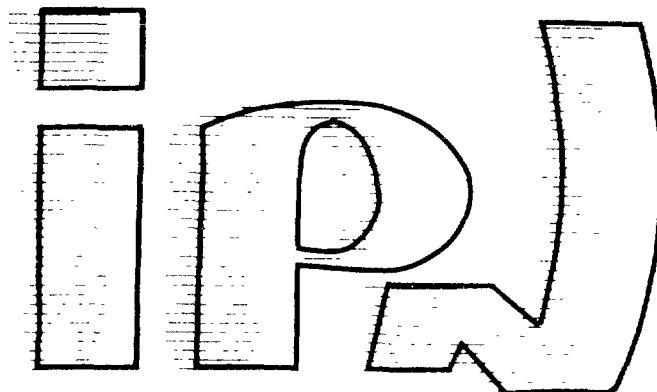


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RADIOCHEMISTRY AND ACTINIDE CHEMISTRY

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## RADIOCHEMISTRY AND ACTINIDE CHEMISTRY

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Radiochemistry is strictly speaking the study of chemical properties of natural or artificial radioactive matter which cannot be conducted using the usual methods and technics of the classical physico-chemistry. Radiochemistry is supported by a single technic : the detection and energy measurement of nuclear rays (or secondary atomic rays) and two types of methods :

1) The ones which allow to read chemical information beared by nuclear process. They do not need a separation of the different species, if any, of a given radionuclide.

2) The others which only use rays emitted by radionuclides as spatial indicators. They need to sort out the chemical species of the radionuclides There are static or dynamic distribution methods into phases systems and transportation or diffusion methods.

Radiochemistry deals with tracer scale amount of radionuclides typically, with  $N$  species (atoms, molecules, ions) by  $\text{cm}^3$  below  $10^{12}$  and, as regard of the  $N$  values, one can speak of tracer scale, atom or single atom chemistry (fig. 1).

As  $N$  decreases from around Avogadro number to less than  $10^{12}$ , we know that we have to be careful when we try to explain the data concerning the behaviour of radionuclides. Some problems occurs (1, 2) In this paper, we should like to deal only with those arising for  $N = 1$  to  $N \approx 100$  or several hundreds ; the other cases ( $N = 1$  and  $100 < N < 10^{12}$  have recently been discussed elsewhere (1, 2).

Isotopes of actinide and transactinide elements can be detected in different situations in such low amount (fig. 2). In these cases, their behaviour can only be studied in the framework of radiochemistry and that is the reason why diluted, or extremely diluted, actinide chemistry is so closely linked to radiochemistry.

Of course, many nuclide, radioactive or not, also exist in very low amount, but as most of the actinide isotopes are  $\alpha$ -emitters, they can be more specifically detected. Furthermore, as actinides display numerous oxidation states, their chemistry is very rich and so far many examples of chemical reactions can be found.

Finally we can note here that the last steps of radioactive matter lead to transitional situations where  $N$  is below some hundreds

Considerations on such systems of extreme high dilution have only a meaning if we can observe them. So, the first point we have to clarify is to define what are observable chemical reactions in the perspective of our purpose.

Observable chemical reactions including minute amount of a given radionuclide can be defined with reference to the following terms :

- . T half-life of the radionuclide,
- . t time given to reactifs to compete,
- .  $\tau$  half-life of equilibrium or steady state chemical reaction,
- .  $\Delta t$  time of collecting data,
- . Class of reactions labelled according t values,
- . Pathway of reactions between micro-macro components.

First of all, it is clear that a reaction will be generally observable if :

$$T > t > \tau > \Delta t$$

Class reaction could be labelled on the following qualitative basis :

If t is in the range of hours, days or year, the A class reactions belong to made man or natural chemistry. If t is very above several years or thousand years, the B class reactions belong to natural earth or space chemistry (fig. 3).

When  $N < 100$ , a given nuclide or radionuclide (or several ones) must be classified as microcomponent : m. Each other element M, such as  $N_M \gg N_m$  is a macrocomponent and watever could arise during the reaction,  $N_M$  remains constant. All the chemical reactions between species of the  $m_i$  or  $M_i$  are going through three pathways type according to micro-macro interactions (fig. 3).

