1,s_2) = g_0(s_1,s_2)
\]

To determine the polydispersity coefficients \( \mu^{(0)} \), \( \mu_{11}^{(1)} \), \( \mu_2^{(1)} \), \( \mu_{11}^{(2)} \) are found as

\[
\mu^{(0)} = G(s_1,s_2) \bigg|_{s_1=s_2=1}
\]
Mathematical model of the flow process vessel for continuous copolymerization of acrylonitrile-vinylacetate at adopted fluid-dynamic model "plug-mixing", steady state and isothermal conditions, is

\[
\begin{align*}
\phi_1(1) &= \left. \frac{\partial G(s_1, s_2)}{\partial s_1} \right|_{s_1 = s_2 = 1} \\
\phi_1(2) &= \left. \frac{\partial G(s_1, s_2)}{\partial s_2} \right|_{s_1 = s_2 = 1} \\
\mu_{11} &= \left. \frac{\partial^2 G(s_1, s_2)}{\partial s_1^2} \right|_{s_1 = s_2 = 1} (13)
\end{align*}
\]

\[
\begin{align*}
V \frac{\partial m}{\partial \tau} &= \int \frac{dM}{(-r_M)p} M_{1,1} \\
V \frac{\partial M_1}{\partial \tau} &= \int \frac{dM_1}{(-r_{M_1})p} M_{1,0} \\
V \frac{\partial M_2}{\partial \tau} &= \int \frac{dM_2}{(-r_{M_2})p} M_{2,0} \\
V \frac{\partial R_1}{\partial \tau} &= \int \frac{dR_1}{(-r_{R_1})p} R_{1,0} \\
V \frac{\partial R_2}{\partial \tau} &= \int \frac{dR_2}{(-r_{R_2})p} R_{2,0}
\end{align*}
\]

(14) \( m = \frac{M_1 - M_2}{Q} \) (15) \( m = \frac{M_{1,1} - M_{1,2}}{Q} \) (16) \( m = \frac{M_{2,1} - M_{2,2}}{Q} \) (17) \( m = \frac{R_{1,1} - R_{1,2}}{Q} \) (18) \( m = \frac{R_{2,1} - R_{2,2}}{Q} \) (19) \( m = \frac{R_{1,1} - R_{1,2}}{Q} \) (20) \( m = \frac{R_{2,1} - R_{2,2}}{Q} \) (21) \( m = \frac{R_{1,1} - R_{1,2}}{Q} \) (22) \( m = \frac{R_{2,1} - R_{2,2}}{Q} \) (23) \( m = \frac{R_{1,1} - R_{1,2}}{Q} \)

where

\[-r_M = \int \frac{dI}{dt} = 2f_k r_I = I\]
\(-r_{M_1}\) = \(- \frac{dM_1}{dt} = \frac{\sqrt{I_{M_1}(r_1M_1+M_2)}}{Z}\)

\(-r_{M_2}\) = \(- \frac{dM_2}{dt} = \frac{\sqrt{I_{M_2}(r_2M_2+M_1)}}{Z}\)

\[Z = (r_1^2M_1^2+2r_1r_2\int M_1M_2+r_2^2M_2^2)^{1/2}\]

\[\int_1 = \frac{\sqrt{k_{11}}}{k_{11}}, \quad \int_2 = \frac{\sqrt{k_{22}}}{k_{22}}, \quad \gamma = \frac{k_{12}^t}{\sqrt{k_{11}k_{22}}}, \quad \phi = \frac{k_{12}^t}{k_{12}^t} \]

\(-r_{R_1}\) = \(- \frac{dR_1}{dt} = -k_{11}^tM_1R_1^t - k_{21}^tM_1R_2^t + k_{12}^tM_2R_1^t + (k_{14}^tR_1^t + k_{12}^tR_2^t)R_1\)

\(-r_{R_2}\) = \(- \frac{dR_2}{dt} = -k_{22}^tM_2R_2^t - k_{12}^tM_2R_1^t + k_{21}^tM_1R_2^t + (k_{24}^tR_1^t + k_{22}^tR_2^t)R_2\)

\[\frac{dR^t}{dt} = 2\gamma k_{11}^tR_1^t - (k_{11}^tM_1 + k_{22}^tM_2)R^t\]

Equations (10), (11), (13) as well the polydispersity coefficient expression are included in the mathematical model too.

