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भारत सरकार
GOVERNMENT OF INDIA
परमाणु ऊर्जा आयोग
ATOMIC ENERGY COMMISSION

DEUTERIUM EXCHANGE BETWEEN LIQUID WATER
AND GASEOUS HYDROGEN

by

S. M. Dave, S. K. Ghosh and H. K. Sadhukhan
Heavy Water Division

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ABSTRACT

The overall separation factors for the deuterium exchange between liquid water and gaseous hydrogen have been calculated over a wide range of temperatures, pressures and deuterium concentrations. These data would be useful in the design and other considerations for heavy water production, based on hydrogen-water exchange.

INIS Subject Category : B 12; D 12

Descriptors

WATER

HYDROGEN

DEUTERIUM

ISOTOPIC EXCHANGE

ISOTOPE SEPARATION

HUMIDITY

SOLUBILITY

QUANTITY RATIO

THEORETICAL DATA

MEDIUM TEMPERATURE

HIGH TEMPERATURE

MEDIUM PRESSURE

HIGH PRESSURE

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1. INTRODUCTION

Hydrogen-water exchange has remained a continuing fascination for heavy water production and there has always been considerable interest in this process because of its many attractive features, such as

- (1) High separation Factors and hence higher recovery, smaller plant volume, lower liquid and gas flows etc.,
- (2) Non-toxic, non-corrosive materials and hence no pollution problems and other hazards,
- (3) Water being the feed material, plant capacity can be increased substantially, thereby leading to overall reduction in the cost of heavy water produced.

However, all the advantages listed above are offset by a single, obstinate fact that the exchange does not proceed spontaneously without a catalyst, and to date no catalyst has emerged or developed which can effectively reduce the cost of heavy water production, so that this process can become competitive with other established methods such as GS and ammonia-hydrogen processes. (1,2)

The interest in this exchange dates back to 1943 and the hydrogen-steam exchange has the distinction of being the first process selected for the commercial development by the Manhattan District and the plant having a capacity of 6 tonnes/year was built at Trail, B.C., Canada^(3,4). Platinum on activated charcoal and nickel on chromium oxide were used as catalysts and the reflux to the exchange column was provided by electrolysis of the enriched water.

For this exchange both types of catalysts - heterogeneous and homogeneous - have been developed and tried by many workers during the last two decades. A brief outline of all these efforts is given below :

Heterogeneous Catalysts

Platinum on charcoal⁽⁵⁾, platinum on alumina⁽⁶⁾, nickel on chromium oxide⁽⁷⁾, colloidal platinum⁽⁷⁾, palladium on charcoal⁽⁸⁾, etc. have been found to catalyse the deuterium exchange between hydrogen and water. The platinum catalysts have been found to give best transfer rates. However, these catalysts lose much of their activity in contact with liquid water and the catalyst inventory becomes prohibitive⁽⁸⁾.

The mass transfer rate depends on⁽⁹⁾

- (1) diffusion of dissolved hydrogen from the gas-liquid interface to the bulk of liquid, and

(3)

(11) diffusion of hydrogen from the bulk to the catalyst surface.

Both the above steps are functions of hydrogen solubility⁽¹⁰⁾ in water which is extremely low (compare - at 200 atms and 25°C, the solubility of hydrogen in water is 0.15 moles/litre while the corresponding solubilities of hydrogen in liquid ammonia (-43°C) is 0.20 moles/litre and in liquid methylamine (-53°C) is 0.48 moles/litre respectively. Thus, even if a very efficient catalyst is developed, the mass transfer rate will be limited.

Recently a new version of the platinum catalyst has been developed; the catalyst consists of highly dispersed platinum metal deposited on activated charcoal and the entire catalyst body is coated with a very thin layer of water repellent material such as teflon etc. The hydrophobic coating helps in reducing the poisoning of the catalyst to a very considerable extent⁽¹¹⁾. A more successful approach has been to deposit platinum on a high surface-area activated charcoal and to bond the platinized charcoal to a variety of column packings by using teflon as both water-proofing and bonding agent⁽¹¹⁾.

Homogeneous Catalysts

The fundamental limitation cited above can be overcome if a homogeneous catalyst is used. In this case, the mass transfer rate is limited by the chemical reaction rate.

It has been observed that many bases such as hydrazine, potassium and sodium hydroxides etc. act as catalyst for deuterium transfer between water and hydrogen^(12,15). The exchange rates are proportional to hydrogen pressure (upto 100 Bar) and increases with increasing hydroxide concentrations. The exchange rates become too slow, below 1% hydroxide concentrations^(16,17). Increasing temperatures and catalyst concentration are not practicable because of highly corrosive nature of alkali solutions.

It has been reported that some transition metal complexes^(14,18) such as ruthenium chloride and cobalt cyanide complexes act as catalyst for this exchange but here also, the exchange rates are not encouraging and the catalyst inventory and catalyst recovery cost become quite prohibitive.

It is possible to combine this catalytic exchange of hydrogen - water (with these improved catalysts) with electrolysis of the enriched water to provide reflux. This process is known as combined Electrolysis and

Catalytic Exchange (CECE)⁽¹⁹⁾. This CECE process combines both - the equilibrium isotope effect in the exchange reaction between liquid water and gaseous hydrogen and the kinetic isotope effect inherent in the electrolytic hydrogen evolution reaction. The two large separation factors are thus combined and this does lead to many advantages. CECE process can be quite competitive or rather it could provide a better route to heavy water production if a market for electrolytic hydrogen can be found⁽²⁾. Electrolytic hydrogen is expensive, but with ever escalating cost of fossil fuel and with increased prospects of using liquid hydrogen as fuel in daily life, the outlook for this process does not look discouraging. It does hold promise.

One of the most important parameters in determining the feasibility of an exchange process is its separation factor which is defined as the degree of enrichment obtainable in a single equilibrium contact. The separation factor determines not only the plant design and process characteristics but also affect the operating cost of the isotope separation plant. Although the deuterium separation factors for the water-hydrogen system have been calculated and measured by many workers, the measured values have been restricted to a narrow

range of experimental conditions, viz. temperature and pressure etc., while the calculations have been mainly restricted to the case of gas phase reactions in low deuterium concentration range only.