Type 1 :  $m_i + m_j$   
 Type 2 :  $M_i + M_j$   
 Type 3 :  $m_i + M_i$  or  $m_j + M_i$ .

Now, we are in position to characterize observable reactions when  $N_m$  is very low.

. Reactions 1A are not observable due to kinetic hindrance,

. Reactions 1B are observable because the previous kinetic hindrance does not exist. When  $m_i$  or  $m_j$ , or both, are radioactive, the collection of data can be supported by system of normal extension. Otherwise(space chemistry), we have to look at very extented system. Important parameters are the  $N_{m_i}$  for 1B reactions.

. Reactions 2A and 2B, which belong to classical chemistry are outside the scope of this paper.

. Reaction 3A and 3B are observable because they are generally kinetically allowed. Observations must bear on the radioactive or not  $m_i$  because, as it was said before, all the  $N_{M_i}$  are constant. Some considerations regarding the spatial extension of the system as the previous ones are still valid. An important parameter is  $\tau$  value for these reactions.

The Fig. 4 gives some examples of 1B, 3A, 3B actinide reactions.

Another point which is important for the following, is the value of the stoichiometric coefficients of the species in which microcomponent are involved :  $v_k(m_i)$ . There are two

categories : the one by one reactions and the others. The one by one reactions will be characterized by all the  $\nu_k(m_j)$  equal to one. We shall see that they fall in a special case. When  $N = 1$ , all the observable reactions belong, of course, to a one by one type.

When  $N_m < 100$ , we cannot consider the number of a given  $m$  species :  $E(m)$  as a continuous variable and consequently :

- we cannot use Stirling approximation to express the partition function  $Z$  of all the  $E(m)$ ,
- we cannot derivate  $Z$  with respect to  $N_{E(m)}$  to get the chemical potential of the  $E(m)$ .

So, as we cannot define the equilibrium of the  $E_j(m_j)$  and the  $E_j(M_j)$  through the chemical potential of the  $E_j(m_j)$ , the main question which arise is : is the law of mass action still working in ultra diluted system ?

To answer this question, first of all, it is necessary to realize that with very low values of a kind of species in which  $m$  can appear,  $E(m)$ , what is significant is the average value of the number of  $N_{E(m)}$  :  $\overline{N}_{E(m)}$ .

We know that :

$$\overline{N}_{E(m)} = \sum P_{N_m} N_{E(m)}$$

where  $P_{N_m}$  is the probability of the existence of  $E(m)$  which depends on  $N_m$ . The  $N_{E(m)}$  discrete values, of course, cannot go over  $N_m$ .

We also know that the limiting value of  $\overline{N}_{E(m)}$  is quickly equal to  $N_{E(m)}$  when  $N_{E(m)}$  takes continuous values over several hundreds.

So, to check if the law of the mass action can apply when the  $N_{m_i}$  are low, we have :

- 1) to calculate all the  $\overline{N}_{E_j(m_j)}$  values according to :

$$\overline{N}_{E_j(m_j)} = \sum P_N N_{E_j(m_j)}$$

$P_N$  being the probability of the realization of the system defined according to partition function of all the  $N_{m_i}$ ,  $N_{M_i}$  species of the system. The summation runs over all the discrete values of the  $N_{E_j(m_j)}$  allowed by the stoichiometric coefficients of the reaction and the  $N_{m_i}$  values. Of course  $\overline{N}_{E_j(M_j)} = N_{E_j(M_j)}$ .

- 2) to evaluate the deviation, if any, between the results given by the expression of the law of mass action expressed with the  $N_{E_j(m_j)}$  and those given by the limiting expression of the law of mass action expressed for the situation for which  $N_{E_j(m_j)}$  is far above several hundreds, that is to say the classical situation of application of the law of mass action. To do this, it is convenient to introduce the ratio of the  $K$  and the classical equilibrium constant  $K$  values given by the former and later expression of the law of mass action. It is clear that the limiting value of  $\rho$  is the unity as the  $N_{m_i}$  increases.