CONCLUSION

Researches have been carried out by the authors bringing to a real mathematical description of a flow process vessel.
A continuous copolymerization of acrylonitrile-vinylacetate in a solution at different process conditions has been studied\(^4\). The age distribution functions are experimentally determined\(^4\). The fluid-dynamic model adopted consists of an active perfectly mixed, a plug flow and completely "dead" region in series\(^5\).

The mathematical model will be used for studying this process via computer simulation, which is a subject of our further investigations.

**NOMENCLATURE**

- \(c_i(l_1, l_2)\): radical distribution of \(i\)-th species
- \(c(l_1, l_2)\): distribution of dead copolymer
- \(\mathfrak{g}_i(s_1, s_2)\): generating function of the radical distribution of \(i\)-th species
- \(\mathfrak{g}_0(s_1, s_2)\): generating function of dead copolymer
- \(\gamma(s_1, s_2)\): generating function of total copolymer
- \(I\): composition vector
- \(l_1, l_2\): number of monomer units and 2 in the binary copolymer
- \(s_1, s_2\): parameters in the generating function
- \(R\): primary radical
- \(M_i\): monomer concentration of \(i\)-th species
- \(R_i\): radical concentration of \(i\)-th species
- \(r\): reaction rates
- \(k\): rate constants
- \(t\): time
- \(\mathbb{1}\): unit matrix (Croncker's symbol)
- \(\mu\): statistical moments
- \(m\): fraction of perfectly mixed region
- \(p\): fraction of plug flow region
- \(V\): total volume of reactor
- \(Q\): flow rate
concentration of initiator before and after the plug flow region and after the perfectly mixed region

monomer concentration before and after the plug flow region and after the perfectly mixed region

radical concentration before and after the plug flow region and after the perfectly mixed region

REFERENCES

The Measurement of Light Transmission through a Fluidized Photocatalytic Reactor
L. Rizzuti, Università di Palermo, Italy.
P.L. Yue, University of Bath, England.

SUMMARY
The transmission of light through an irradiated fluidized bed with flat walls containing catalytic particles has been experimentally studied. This type of reactor is suitable for the utilisation of solar energy in heterogeneous photo-assisted catalysis, which is an increasingly important field of research. No experimental work using flat reactors has been reported in literature so far.

A reactor with 100 x 50mm irradiated area was used. The amount of light transmitted through the reactor at different bed heights was measured by a photocell. The experimental variables studied included: (i) gas flow rate, varying from two to ten times that required for minimum fluidization; (ii) particle size, ranging from 0.131 to 0.262mm; and (iii) internal bed thickness from 2 to 5mm.

Results show that the amount of light transmission by flat fluidized reactors is very low. Light transmission was found to be a function of gas flow rate, particle size, bed height and internal bed thickness. The average percentage of light transmitted per unit irradiated area was correlated with the average bubble voidage of the bed $e_B$ and the ratio of internal bed thickness to particle size $6$.

INTRODUCTION
Recently research efforts in converting solar energy to chemical energy have greatly intensified (1-4). Many of these studies found the use of heterogeneous catalytic systems effective in promoting the reactions of interest. Batch or continuous gas-liquid, gas-solid or gas-liquid-solid reactors have been used to perform these photosensitised reactions. Cassano, Silveston and Smith (5) in their excellent review of photochemical reactor design have pointed out the complexity of modelling multiphase photoprocesses in flow reactors. These reactors are more difficult to treat than conventional reactors because of the effects of the absorption and distribution of light on the chemical kinetics. Jacob and Dranoff (6) have tackled the design and analysis of perfectly mixed systems. A rigorous approach making use of radiant energy transfer theory to model photochemical reactors has been advanced by Santarelli and co-workers (7, 8). The theoretical basis of this approach is very sound.
but experimental verification in specific types of continuous flow reactor is needed.

Gas-solid fluidized beds have been used for conducting photoassisted ammonia synthesis \(^{(3, 9)}\). This type of heterogeneous system has the advantage of good and frequent contact between reactants, photons and catalysts. Rigorous mathematical modelling of a gas-solid fluidized bed photoreactor is, however, far from simple. From the point of view of design it may be attractive to experimentally investigate some important aspects of fluidized photoreactor before attempting a fundamental analysis of the general problem.

The effect of the physical and transport parameters of a fluidized photoreactor on the absorption of light is one interesting aspect which deserves careful study. As a first step of such study, it will be adequate to examine the problem without introducing the complication of kinetics. This paper presents the results of an experimental investigation on the transmission of light through a fluidized bed.