However, in practice, in order to establish an effective countercurrent flow for achieving the concentration build-up of the desired isotope, water must be kept in the liquid phase and gradually the deuterium concentration builds up in water phase. It is the purpose of the present work to report a detailed theoretical investigation of the separation factors for this process over a wide range of temperature, pressure and deuterium concentrations for both gas-gas and liquid-gas exchanges.

2. THEORY

The separation factor, α , which denotes the degree of separation achieved when gaseous hydrogen and water vapour are in equilibrium can be represented as

$$\alpha = \frac{X/(1-X)}{Y/(1-Y)} \quad \dots (1)$$

Where X and Y denote the deuterium atom fractions in water and hydrogen respectively and can be expressed as

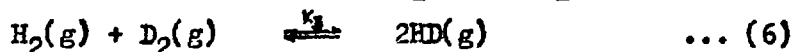
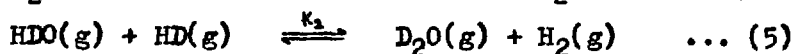
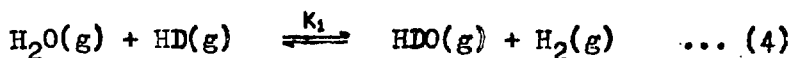
$$X = \frac{\frac{1}{2} [\text{HDO}] + [\text{D}_2\text{O}]}{[\text{H}_2\text{O}] + [\text{HDO}] + [\text{D}_2\text{O}]}, \quad \dots (2)$$

(7)

$$\text{and } Y = \frac{\frac{1}{2} [\text{HD}] + [\text{D}_2]}{[\text{H}_2] + [\text{HD}] + [\text{D}_2]} \quad \dots (3)$$

Here the bracketed quantities denote the atom fractions of different species in the mixture.

In a mixture of gaseous hydrogen and water vapour, the following chemical exchange equilibria exist :



The overall separation factor, α , can be evaluated as a function of either X , the deuterium fraction in water, or Y , the deuterium fraction in hydrogen. These separation factors can be expressed as^(20,21)

$$\alpha_x = \frac{(K_1 + 2K_2A)(2K_1 + A)}{(A + 2)(K_1 + 2A/K_3)} \quad \dots (7)$$

$$\text{and } \alpha_y = \frac{(K_1 + 2K_1K_2B)(B+2)}{(K_1B + 2)(1+2B/K_3)} \quad \dots (8)$$

Where K_1 , K_2 and K_3 are the equilibrium constants and A and B can be expressed as

$$A = \frac{[\text{HDO}]}{[\text{H}_2\text{O}]} = \frac{(2x-1) \pm \left[(1-2x)^2 + 16x(1-x)K_2/K_1 \right]^{\frac{1}{2}}}{4 K_2(1-x)/K_1} \quad \dots (9)$$

(8)

$$\text{and } B = \frac{[\text{HD}]}{[\text{H}_2]} = \frac{(2Y-1) \pm \left[(1-2Y)^2 + 16Y(1-Y)/K_3 \right]^{\frac{1}{2}}}{4(1-Y)/K_3} \dots (10)$$

Thus, one can evaluate the separation factors from a knowledge of equilibrium constants. The deuterium concentrations X and Y can be varied from their natural abundance of 10^{-4} to 0.99 atom fractions. At low deuterium concentrations, both X and Y become equal to K_1 .

So far, only the gas-phase separation factor, α , has been considered. In actual practice, however, it is the separation factor, β , for the liquid-gas exchange which is more important. The magnitude of β will depend on several factors viz. the solubility of hydrogen in water, entrapment of water vapour in hydrogen known as humidity, the vapour pressure ratios of the different isotopic water molecules and the gas phase equilibrium constants of different exchange reactions.

For an equilibrium between gaseous hydrogen and liquid water, the separation factor, β , is defined as the ratio of deuterium fractions in liquid and gas phases and is given by

$$\beta = \frac{(\text{D/H})_{\text{liq.}}}{(\text{D/H})_{\text{gas}}} \dots (11)$$

β can be expressed explicitly as^(1,22)

$$\beta = \frac{P_2[S + \{X_D + K_1(1 - X_D)\}][K_1S \{X_D + P_2K_1(1 - X_D)\} + HS\{X_D + P_2(1 - X_D)\} \{X_D + K_1(1 - X_D)\}^2]}{[K_1S + \{X_D + K_1(1 - X_D)\}][S\{X_D + P_2K_1(1 - X_D)\} + HS\{X_D + P_2(1 - X_D)\} \{X_D + K_1(1 - X_D)\}^2]} \dots$$

Where P_2 is the relative volatility of HDO i.e., the ratio of vapour pressures of HDO and H_2O , H is the humidity which represents the ratio of the moles of water to those of hydrogen in the gas phase; S is the solubility expressed as the moles of gas dissolved per mole of liquid and X_D is the deuterium atom fraction in the liquid phase.

For very low deuterium concentration, $X_D \approx 0$ and the expression of β simplifies to

$$\beta = \frac{P_2(S + K_1)(1 + H)}{(1 + K_1)(1 + S)}, \quad \dots (13)$$

while for high deuterium concentration, $X_D \approx 1$ and becomes

$$\beta = \frac{P_2(H + K_1)(1 + S)}{(1 + K_1)(1 + H)}. \quad \dots (14)$$

3. METHOD OF CALCULATION

The separation factors α and β can be calculated from the knowledge of the equilibrium constants for the exchange reactions (4) - (6). The latter can be calculated theo-

(10)

retically through the evaluation of the reduced partition function (RPF) ratios for different isotopic pairs. The equilibrium constant, K, of an isotopic exchange reaction, say,



where the primed species refers to the species containing lighter isotope, can thus be expressed as^(22,23)

$$K = \frac{[S/S', f \{A/A'\}] (\sigma_B'/\sigma_{B'})}{[S/S', f \{B/B'\}] (\sigma_A'/\sigma_A)} \quad \dots (16)$$

Here $[S/S', f \{X/X'\}]$ refers to the RPF ratio for the isotopic pair X and D' and σ_X denotes the symmetry number of the molecule X. The RPF ratio consists of vibrational and rotational contributions. Thus, Eq. (16) becomes

$$K = \frac{[S/S', f \{A/A'\}]_{\text{vib.}}}{[S/S', f \{B/B'\}]_{\text{vib.}}} \frac{[S/S', f \{A/A'\}]_{\text{rot.}}}{[S/S', f \{B/B'\}]_{\text{rot.}}} \frac{(\sigma_B'/\sigma_{B'})}{(\sigma_A'/\sigma_A)} \quad \dots (17)$$