The general expression of  $P_N$  is (3) :

$$P_N = \frac{Z_0}{Z} Z(\text{TVN})$$

with :

$$Z(\text{TVN}) = \prod_{ji} \left[ \frac{z_{E_j(m_i)}^{(T)} V}{\Gamma_{E_j(m_i)}} \right]^{N_{E_j(m_i)}} \frac{1}{N_{E_j(m_i)}!}$$

and :

$$N = \sum_j \sum_i N_{E_j(m_i)}$$

- $Z_0$  is the partition function of all the  $E_j(M_i)$ ,
- $Z(\text{TVN})$  is the partition function of all the  $E_j(m_i)$ ,
- $Z$  is the partition function of all the species ; it is a factor of normalization,
- $z_{E_j(m_i)}^{(T)} V$  is the partition function of a  $E_j(m_i)$  in a gaseous phase of a volume  $V$ ,
- $\Gamma_{E_j(m_i)}$  is a characteristic coefficient of a  $E_j(m_i)$  in the system.

There is no general expression of  $\rho$ . Each one depends on the stoichiometry of the reaction as we shall see later.

Computation of all the  $\overline{N_{E_j(m_i)}}$  and  $\rho$  values for all the  $N_{E_j(m_i)}$  values are easily done with the help of a computation programme, or need it.

The general results we got for close systems are the following ones.

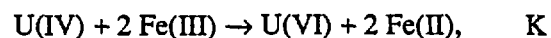
For one by one reactions,  $\rho$  is independent of  $N$  and of the equilibrium constant  $K$  values. That means that law of mass action holds without restriction when  $N$  is very low and, even when  $N = 1$ , to predict the behaviour of matter in state of extreme dilution.

For other reactions, variation of  $\rho$  versus  $N$ , first depends on  $N$  and equilibrium constant values  $K$ , and then reaches a constant unity value as  $N$  increases. That means that deviations from the classical law of mass action can occurs. So, the behaviour of some species in very few amount could be different of the predicted behaviour from classical law of mass action.

We shall give two simple examples to illustrate that general and important results.

#### One by one reaction.

Let be the reaction :



with U as microcomponent.

The classical equilibrium constant K is a function of pH. It is obvious that  $E_1(U) = U(IV)$ ,  $E_2(U) = U(VI)$ . For the sake of simplicity, we can label all the previous introduced symbols which refer to U(IV) and U(VI) with subscripts 1 and 2.

If the advance of the reaction,  $i$ , is measured by  $N_2$ , the probability that  $i$  species of U(VI) and  $N-i$  species of U(IV) coexist is :

$$P_N^{(i)} = P_i = \frac{Z_0}{Z} \left( \frac{z_1 V}{\Gamma_1} \right)^N \left( \frac{z_2 \Gamma_1}{z_1 \Gamma_2} \right)^i \frac{1}{(N-i)! i!}$$

which, with :

$$k = \frac{Z_0}{Z} \left( \frac{z_1 V}{\Gamma_1} \right)^N \quad \chi = \frac{z_2 \Gamma_1}{z_1 \Gamma_2} \quad \theta_i = \frac{\chi^i}{(N-i)! i!}$$

transforms to :

$$P_i = k \theta_i$$

As :

$$\sum_{i=1}^N P_i = 1$$

we have :

$$k = \frac{1}{\sum_{i=1}^N \theta_i} = \frac{1}{S}$$

So :

$$S \bar{N}_1 = \sum_{i=0}^N (N-i) \theta_i$$

$$S \bar{N}_1 = \sum_{i=0}^N i \theta_i$$

$$S \bar{N}_1 = \frac{1}{(N-1)!} + \frac{\chi}{(N-2)!} + \frac{\chi^2}{(N-3)!2!} + \dots + \frac{\chi^{N-1}}{(N-1)!}$$

$$S \bar{N}_2 = \frac{\chi}{(N-1)!} + \frac{\chi^2}{(N-2)!} + \frac{\chi^3}{(N-3)!2!} + \dots + \frac{\chi^N}{(N-1)!}$$

and :

$$\frac{\overline{N_2}}{\overline{N_1}} = \chi$$

It follows :

$$\overline{K} = \frac{[N_{Fe(II)}]^2}{[N_{Fe(III)}]^2} \chi$$

When N ( $N_2$  and  $N_1$ ) increases,  $P_i$  and  $P_{i-1}$  comes closer and closer and the limiting values of :

$$\frac{P_i}{P_{i-1}} = \chi \frac{N-i+1}{i}$$

is unity, so :

$$\chi = \frac{i}{N-i} = \frac{N_2}{N_1}$$

and we have :