**EXPERIMENTAL**

The reactor used had two vertical parallel flat walls separated by a small gap. This type of reactor geometry is suitable for solar irradiation application. It offers a very high irradiation area per unit volume of catalyst, thus greatly increasing the exposure of the catalyst to irradiation. A flat fluidized reactor has been demonstrated \(^{(9)}\) to be more effective than a cylindrical one with a reflector. The reactor walls were made of 2mm thick soda-lime glass. Nitrogen was introduced into the fluidized bed through a porous sintered plate which supported particles of \(\gamma\)-alumina. These particles are often used as catalyst or catalyst support \(^{(3, 9)}\). Values of the mean diameter of the particles used and bed thicknesses are given in Table 1. Experiments were performed at various gas flow rates for each particle size using all four reactors. The static height of the particles in the bed was about 85mm. The internal bed thicknesses, i.e. the gap between the flat walls, is an important design variable. A small thickness will increase the exposure of all the particles to irradiation but will also increase the amount of light transmitted through the reactor as well as decrease the effective reactor volume. If the bed thickness is too high, some of the catalyst may not have much contact with photons and product yield would be reduced.
Since the reactor was made of glass, the behaviour of the fluidized bed could be visually observed. Flow distribution was very uniform throughout the bed. The variation of bed pressure drop with gas flow rate was measured for each size of particles used. From these results the point of minimum fluidization was determined according to the method suggested by Richardson (10). The bed height at this point was also measured.

Gas flow rate was determined downstream of the fluidized bed. The reactor was irradiated by a light source in the form of a 50 x 1.5 mm horizontal slit which was formed by a bundle of optical fibres. The fibres were aligned in a metal case with the slit at one end and a cylindrical section of 7.5 mm O.D. at the other end. The cylindrical end was attached to a 10 mm O.D. light bulb which was fitted to a metal housing. A voltage regulator was used to keep the voltage input to the light bulb constant.

The light coming through the slit was collimated by a cylindrical glass rod. The reactor was placed in the focal plane of the collimated light beam. Thus only a very thin slit of the reactor wall was irradiated at a given beam height. Light which passed through the reactor without being absorbed was directed by another collimator and optical fibre bundle arranged in reverse order to a detecting photocell. The output of the photocell was measured by a digital voltmeter and recorded continuously on a chart recorder.

The photocell output was calibrated by the following method. The collimated light was allowed to pass through a vertical slit of precisely known width placed in front of the empty reactor. The irradiation received by the photocell corresponded to that which passed through the reactor without being absorbed. The photocell output was calibrated against the percentage of light transmission through the reactor by using a series of slits of different known widths. For a given particle size and gas flow rate, light transmission was measured at different bed heights above the distributor.

RESULTS

In this section the term light transmission \( E \) means the fraction of light transmitted through the reactor. Assuming that very little light was reflected from the reactor wall which was irradiated, \( (1-E) \) therefore represents the fraction of light energy absorbed by the fluidized particles. \( E \) was found to vary considerably at different heights above the distributor, \( h \). The measurement of \( E \) at different \( h \) in reactor D containing particles
of 0.157 mm mean diameter is illustrated in fig 1. The figure shows very little light passed through the first 10 mm above the distributor. From a height of 20 mm upward E varied roughly linearly with h for all flow rates up to ten times \( Q_{mf} \), the flow rate at minimum fluidization. The distribution of bubble size observed visually was characteristic of a freely bubbling fluidized bed. Small bubbles were formed near the distributor. As the bubbles moved up the bed and coalesced, voidage in the bed increased.

The performance of reactor A containing particles of 0.220 mm mean diameter is illustrated in fig 2. In this case light transmission started immediately above the distributor and initially increased very rapidly with height. Further up the bed the increase in E gradually declined. The variation of E with h was therefore highly nonlinear, especially at higher flow rates. Visual observation of the bed showed that the fluidization of particles near the distributor was more rigorous than in the previous case. Bubble voidage in the bed was also more evenly distributed throughout the bed except at the very top. The average light transmission \( \bar{E} \) over the entire irradiated area was obtained by integrating the area under the E versus h curves. \( \bar{E} \) increased approximately linearly with increase in gas flow rate up to about six times \( Q_{mf} \) for all the reactors with the exception of reactor A. Thereafter the increase in \( \bar{E} \) with increasing flow rate slowed down. The behaviour of reactor A was much more nonlinear. An interesting point to note is that the flow rate at which light began to pass through the bed was about 1.7 to 2.2 times \( Q_{mf} \). The transition point corresponds approximately to \( Q_{mb} \), the flow rate at which bubbling begins. Visual observation also confirmed this phenomenon. It can be concluded that light passes through a fluidized bed via the bubbles. The variation of \( \bar{E} \) with particle size is roughly linear, though a little less so with reactor D. Extrapolation of plots of \( \bar{E} \) versus \( d_p \) suggest that below a certain particle size no light energy will pass through the bed. This critical particle diameter was found to vary from .08 to 0.12 mm for the reactors used.