The vibrational contribution to RPF ratio can be calculated from the knowledge of the vibrational frequencies, using the relation

$$\left[\frac{S/S', f \{A/A'\}}{S/S', f \{B/B'\}} \right]_{\text{vib.}} = e^{-(Z_A - Z_{A'})/kT} \prod_{i=1}^{3N-6} \left\{ \frac{u_i/(1 - e^{-u_i})}{u_i'/(1 - e^{-u_i'})} \right\} \dots (18)$$

where Z_A and $Z_{A'}$ are the zero-point energies of A and A' respectively and u_i is related to the i th vibrational frequency ν_i by the expression

$$u_i = \frac{hc \nu_i}{kT} = 1.4385 \nu_i / T. \quad \dots (19)$$

The rotational contribution to the RPF for water molecule can be calculated from the values of the rotational constants A, B and C, using the relation

$$\left[\frac{S}{S'} f(X) \right]_{\text{rot}} = 1 + (BC)^{\frac{1}{2}} \left[1 - \frac{(BC)^{\frac{1}{2}}}{A} \right] \frac{hc}{kT} \quad \dots (20)$$

Here X refers to H_2O , HDO or D_2O .

The rotational RPF ratio for hydrogen molecules is given by the relation

$$\left[\frac{S}{S'} f(A/A') \right]_{\text{rot.}} = 1 + \frac{(\delta - \delta')}{9} + \frac{(\delta - \delta')^2}{9} \quad \dots (21)$$

where $\delta = h^2 / 8\pi^2 I kT$ and I is the moment of inertia. Here δ corresponds to the isotopic species A and δ' to A'.

The vibrational frequencies to be used in Eq. (18) for the calculation of vibrational RPF ratio should be harmonic frequencies which can be calculated from a knowledge of the experimentally observed spectroscopic frequencies either through the use of force field calculations or by using the Dennison's rule. According to Dennison's rule, the harmonic and the observed frequencies are related by

$$\nu_i = \omega_i (1 - x_i), \quad \dots (22)$$

where ω_i is the i th harmonic frequency and x_i is the anharmonicity constant. Thus, using the data on x_i , one can calculate ω_i values. The values of x_i for stretching and bending vibrations of O-H and H-H bonds are respectively :

$$x_{\nu_{\text{O-H}}} = 0.04, \quad x_{\delta_{\text{O-H}}} = 0.02, \quad \text{and} \quad x_{\nu_{\text{H-H}}} = 0.04.$$

The zero-point energy should, however, be corrected for the anharmonicity of vibrations. Thus, the anharmonic correction is to be added to the harmonic frequencies, calculated by using Dennison's rule.

Using these values, the equilibrium constants for different reactions can be calculated.

The harmonic vibrational frequencies of water as well as hydrogen molecules have been calculated using Dennison's rule from the reported frequencies^(24,25) and are given in Tables 1 and 2 respectively. The anharmonicity corrections, G_0 to the zero-point energy values have also been included. The rotational constants have been reported in Table 3.

The vapour pressure (vp) ratios of the isotopic water molecules have been measured by many workers^(26,27).

Expressions have also been derived for vp ratio by fitting the experimental data.

We have used the following equation derived from the result of Jones⁽²⁷⁾.

$$\ln \frac{P_{\text{HDO}}}{P_{\text{H}_2\text{O}}} = \frac{35}{T} - \frac{16815}{T^2} \quad \dots (23)$$

The vapour pressure of water, P_w , has been calculated using the following set of equations proposed by Bridgeman and Aldrich⁽²⁸⁾. Thus,

$$\log P_w(\text{atm}) = A + Y_1 - B(1 + Ct)Y_2, \quad \dots (24)$$

where $Y_1 = D(t-187)/(t+E)$,

$$100 Y_2 = \frac{3\sqrt{3}}{2 \times 1.87^3} (X - 0.01\alpha) \{1.87^2 - (X - 0.01\alpha)^2\},$$

$$X = 0.01(t-187),$$

$$\alpha = Z^2(1.87^2 - Z^2)/F(1 + Gt),$$

$$Z = -1.87 + 3.74\{H - K \cosh^{-1} L/(t+M)\},$$

with	$A = 1.06423320$	$G = 3.377565 \times 10^{-3}$
	$B = 1.0137921$	$H = 1.152894$
	$C = 5.83531 \times 10^{-4}$	$K = 0.745794$
	$D = 4.16385282$	$L = 654.2906$
	$E = 237.098157$	$M = 266.778$
	$F = 0.30231574$	

The vapour pressure values have been used to evaluate the humidity at the desired temperature and a total pressure P by the relation

$$H = \frac{P_w}{P - P_w} \quad \dots (25)$$

The humidity, H, calculated have been given in Table 4. The solubility of Hydrogen gas in water over a wide range of temperature and pressures has been reported by Pray et.al⁽²⁰⁾. From their graphs, the solubility values have been calculated at the desired temperatures and pressures. The solubility data have been presented in Table 5.

4. RESULT AND DISCUSSION

The equilibrium constants for the three exchange reactions (Eqs. (4)-(6)) have been calculated and the values are reported in Table 6. The gas-phase separation factors α_x and α_y have been calculated as a function of temperature and the deuterium atom fractions x and y respectively. They are shown in Table 7 and 8. The overall separation factors have been evaluated as a function of temperature and pressure for a number of deuterium concentrations i.e. at several stages of enrichment. These values are given in Tables 9-12.

From the above tables, it can be seen that both the gas-gas and liquid-gas separation factors are highly dependent on temperature and they both decrease with increasing temperatures.

The dependence of α and β with deuterium concentration is not much pronounced, but, in general, they both

increase with increasing deuterium concentration.

The pressure dependence of β follows a somewhat less straight forward pattern. At lower temperatures, β increases with pressure, passes through a maximum and then decreases, while at higher temperatures, it increases very slowly.