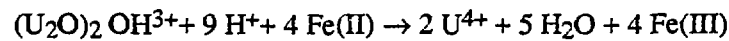
$$K = \frac{[N_{Fe(II)}]^2}{[N_{Fe(III)}]^2} \chi$$

which leads to :

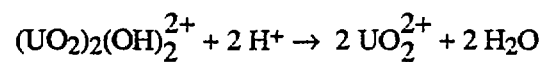
$$\rho = 1$$

#### Other type reactions.

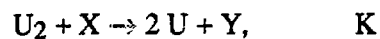
Let be with U as microcomponent the reactions :



and



which belong to the general process :



K depending on the pH and on the constant ratio of macrocomponents X and Y. As we have done above, we shall labell all the symbols which refer to the monomeric species with subscript 2 and those of the dimeric species with subscript 1. When the advancement of the reaction is i there are  $N_2 = 2 i$  monomeric species and  $N_1 = \frac{N}{2} - i$  dimeric one. The probability of realization of such state is :



$$P_N^{(i)} = P_i = \frac{Z_0}{Z} \left( \frac{z_1 V}{\Gamma_1} \right)^{N/2} \left( \frac{z_2^2 V \Gamma_1}{z_1 \Gamma_2} \right)^i \frac{1}{\left( \frac{N}{2} - i \right)! 2i!}$$

which, with :

$$k = \frac{Z_0}{Z} \left( \frac{z_1 V}{\Gamma_1} \right)^{N/2} \quad \chi = \left( \frac{z_2^2 V \Gamma_1}{z_1 \Gamma_2} \right) \quad \theta_i = \frac{\chi^i}{\left( \frac{N}{2} - i \right)! 2i!}$$

transforms, after normalization, to :

$$P_i = \frac{\theta_i}{S}$$

with

$$S = \sum_{i=1}^N \theta_i$$

The average values of  $N_1$  and  $N_2$  are given by :

$$S N_1 = \frac{1}{\left( \frac{N}{2} - 1 \right)!} + \frac{\chi}{\left( \frac{N}{2} - 2 \right)!} + \frac{\chi^2}{\left( \frac{N}{2} - 3 \right)! 2!} + \dots + \frac{\chi^{N-1}}{\left( \frac{N}{2} - 1 \right)!}$$

$$S N_2 = \frac{\chi}{\left( \frac{N}{2} - 1 \right)!} + \frac{\chi^2}{\left( \frac{N}{2} - 2 \right)! 3!} + \frac{\chi^3}{\left( \frac{N}{2} - 3 \right)! 5!} + \dots + \frac{\chi^N}{\left( \frac{N}{2} - 1 \right)!}$$

There is no more simple relation between average values of  $N_1$  and  $N_2$ .

To calculate  $\overline{N_1}$  and  $\overline{N_2}$ , we need to know the meaning of  $\chi$ . It is easy to find it in the following way.

When  $N$  increases the limiting values of :

$$\frac{P_i}{P_{i-1}} = \chi \frac{\frac{N}{2} - i + 1}{2i(2i-1)}$$

is, as we have seen, the unity. So :

$$\chi = \frac{(2i)^2}{\frac{N}{2} - i} = \frac{N_2^2}{N_2}$$

and  $\chi$  can be linked to K through the classical law of mass action :

$$\chi = K \frac{[X]}{[Y]} = K'$$

We see that :

$$\bar{K} = \frac{[X]}{[Y]} \frac{N_2^2}{N_1}$$

is a quite complicated function of K' or K as  $\rho$  is.

The figures 5 and 6 give the results of computer calculations for :

$$[X] = [Y]$$

that is to say for :

$$\chi = K.$$

They show the variations of :

$$\rho = \frac{N_2^2}{N_1 K}$$

versus N for different K values.