It would seem reasonable that the average light energy transmitted through a flat fluidized bed might be correlated with the average bed voidage \( e_B \), particle size \( d_p \), and bed thickness \( d_n \). \( e_B \) was determined by an empirical correlation proposed by Geldart (11). For group B particles, that is, sand type particles, which cover the range of particle size and density of \( \gamma \)-alumina used in this study,
where \( \alpha = 0.915 \) \( (U - U_{mf})^{0.4} \) 
\[
e_{B} = \frac{2}{\beta} \sqrt{\frac{2}{g} \left( U - U_{mf} \right) \left[ (\alpha + \beta H_{mf})^{1 - \alpha} \right]} 
\]
(1)

\( \beta = 0.027 \) \( (U - U_{mf})^{0.94} \) 

\( H_{mf} \) = bed height at minimum fluidization in cm 
\( U_{mf} \) = minimum fluidization velocity in cm s\(^{-2}\) 
\( g \) = acceleration due to gravity in cm s\(^{-2}\)

Linear regression of all the data yielded the following correlation,
\[
E \delta = -0.206 + 3.39 e_{B} 
\]
(4)

where \( \delta \) is the ratio of \( d_{r} \) to \( d_{p} \).

The regression equation together with the experimental data have been plotted in Fig 3. The R-square value of the correlation is about 90 which indicates goodness of fit. The negative value of the intercept means that light energy will not be transmitted through the bed until \( e_{B} \) reaches a certain value.

The above attempt in correlating the experimental data is based on the macroscopic behaviour of the photoreactor. The analysis shows that the ratio of bed thickness of particle diameter and bubble voidage are important design parameters.

In order to analyse the absorption of light energy by the fluidized particles it will be necessary to examine the problem from a microscopic viewpoint. The effect of geometrical and optical properties of the particles and the interaction of particles with incident light will have to be studied.

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Table 1 Particle Size and Bed Thickness

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<th>Bed Thickness $d_r$, mm</th>
<th>Mean Particle Diameter $d_p$, mm</th>
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<tr>
<td>A</td>
<td>2.0</td>
<td>0.131</td>
</tr>
<tr>
<td>B</td>
<td>3.0</td>
<td>0.157</td>
</tr>
<tr>
<td>C</td>
<td>4.0</td>
<td>0.187</td>
</tr>
<tr>
<td>D</td>
<td>5.0</td>
<td>0.220</td>
</tr>
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0.262
Fig. 1 Light transmission at different bed heights in Reactor D  $d_p = 0.157$ mm