Fig.1 shows the temperature dependence of the separation factors for water-hydrogen system for very low deuterium concentrations. This graph also incorporates the values of separation factors by other workers for the sake of comparison. It can be observed that our values are in good agreement with those reported by other workers.

5. CONCLUSION

This is the first time a systematic calculation of separation factors for liquid water-gaseous hydrogen has been carried out over a wide range of temperatures, pressures and deuterium concentrations. Such data will be very helpful in design calculations for heavy water plants based on this process.

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Table 1. Harmonic Vibrational Frequencies for Water

	H ₂ O	HDO	D ₂ O
ω_1	3825.0	2818.5	2557.9
ω_2	1653.8	1449.6	1212.2
ω_3	3953.8	3882.5	2883.5
G_0	-76.4	-58.6	-40.7

Table 2. Harmonic Vibrational frequencies for Hydrogen

	H ₂	HD	D ₂
ω_1	4405.3	3817.1	3117.9
G ₀	-21.0	-15.8	-10.5

Table 3. Rotational Constants for Water and Hydrogen

	H_2O	HDO	D_2O	H_2	HD	D_2
A	27.8778	14.5092	9.2869	-	-	-
B	23.3790	9.1020	6.4170	-	-	-
C	15.3846	7.2716	4.8458	-	-	-
Moment of Inertia	-	-	-	0.459	0.612	0.920

Table 4. Humidity in the saturated water vapour - Hydrogen mixture [(moles of H₂O per mole of H₂) × 10³]

Temp °C	Press atm	1	20	40	60	80	100	120	140
0		6.066	0.3017	0.1508	0.1005	0.0754	0.0603	0.0503	0.0431
20	23.60	1.154	0.5768	0.3843	0.2883	0.2306	0.1922	0.1647	
40	78.55	3.654	1.824	1.214	0.9103	0.7282	0.6068	0.5201	
60	244.9	9.933	4.918	3.278	2.459	1.967	1.639	1.405	
80	877.1	23.93	11.83	7.792	5.844	4.675	3.896	3.339	
100	-	52.63	25.64	16.95	12.66	10.10	8.403	7.194	
120	-	108.6	51.50	33.78	25.12	19.99	16.60	14.20	
140	-	217.1	97.89	63.20	46.66	36.98	30.63	26.14	
160	-	438.8	179.9	113.2	82.54	64.96	53.55	45.55	
180	-	979.8	328.8	197.5	141.2	109.8	89.88	76.07	
200	-	3301.0	622.6	343.7	237.4	181.3	146.7	123.1	
220	-	-	1339.0	617.2	401.0	297.0	235.8	195.5	
240	-	-	4747.0	1226.0	703.0	493.2	379.8	308.8	
260	-	-	-	3386.0	1375.0	863.0	628.7	494.5	
280	-	-	-	-	3805.0	1729.0	1118.0	826.5	
300	-	-	-	-	-	5575.0	2408.0	1876.0	

Table 4. (Contd.)

Temp °C \ Press atm	160	180	200	220	240	260	280	300
0	0.0377	0.0335	0.0302	0.0274	0.0251	0.0232	0.0215	0.0201
20	0.1441	0.1281	0.1153	0.1048	0.0961	0.0887	0.0824	0.0769
40	0.4551	0.4046	0.3641	0.3310	0.3034	0.2801	0.2601	0.2427
60	1.229	1.093	0.9835	0.8941	0.8196	0.7565	0.7025	0.6557
80	2.922	2.597	2.338	2.125	1.948	1.798	1.670	1.558
100	6.289	5.587	5.025	4.566	4.184	3.861	3.584	3.344
120	12.40	11.01	9.895	8.987	8.232	7.594	7.048	6.575
140	22.80	20.21	18.15	16.48	15.08	13.91	12.90	12.03
160	39.63	35.08	31.46	28.52	26.08	24.02	22.27	20.75
180	65.93	58.18	52.06	47.10	43.03	39.58	36.65	34.12
200	106.1	93.21	83.21	74.99	68.32	62.73	57.99	53.92
220	167.0	145.8	129.3	116.2	105.5	96.57	89.06	82.66
240	260.2	224.8	197.9	176.7	159.6	145.6	133.8	123.8
260	407.5	346.5	301.4	266.7	239.2	216.8	198.2	182.6
280	655.5	543.1	463.6	404.4	358.6	322.1	292.4	267.7
300	1127.0	890.6	736.0	627.1	546.3	483.9	434.4	394.0

Table 5. Solubility of Hydrogen in Water (ml(NTP) of dissolved H₂ per gram of H₂O)

Temp °C	Press. atm	1	20	40	60	80	100	120	140
0		0.0209	0.4199	0.8398	1.260	1.680	2.100	2.520	2.940
20		0.0201	0.4110	0.8220	1.234	1.645	2.057	2.468	2.879
40		0.0185	0.3983	0.7980	1.198	1.597	1.997	2.397	2.797
60		0.0148	0.3637	0.7309	1.098	1.466	1.833	2.200	2.567
80		0.0092	0.3372	0.6825	1.028	1.373	1.718	2.063	2.409
100		-	0.3249	0.6670	1.009	1.351	1.693	2.035	2.377
120		-	0.3114	0.6567	1.002	1.347	1.692	2.038	2.383
140		-	0.3017	0.6690	1.036	1.404	1.771	2.138	2.505
160		-	0.2780	0.6790	1.079	1.479	1.879	2.280	2.681
180		-	0.2450	0.7300	1.214	1.699	2.184	2.668	3.154
200		-	0.1229	0.6520	1.181	1.710	2.239	2.767	3.296
220		-	-	0.5650	1.226	1.887	2.548	3.209	3.870
240		-	-	0.3195	1.238	2.155	3.074	3.992	4.910
260		-	-	-	0.7940	1.954	3.115	4.276	5.436
280		-	-	-	-	1.113	2.449	3.786	5.123
300		-	-	-	-	-	1.313	3.040	4.766

Table 5. (Contd.)