It is clear from these figures, that the behaviour of very few dimeric species of U(VI), appearing for instance after an instantaneous very high dilution of a concentrated uranium solution, is different as the predicted one by the classical law of mass action.

In conclusion, as actinides can be detected at very high dilution and, as they have a very rich chemistry due to their numerous oxidation state, we have to be very careful in interpreting the data obtained in that conditions to identify oxidation states and species.

The data come very frequently from partition experiments. So, we have to check if corrections have to be done to take into account deviations from the prediction given by the law of mass action applied both to the reactions which run in the initial system and the two phase partition systems. Moreover, we do not forget that partition experiments could disturb the true initial system (2).

Actinide chemistry as a function of concentration down to high dilution, when suitable isotopes are available, has to be deeply investigated for many reasons, but also in order to get fundamental and general information about the behaviour of matter in very few amount.

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Figure 1

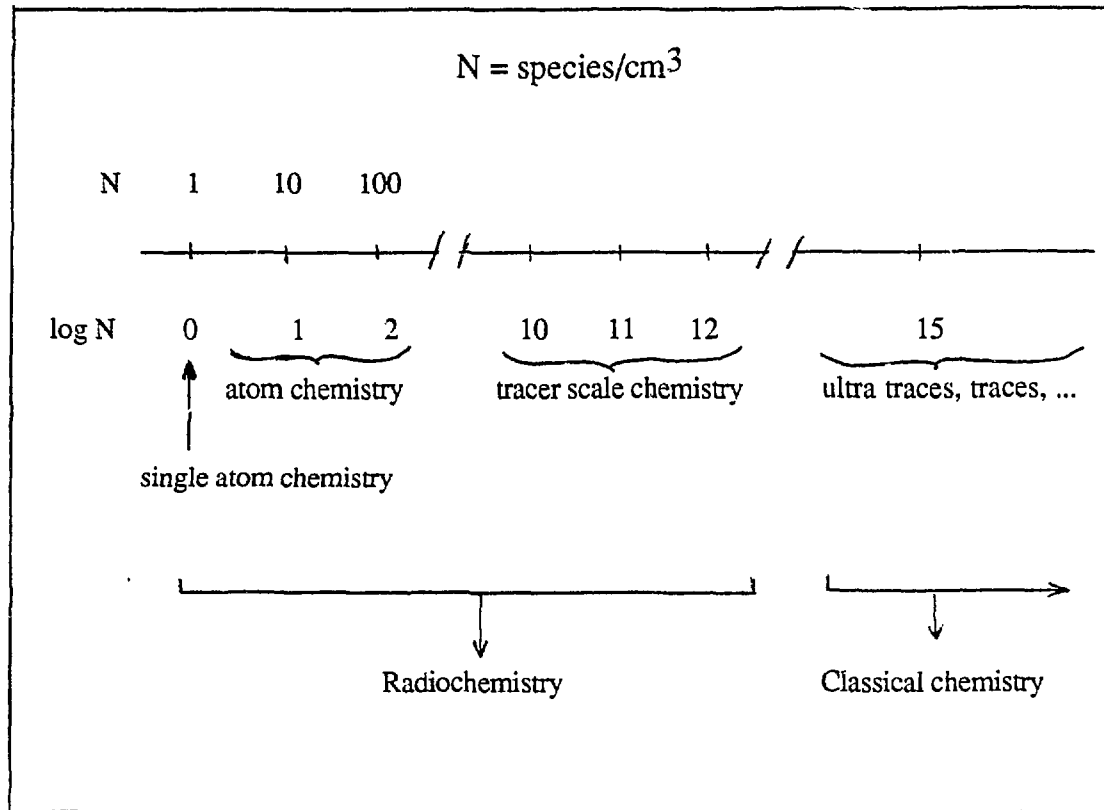


Figure 2

Usual case of actinides in minute amount

- Actinides of nuclear fuel cycle in hydrosphere, geosphere, biosphere,
- Actinides of nuclear fuel cycle in living material,
- Heavy actinides in laboratory experiments,
- Transactinides in laboratory experiments.