Fig. 2 Light transmission at different bed heights in Reactor A  $d_p = 0.220$
Fig. 3 Correlation between light transmission, bed thickness, particle diameter and bed voidage
<table>
<thead>
<tr>
<th>Authors</th>
<th>Page</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALESSANDRINI A.</td>
<td>230</td>
<td>KEMENY S.</td>
<td>106, 208</td>
</tr>
<tr>
<td>ALESSI P.</td>
<td>114, 223, 230</td>
<td>KIKIC I.</td>
<td>98, 223, 230</td>
</tr>
<tr>
<td>ANNESINI M.C.</td>
<td>88</td>
<td>KIPRIJANOVA-RADANOVIC R.</td>
<td>562</td>
</tr>
<tr>
<td>ARLT W.</td>
<td>153</td>
<td>KLEINHENV K.</td>
<td>153</td>
</tr>
<tr>
<td>BALDI G.</td>
<td>476</td>
<td>KOLLAR-HUNEK K.</td>
<td>208</td>
</tr>
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<td>BALOG Gy.</td>
<td>106</td>
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<td>389</td>
</tr>
<tr>
<td>BOYADZHEV L.</td>
<td>349</td>
<td>KURTANEC Z.</td>
<td>519</td>
</tr>
<tr>
<td>CANEPA P.</td>
<td>341</td>
<td>LAPASIN R.</td>
<td>98</td>
</tr>
<tr>
<td>CARASSITI F.</td>
<td>373</td>
<td>LEVEL J.</td>
<td>527</td>
</tr>
<tr>
<td>CARVOLI G.</td>
<td>188</td>
<td>LIUZZO G.</td>
<td>373</td>
</tr>
<tr>
<td>CHUCHVALEC A.</td>
<td>257</td>
<td>MAHENDRU H. L.</td>
<td>333</td>
</tr>
<tr>
<td>CIBULKA L.</td>
<td>130</td>
<td>MALJJEVSKY A.</td>
<td>200</td>
</tr>
<tr>
<td>CONTI R.</td>
<td>476</td>
<td>MANCZINGER J.</td>
<td>208</td>
</tr>
<tr>
<td>CORI L.</td>
<td>188</td>
<td>MARELLI L.</td>
<td>88</td>
</tr>
<tr>
<td>CRESSI E.</td>
<td>223</td>
<td>MARKOVSKA L.</td>
<td>562</td>
</tr>
<tr>
<td>DELOGU P.</td>
<td>188</td>
<td>MARR R.</td>
<td>432</td>
</tr>
<tr>
<td>DJORDJEVIC B.</td>
<td>238</td>
<td>MARTON G.</td>
<td>484</td>
</tr>
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<td>DOLECEK V.</td>
<td>300</td>
<td>MATOUS J.</td>
<td>122</td>
</tr>
<tr>
<td>FERMEGLIA M.</td>
<td>98, 138, 230</td>
<td>MELZNER D.</td>
<td>358</td>
</tr>
<tr>
<td>v. FISCHER E.</td>
<td>424</td>
<td>MIHAJLOV A.</td>
<td>80</td>
</tr>
<tr>
<td>GAUBINGER W.</td>
<td>432</td>
<td>MITROVIC M.</td>
<td>367</td>
</tr>
<tr>
<td>GIRONI F.</td>
<td>88</td>
<td>MODIL R.</td>
<td>495</td>
</tr>
<tr>
<td>GIUDICE S.</td>
<td>500</td>
<td>MOHRMANN A.</td>
<td>358</td>
</tr>
<tr>
<td>GOLAB J.</td>
<td>300, 445</td>
<td>MOLZAHN M.</td>
<td>267</td>
</tr>
<tr>
<td>GOMZI Z.</td>
<td>509</td>
<td>MORELLI A.</td>
<td>373</td>
</tr>
<tr>
<td>GREGOR W.</td>
<td>406</td>
<td>MOSE R.</td>
<td>143</td>
</tr>
<tr>
<td>GRILC V.</td>
<td>300, 445</td>
<td>MUNARI S.</td>
<td>341</td>
</tr>
<tr>
<td>GRIZO A.N.</td>
<td>381</td>
<td>NICCHIA M.</td>
<td>341</td>
</tr>
<tr>
<td>GULIC V.</td>
<td>300</td>
<td>NOVAK J.P.</td>
<td>122, 180, 200</td>
</tr>
<tr>
<td>HACKL A.</td>
<td>333</td>
<td>OLIVERI del CASTILLO G.</td>
<td>492</td>
</tr>
<tr>
<td>HALWACHS W.</td>
<td>358</td>
<td>ORLANDINI - VISALBERGI M.14, 138</td>
<td></td>
</tr>
<tr>
<td>HARTLAND S.</td>
<td>397, 424</td>
<td>PAUVISON R.</td>
<td>72, 80</td>
</tr>
<tr>
<td>HAVAS-DENCS J.</td>
<td>484</td>
<td>PAYKO A.</td>
<td>327</td>
</tr>
<tr>
<td>HENTRICH P.</td>
<td>318</td>
<td>PETRUS L.</td>
<td>535</td>
</tr>
<tr>
<td>HUDCOVA L.</td>
<td>257</td>
<td>PICK J.</td>
<td>180</td>
</tr>
<tr>
<td>HUEMER H.</td>
<td>145, 267</td>
<td>POPOVSKA F.A.</td>
<td>381</td>
</tr>
<tr>
<td>HUSUNG G.</td>
<td>432</td>
<td>POPPE W.</td>
<td>358</td>
</tr>
<tr>
<td>JOOSTEN G.E.H.</td>
<td>535</td>
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<td></td>
</tr>
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<td>80</td>
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<tr>
<td>Name</td>
<td>Page 1</td>
<td>Page 2</td>
<td>Page 3</td>
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<td>-----------------------------</td>
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<tr>
<td>QIULIN W.</td>
<td>367</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RASSMUSSEN P.</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>REISSINGER K.H.</td>
<td>412</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RIVOLTA L.</td>
<td>492</td>
<td></td>
<td></td>
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<tr>
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<td>550</td>
<td></td>
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</tr>
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<td>397, 626</td>
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