Temp °C	Press. atm.	160	180	200	220	240	260	280	300
0		3.360	3.780	4.200	4.620	5.040	5.460	5.880	6.300
20		3.291	3.702	4.114	4.525	4.936	5.348	5.759	6.171
40		3.196	3.596	3.996	4.395	4.795	5.195	5.595	5.994
60		2.935	3.302	3.669	4.037	4.404	4.771	5.139	5.510
80		2.754	3.092	3.445	3.789	4.135	4.480	4.826	5.171
100		2.719	3.061	3.403	3.745	4.087	4.429	4.771	5.113
120		2.728	3.074	3.419	3.764	4.109	4.455	4.799	5.150
140		2.873	3.240	3.607	3.975	4.342	4.709	5.077	5.440
160		3.081	3.481	3.882	4.282	4.683	5.083	5.483	5.880
180		3.638	4.123	4.608	5.093	5.578	6.062	6.547	7.030
200		3.825	4.354	4.883	5.412	5.941	6.470	6.998	7.530
220		4.531	5.192	5.853	6.514	7.175	7.836	8.497	9.158
240		5.830	6.750	7.665	8.580	9.502	10.42	11.34	12.26
260		6.597	7.757	8.918	10.08	11.24	12.40	13.56	14.72
280		6.460	7.796	9.134	10.47	11.80	13.14	14.48	15.82
300		6.490	8.219	9.946	11.67	13.40	15.13	16.85	18.58

Table 6. Equilibrium constants for the deuterium exchange reactions.

Temp °C	K ₁	K ₂	K ₃
0	4.34	1.70	3.17
20	3.84	1.45	3.23
40	3.46	1.26	3.29
60	3.15	1.12	3.34
80	2.90	1.00	3.39
100	2.70	0.91	3.43
120	2.53	0.84	3.47
140	2.38	0.77	3.50
160	2.26	0.72	3.53
180	2.15	0.67	3.56
200	2.06	0.64	3.59
220	1.97	0.61	3.61
240	1.90	0.58	3.63
260	1.84	0.55	3.65
280	1.78	0.53	3.67
300	1.73	0.51	3.69

Table 7. Gas Phase Separation Factors, α_x

Temp. $^{\circ}\text{C}$ \ x	0.00015	0.0005	0.001	0.005	0.010	0.050	0.075	0.100	0.200	0.300
0.000	4.340	4.341	4.342	4.351	4.362	4.446	4.497	4.546	4.733	4.905
20.000	3.840	3.841	3.842	3.849	3.857	3.923	3.963	4.002	4.149	4.285
40.000	3.460	3.461	3.461	3.467	3.474	3.526	3.558	3.589	3.706	3.814
60.000	3.150	3.151	3.151	3.156	3.161	3.205	3.231	3.257	3.355	3.445
80.000	2.900	2.900	2.901	2.905	2.909	2.945	2.966	2.987	3.067	3.141
100.000	2.700	2.700	2.701	2.704	2.708	2.738	2.756	2.774	2.841	2.903
120.000	2.530	2.530	2.531	2.533	2.537	2.563	2.579	2.595	2.654	2.708
140.000	2.380	2.380	2.381	2.383	2.386	2.407	2.420	2.433	2.482	2.527
160.000	2.260	2.260	2.260	2.262	2.265	2.284	2.295	2.307	2.349	2.389
180.000	2.150	2.150	2.150	2.152	2.154	2.170	2.179	2.189	2.225	2.258
200.000	2.060	2.060	2.060	2.062	2.064	2.079	2.088	2.097	2.131	2.163
220.000	1.970	1.970	1.970	1.972	1.974	1.988	1.996	2.005	2.037	2.067
240.000	1.900	1.900	1.900	1.902	1.903	1.916	1.923	1.931	1.959	1.985
260.000	1.840	1.840	1.840	1.841	1.843	1.853	1.859	1.865	1.889	1.911
280.000	1.780	1.780	1.780	1.781	1.782	1.792	1.798	1.804	1.826	1.847
300.000	1.730	1.730	1.730	1.731	1.732	1.741	1.746	1.752	1.772	1.791

(27)

Table 7. (Contd.)

Temp. °C	x	0.400	0.0500	0.600	0.700	0.800	0.900	0.925	0.950	0.975	0.990
0.000		5.067	5.220	5.362	5.487	5.581	5.598	5.578	5.541	5.482	5.431
20.000		4.412	4.530	4.640	4.735	4.805	4.818	4.805	4.781	4.742	4.710
40.000		3.915	4.009	4.094	4.168	1.221	4.233	4.225	4.209	4.183	4.152
60.000		3.529	3.607	3.678	3.739	3.784	3.797	3.792	3.782	3.766	3.752
80.000		3.209	3.272	3.329	3.378	3.414	3.427	3.424	3.417	3.406	3.397
100.000		2.961	3.014	3.062	3.103	3.133	3.145	3.144	3.140	3.132	3.126
120.000		2.759	2.806	2.849	2.886	2.914	2.928	2.928	2.926	2.922	2.918
140.000		2.569	2.607	2.641	2.671	2.693	2.704	2.704	2.703	2.700	2.697
160.000		2.425	2.459	2.489	2.515	2.535	2.546	2.547	2.547	2.545	2.543
180.000		2.288	2.316	2.341	2.363	2.379	2.388	2.389	2.389	2.387	2.386
200.000		2.192	2.220	2.244	2.266	2.284	2.295	2.297	2.298	2.298	2.298
220.000		2.095	2.121	2.144	2.166	2.184	2.197	2.199	2.201	2.202	2.202
240.000		2.010	2.033	2.054	2.072	2.088	2.100	2.102	2.104	2.105	2.105
260.000		1.931	1.950	1.967	1.982	1.994	2.004	2.005	2.006	2.007	2.007
180.000		1.867	1.885	1.902	1.917	1.929	1.939	1.941	1.943	1.944	1.945
300.000		1.809	1.825	1.841	1.854	1.866	1.876	1.878	1.879	1.881	1.881