Figure 3

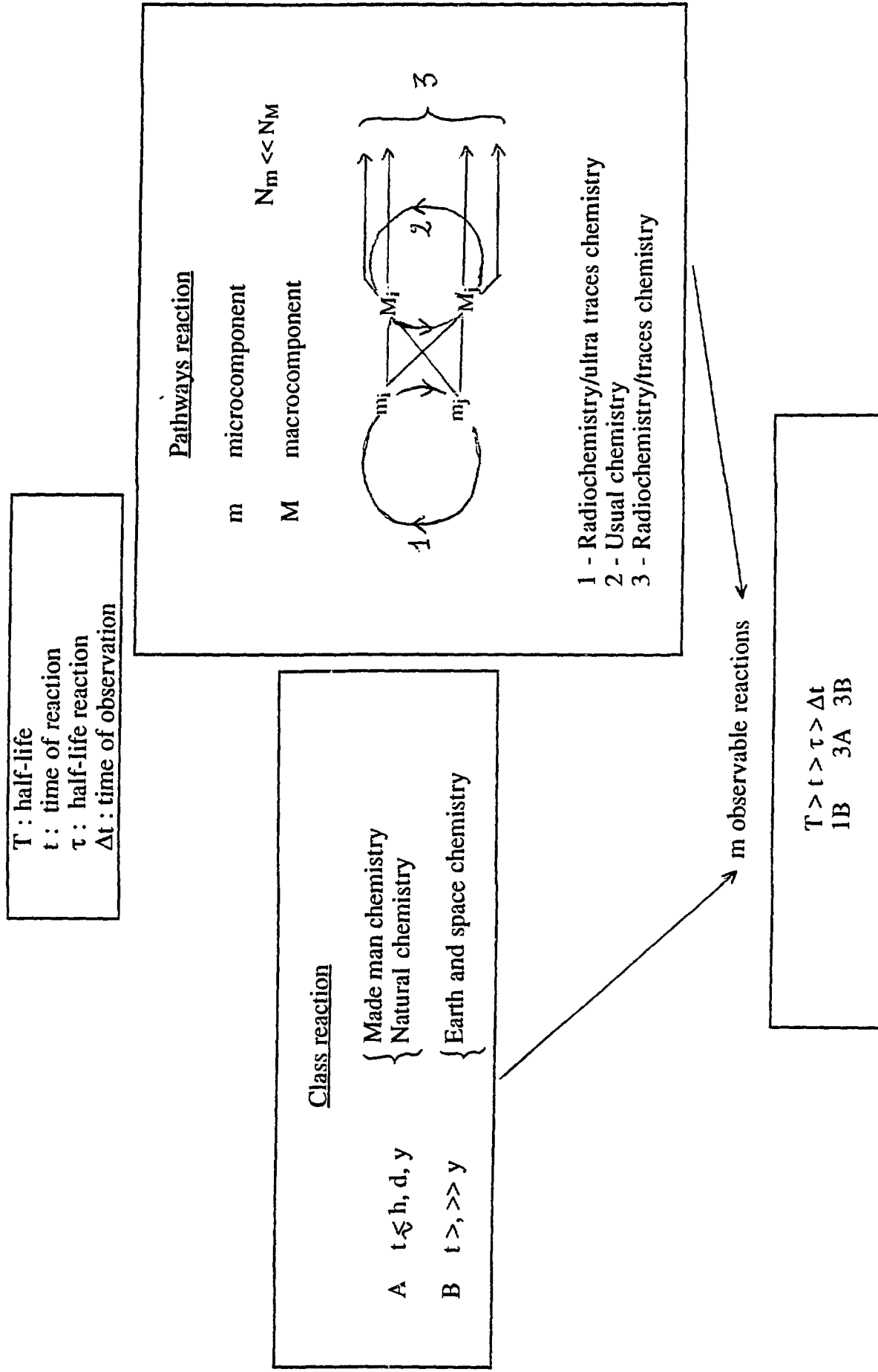
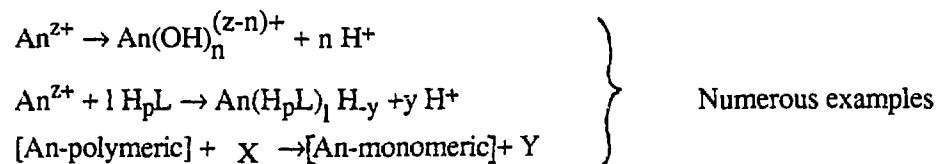