Table 8. Gas Phase Separation Factors, K_y

Temp. T °C	0.00015	0.0005	0.001	0.005	0.010	0.050	0.075	0.100	0.200	0.300
0.000	4.338	4.342	4.347	4.384	4.429	4.728	4.874	4.995	5.319	5.486
20.000	3.843	3.846	3.849	3.875	3.906	4.119	4.226	4.317	4.568	4.707
40.000	3.458	3.460	3.462	3.480	3.503	3.660	3.741	3.810	4.009	4.125
60.000	3.151	3.152	3.154	3.168	3.185	3.304	3.366	3.420	3.580	3.678
80.000	2.902	2.903	2.905	2.915	2.928	3.020	3.069	3.113	3.244	3.327
100.000	2.697	2.698	2.699	2.708	2.718	2.791	2.830	2.865	2.973	3.045
120.000	2.526	2.527	2.527	2.534	2.542	2.601	2.633	2.662	2.753	2.814
140.000	2.381	2.381	2.382	2.387	2.394	2.442	2.469	2.493	2.570	2.623
160.000	2.257	2.257	2.258	2.262	2.267	2.307	2.330	2.350	2.416	2.463
180.000	2.149	2.150	2.150	2.154	2.158	2.192	2.211	2.228	2.285	2.327
200.000	2.056	2.056	2.057	2.060	2.064	2.092	2.108	2.123	2.173	2.210
220.000	1.974	1.974	1.975	1.977	1.981	2.005	2.019	2.032	2.076	2.109
240.000	1.902	1.902	1.902	1.905	1.907	1.929	1.941	1.952	1.991	2.020
260.000	1.838	1.838	1.838	1.840	1.842	1.861	1.872	1.882	1.916	1.943
280.000	1.780	1.780	1.780	1.782	1.784	1.801	1.810	1.819	1.850	1.874
300.000	1.728	1.729	1.729	1.730	1.732	1.747	1.755	1.763	1.791	1.813

Table 8. (Contd.)

Temp. °C	0.400	0.500	0.600	0.700	0.800	0.900	0.925	0.950	0.975	0.990
0.000	5.569	5.600	5.597	5.570	5.525	5.463	5.445	5.426	5.407	5.394
20.000	4.782	4.816	4.823	4.810	4.781	4.739	4.726	4.713	4.699	4.691
40.000	4.192	4.226	4.238	4.234	4.216	4.188	4.179	4.169	4.159	4.153
60.000	3.738	3.771	3.786	3.786	3.776	3.757	3.751	3.744	3.737	3.732
80.000	3.379	3.411	3.427	3.431	3.426	3.413	3.409	3.404	3.399	3.396
100.000	3.091	3.121	3.137	3.144	3.143	3.134	3.131	3.128	3.124	3.122
120.000	2.856	2.883	2.900	2.908	2.909	2.904	2.902	2.900	2.897	2.896
140.000	2.661	2.686	2.702	2.711	2.714	2.712	2.711	2.709	2.707	2.706
160.000	2.497	2.520	2.536	2.545	2.549	2.549	2.548	2.547	2.546	2.545
180.000	2.357	2.379	2.394	2.403	2.408	2.410	2.409	2.409	2.408	2.408
200.000	2.237	2.258	2.272	2.282	2.287	2.289	2.290	2.289	2.289	2.289
220.000	2.134	2.152	2.166	2.176	2.182	2.185	2.185	2.185	2.185	2.185
240.000	2.043	2.061	2.074	2.083	2.090	2.093	2.094	2.094	2.094	2.094
260.000	1.964	1.980	1.993	2.002	2.008	2.012	2.013	2.014	2.014	2.014
280.000	1.893	1.909	1.921	1.930	1.936	1.941	1.941	1.942	1.943	1.943
300.000	1.831	1.845	1.857	1.865	1.872	1.877	1.877	1.878	1.879	1.879

Table 9. The overall separation factors, β , for liquid-gas exchange
($x_D = 0.0001$).

Temp °C	Press. atm.	1	20	40	60	80	100	120	140
0		4.678	4.767	4.767	4.767	4.766	4.765	4.764	4.763
20		3.886	4.126	4.132	4.133	4.133	4.133	4.132	4.131
40		3.109	3.631	3.647	3.651	3.653	3.654	3.654	3.654
60		2.316	3.227	3.261	3.271	3.276	3.279	3.281	3.282
80		1.590	2.876	2.938	2.959	2.969	2.975	2.978	2.981
100		-	2.551	2.654	2.690	2.708	2.719	2.726	2.731
120		-	2.238	2.394	2.449	2.479	2.496	2.508	2.516
140		-	1.935	2.146	2.227	2.269	2.296	2.314	2.326
160		-	1.644	1.908	2.016	2.074	2.111	2.136	2.154
180		-	1.375	1.679	1.813	1.887	1.935	1.968	1.993
200		-	1.136	1.463	1.618	1.709	1.768	1.809	1.841
220		-	-	1.264	1.435	1.538	1.608	1.658	1.696
240		-	-	1.084	1.263	1.378	1.456	1.513	1.557
260		-	-	-	1.107	1.228	1.313	1.376	1.426
280		-	-	-	-	1.090	1.179	1.248	1.301
300		-	-	-	-	-	1.057	1.128	1.157

Table 9 (Contd.)

Temp °C	Press. atm.	160	180	200	220	240	260	280	300
0		4.762	4.761	4.759	4.758	4.757	4.756	4.755	4.754
20		4.131	4.130	4.129	4.128	4.127	4.126	4.125	4.124
40		3.654	3.653	3.653	3.652	3.652	3.651	3.651	3.650
60		3.282	3.282	3.282	3.282	3.282	3.282	3.282	3.281
80		2.983	2.984	2.985	2.986	2.986	2.987	2.987	2.987
100		2.734	2.737	2.739	2.741	2.742	2.743	2.744	2.745
120		2.523	2.528	2.531	2.534	2.537	2.538	2.540	2.542
140		2.336	2.344	2.349	2.354	2.358	2.361	2.364	2.366
160		2.167	2.178	2.186	2.194	2.199	2.204	2.208	2.212
180		2.011	2.026	2.037	2.047	2.055	2.062	2.067	2.072
200		1.864	1.883	1.898	1.911	1.921	1.931	1.938	1.945
220		1.725	1.748	1.767	1.783	1.796	1.808	1.817	1.826
240		1.591	1.619	1.642	1.661	1.677	1.691	1.703	1.713
260		1.464	1.496	1.523	1.545	1.564	1.580	1.594	1.607
280		1.345	1.380	1.409	1.435	1.457	1.475	1.492	1.506
300		1.231	1.269	1.302	1.330	1.354	1.375	1.393	1.409

Table 10. The Overall Separation Factors, β ,
for Liquid-Gas Exchange ($X_D = 0.10$)

Temp. °C	Press. atm.	1	20	40	60	80	100	120	140
0		4.686	4.767	4.767	4.767	4.766	4.765	4.764	4.763
20		3.904	4.127	4.132	4.133	4.133	4.132	4.132	4.131
40		3.142	3.634	3.648	3.652	3.654	3.654	3.654	3.654
60		2.357	3.232	3.263	3.272	3.277	3.279	3.281	3.282
80		1.619	2.884	2.942	2.962	2.971	2.976	2.979	2.982
100		-	2.563	2.661	2.695	2.712	2.722	2.728	2.733
120		-	2.255	2.403	2.456	2.484	2.501	2.512	2.519
140		-	1.953	2.159	2.236	2.277	2.302	2.319	2.331
160		-	1.662	1.923	2.027	2.083	2.118	2.142	2.159
180		-	1.389	1.694	1.826	1.898	1.945	1.976	1.999
200		-	1.142	1.477	1.631	1.721	1.778	1.819	1.849
220		-	-	1.274	1.446	1.550	1.619	1.668	1.705
240		-	-	1.088	1.273	1.389	1.467	1.524	1.567
260		-	-	-	1.112	1.235	1.322	1.386	1.435
280		-	-	-	-	1.094	1.186	1.255	1.310
300		-	-	-	-	-	1.059	1.133	1.163

Table 10 (Contd.)

Temp. °C	Press. atm.	160	180	200	220	240	260	280	300
0		4.761	4.760	4.759	4.757	4.756	4.755	4.754	4.752
20		4.130	4.129	4.128	4.127	1.126	1.125	1.124	4.123
40		3.654	3.653	3.652	3.652	3.651	3.651	3.650	3.649
60		3.282	3.283	3.283	3.283	3.282	3.282	3.281	3.281
80		2.984	2.985	2.986	2.986	2.986	2.987	2.987	2.987
100		2.736	2.739	2.741	2.742	2.743	2.744	2.745	2.746
120		2.525	2.529	2.533	2.536	2.538	2.540	2.541	2.543
140		2.339	2.347	2.352	2.357	2.360	2.363	2.366	2.368
160		2.172	1.183	2.190	2.197	2.202	2.207	2.211	2.214
180		2.017	2.031	2.042	2.052	2.059	2.066	2.071	2.076
200		1.872	1.890	1.905	1.917	1.927	1.936	1.943	1.949
220		1.733	1.756	1.774	1.790	1.803	1.813	1.823	1.831
240		1.601	1.628	1.650	1.669	1.684	1.698	1.709	1.719
260		1.474	1.505	1.531	1.553	1.572	1.588	1.601	1.613
280		1.353	1.389	1.418	1.443	1.465	1.483	1.499	1.513
300		1.238	1.277	1.309	1.338	1.361	1.382	1.400	1.416

Table 11. The Overall Separation Factors, β ,
for Liquid-Gas Exchange ($X_D = 0.50$)

Temp. °C	Press. atm.	1	20	40	60	80	100	120	140
0		4.716	4.767	4.767	4.765	4.764	4.762	4.760	4.758
20		3.978	4.131	4.133	4.133	4.132	4.131	4.130	4.128
40		3.282	3.643	3.652	3.654	3.654	3.654	3.654	3.653
60		2.544	3.250	3.272	3.278	3.281	3.282	3.283	3.283
80		1.765	2.916	2.958	2.972	2.978	2.982	2.984	2.986
100		-	2.613	2.688	2.713	2.725	2.732	2.737	2.740
120		-	2.324	2.443	2.485	2.505	2.518	2.525	2.531
140		-	2.036	2.212	2.275	2.307	2.326	2.339	2.348
160		-	1.747	1.987	2.076	2.122	1.151	2.169	2.183
180		-	1.457	1.763	1.882	1.946	1.985	2.011	2.030
200		-	1.175	1.541	1.692	1.773	1.825	1.860	1.885
220		-	-	1.322	1.503	1.604	1.669	1.714	1.746
240		-	-	1.108	1.317	1.437	1.515	1.569	1.610
260		-	-	-	1.135	1.273	1.364	1.429	1.477
280		-	-	-	-	1.113	1.217	1.291	1.347
300		-	-	-	-	-	1.072	1.156	1.189

Table 11. (Contd.)

Temp. °C	Press. atm.	160	180	200	220	240	260	280	300
0		4.756	4.754	4.752	4.750	4.748	4.746	4.744	4.742
20		4.127	4.125	4.123	4.122	4.121	4.119	4.117	4.116
40		3.652	3.651	3.649	3.649	3.648	3.646	3.645	3.644
60		3.282	3.282	3.281	3.281	3.280	3.279	3.279	3.278
80		2.986	2.987	2.987	2.987	2.986	2.986	2.985	2.985
100		2.742	2.743	2.744	2.745	2.745	2.745	2.745	2.745
120		2.535	2.538	2.541	2.542	2.544	2.545	2.546	2.547
140		2.355	2.360	2.364	2.367	2.369	2.372	2.374	2.375
160		2.193	2.201	2.207	2.212	2.216	2.219	2.222	2.225
180		2.045	2.055	2.064	2.071	2.077	2.082	2.086	2.089
200		1.905	1.920	1.932	1.942	1.950	1.957	1.963	1.968
220		1.771	1.791	1.806	1.819	1.830	1.839	1.847	1.854
240		1.641	1.665	1.685	1.701	1.715	1.726	1.736	1.745
260		1.515	1.544	1.568	1.588	1.605	1.619	1.631	1.642
280		1.391	1.426	1.455	1.479	1.499	1.516	1.530	1.543
300		1.270	1.310	1.343	1.371	1.394	1.414	1.431	1.447

Table 12. The Overall Separation Factors, β ,
for Liquid-Gas Exchange ($X_D = 0.99$)

Temp. °C	Press. atm.	1	20	40	60	80	100	120	140
0		4.749	4.766	4.762	4.756	4.752	4.746	4.741	4.736
20		4.068	4.133	4.131	4.128	4.125	4.121	4.117	4.114
40		3.471	3.652	3.654	3.653	3.651	3.648	3.646	3.644
60		2.846	3.272	3.281	3.283	3.282	3.282	3.280	3.279
80		2.075	2.956	2.978	2.984	2.986	2.987	2.987	2.986
100		-	2.678	2.721	2.734	2.741	2.744	2.745	2.746
120		-	2.418	2.494	2.519	2.531	2.537	2.541	2.544
140		-	2.158	2.283	2.324	2.345	2.356	2.363	2.369
160		-	1.884	2.077	2.142	2.173	2.192	2.204	2.213
180		-	1.583	1.868	1.963	2.010	2.038	2.056	2.069
200		-	1.244	1.648	1.782	1.849	1.889	1.916	1.934
220		-	-	1.409	1.594	1.686	1.741	1.777	1.803
240		-	-	1.149	1.394	1.517	1.590	1.639	1.673
260		-	-	-	1.180	1.339	1.434	1.497	1.542
280		-	-	-	-	1.150	1.271	1.351	1.408
300		-	-	-	-	-	1.098	1.198	1.235

Table 12 (Contd.)