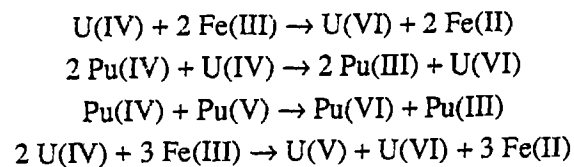
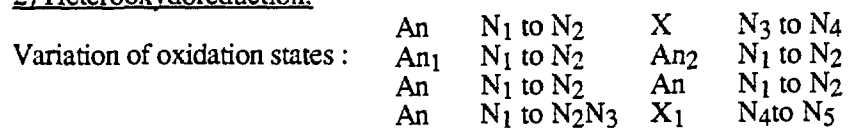
Figure 4

An = actinide      X, Y, ... = other micro/macroelement

1) Acid base type :

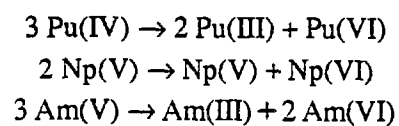


2) Heterooxydoreduction.



3) Autooxydoreduction :

Variation of oxidation state : An N<sub>1</sub> to N<sub>2</sub> N<sub>3</sub>



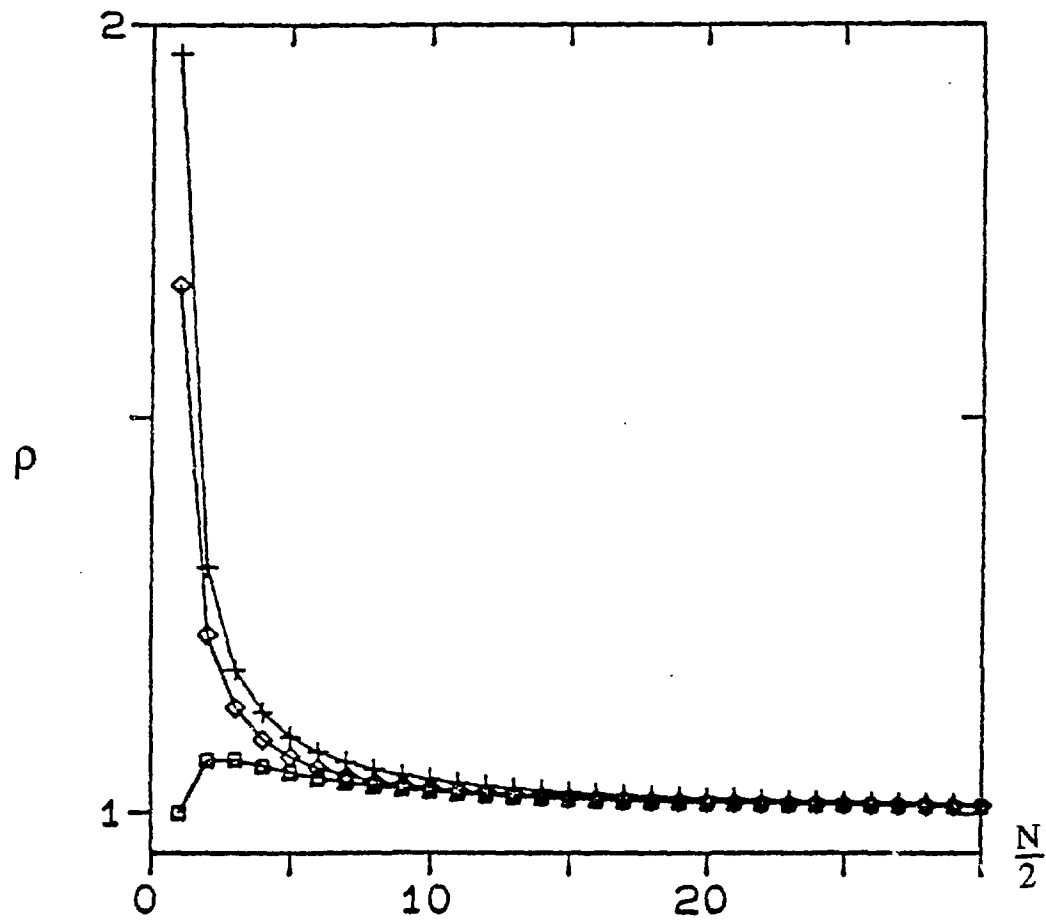
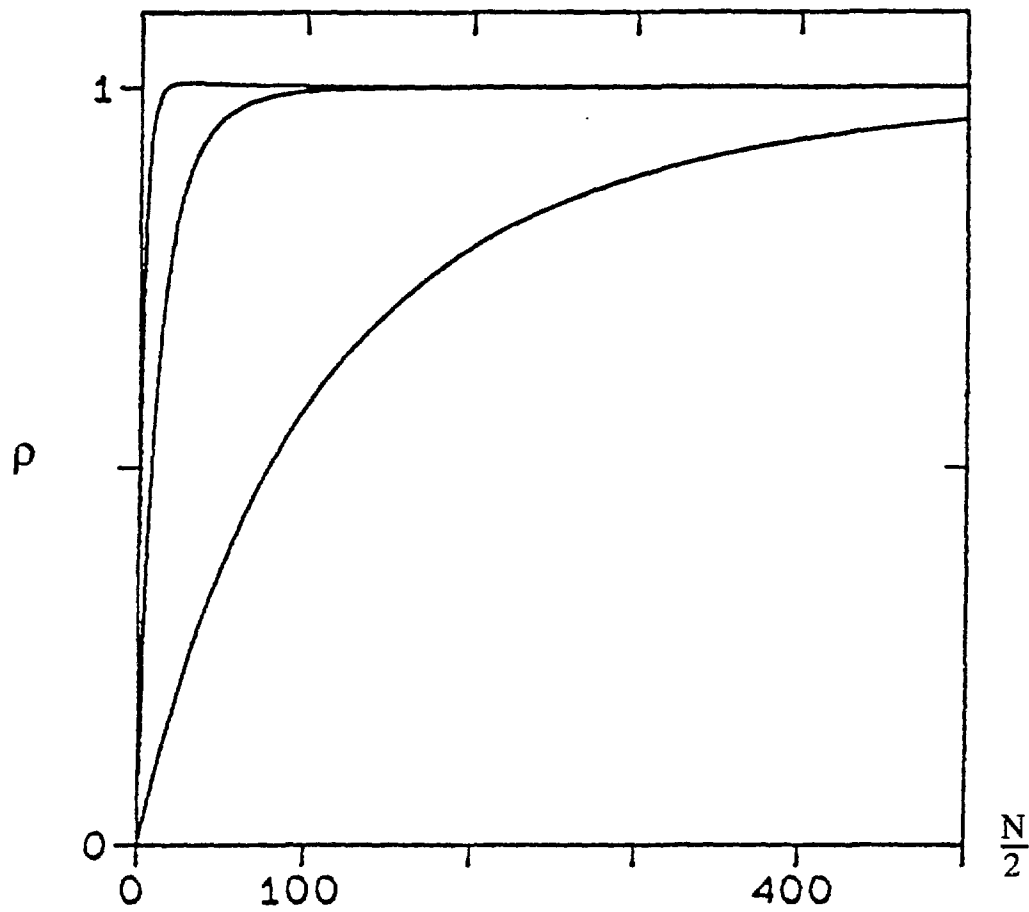


Fig. 5: Variation of  $\rho$  as a function of  $N$  (see the text).  $K$  values are equal to  $10^2$ , 10 and 2 from up. to down





**Fig. 6:** Variation of  $\rho$  as a function of  $N$  (see the text)  $K$  values are equal to  $5 \cdot 10^{-1}$ ,  $10^{-1}$  and  $10^{-2}$  from up to down.