Temp. °C	Press. atm.	160	180	200	220	240	260	280	300
0		4.731	4.726	4.721	4.716	4.711	4.706	4.701	4.696
20		4.110	4.107	4.103	4.099	4.096	4.092	4.088	4.085
40		3.641	3.639	3.636	3.633	3.631	3.628	3.625	3.622
60		3.277	3.275	3.274	3.272	3.270	3.268	3.266	3.264
80		2.985	2.985	2.984	2.983	2.982	2.980	2.979	2.978
100		2.747	2.746	2.746	2.745	2.745	2.744	2.744	2.743
120		2.546	2.547	2.547	2.547	2.548	2.548	2.547	2.547
140		2.372	2.375	2.376	2.377	2.378	2.379	2.380	2.380
160		2.219	2.223	2.226	2.229	2.231	2.233	2.234	2.235
180		2.078	2.085	2.091	2.095	2.099	2.101	2.104	2.105
200		1.948	1.958	1.966	1.973	1.978	1.983	1.986	1.989
220		1.822	1.836	1.848	1.857	1.865	1.871	1.876	1.881
240		1.698	1.718	1.733	1.745	1.756	1.764	1.771	1.777
260		1.575	1.601	1.621	1.637	1.650	1.661	1.671	1.679
280		1.451	1.483	1.509	1.530	1.547	1.562	1.574	1.584
300		1.322	1.363	1.395	1.422	1.443	1.461	1.476	1.489

(39)

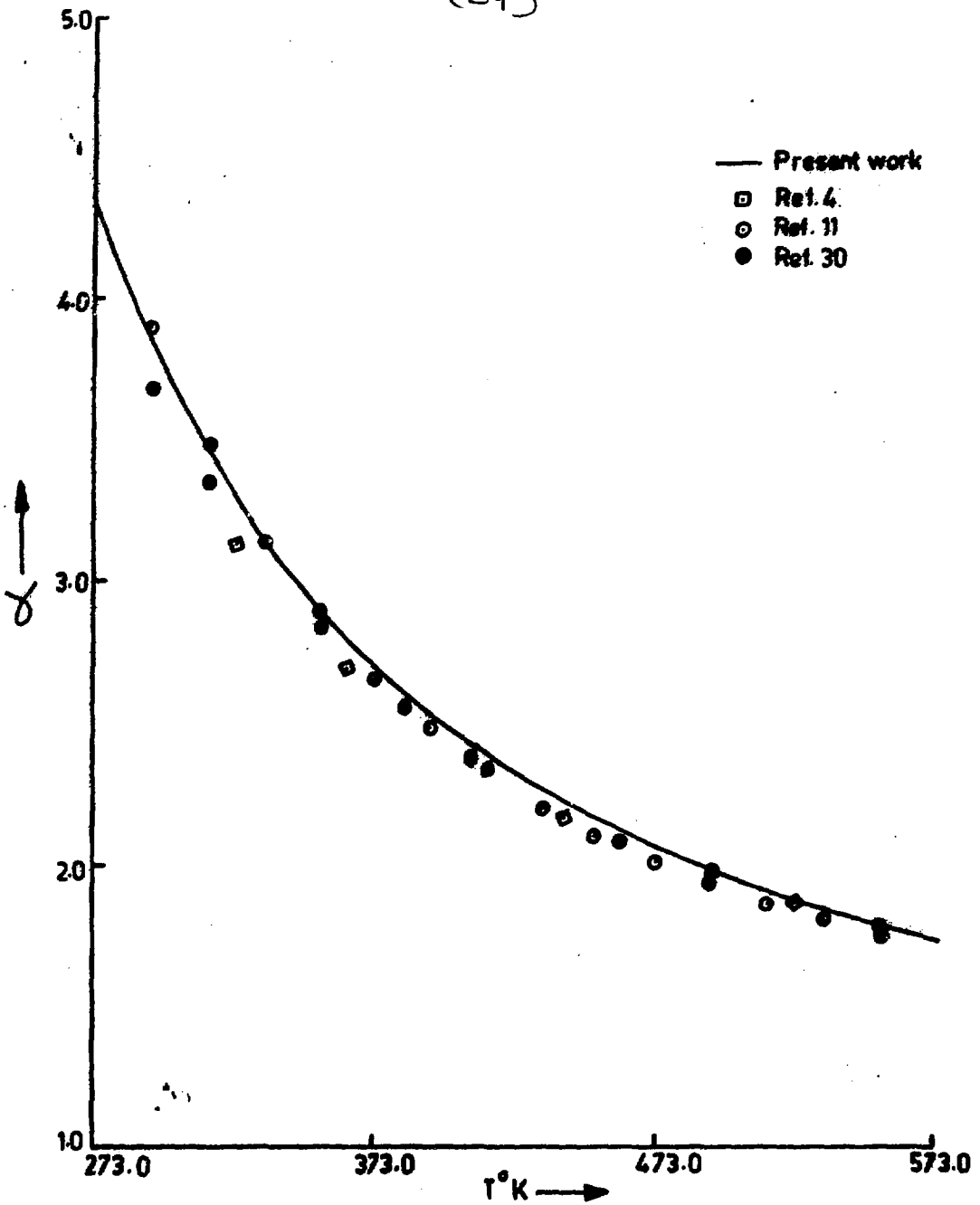


Fig.1. Plot of Separation factor α Vs Temperature T .