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Solvation and Ion-pair Formation of Lithium Bromide in Acetone-methanol and Acetone-ethanol Mixtures Studied by Reaction Kinetics

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Kinetic data at 25 °C for the exchange of bromine between lithium bromide and butyl bromide in acetone-methanol and acetone-ethanol mixtures containing between 0.1 and 1.0 wt-% of the hydroxylic compound are reported. The data have been analyzed by means of the McKay and Acree equations. The exchange appears to be of S_N2-type. The second-order rate constant for the exchange between free bromide ions and the organic bromide decreases strongly with increasing concentration of the hydroxylic constituent of the solvent medium. Ion-pairs of lithium bromide have been found to be kinetically inactive. The dependence of the kinetics on the composition of the solvent mixture is discussed in terms of preferential solvation of the ionic bromide. Transfer activity coefficients, estimated from the kinetic data, are used to obtain information about solvation of lithium bromide ion-pairs in the solvent mixtures investigated.

The kinetics of the exchange of ^{82}Br between butyl bromide and lithium bromide in acetone-water mixtures was studied in earlier investigations.[1,2] The water present in the solvent was found to have a strong inhibitory effect on the exchange reaction. This effect was interpreted as a difference in solvation of the activated complex and the reactants caused by hydrogen bond formation.

The main purpose of the present investigation was to study how the same exchange reaction is affected upon substituting the water in the solvent mixture by methanol and ethanol, respectively.

Measurements were performed at several different lithium bromide concentrations between 2×10^{-4} and 8×10^{-3} M. The concentration of the protic component in the solvent mixture varied between 0.1 and 1.0 wt-%. At these low concentrations of protic component in acetone, the self-association of hydroxylic molecules is minimized and the macroscopic permittivity is retained at almost a constant value.

EXPERIMENTAL

The acetone used (Merck, *p.a.*) was purified according to Ref. 1. Its density at 25 °C was 0.7843 kg dm^{-3}.

Methanol (Merck, *p.a.*) was dried over a molecular sieve (Fischer Sci. Co. type 4 A) and fractionally distilled in a Widmer column. The same procedure was used to purify "absolute" ethanol (99.9 %).

After purification the densities of methanol and ethanol were 0.7867 kg dm^{-3} and 0.7851 kg dm^{-3}, respectively.

Solvent mixtures of acetone-methanol and acetone-ethanol were prepared by weight at 25 °C.

Butyl bromide (Fluka, *puriss*) was dried over phosphorus pentaoxide and fractionally distilled.

Lithium bromide (Fluka, *suprapur*) was dried at 200 °C for 6 h and cooled in a vacuum desiccator.

The method employed to convert inactive lithium bromide to radiobromide and the preparation of solutions of lithium radiobromide of different concentrations has been reported.[1]

The course of the exchange reaction was followed electroanalytically by anodic deposition of bromide on silver electrodes according to Refs. 3 – 4.

The electrode reaction, $Ag+Br^-\rightarrow AgBr+e^-$, was investigated with respect to the dependence

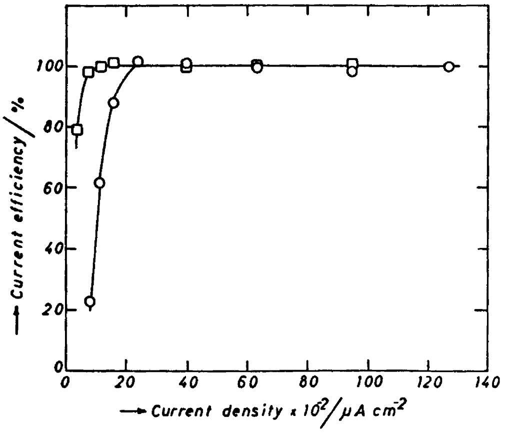

Fig. 1. Graphs of current efficiency *vs.* current density for 5.1×10^{-4} M (squares) and 2.04×10^{-3} M (open circles) solutions of lithium bromide in acetone containing 0.1 wt-% methanol at 25 °C.

of the current efficiency on the current density. Fig. 1 representatively illustrates how the shape of the current efficiency-current density curve depends on the concentration of lithium bromide at constant solvent composition (acetone-methanol containing 0.1 wt-% of the hydroxylic constituent).

RESULTS AND DISCUSSION

The kinetic data were analyzed by means of the McKay equation [5] using the method of least squares. The results are summarized in Tables 1–2, in which the second-order rate constant, k, is defined by the expression,

$$k=R/(bc) \qquad (1)$$

where R is the total rate of exchange, b is the concentration of butyl bromide, and c is the concentration of lithium bromide.

The degree of dissociation of the inorganic bromide, α, was calculated from ion-pair association constants, K_A, of lithium bromide in the various solvent mixtures investigated.

The association constants listed in Table 3 were evaluated from electrical conductance data [6,7] by means of the Fuoss-Hsia conductance equation [8,9] in the form developed by Fernandez-Prini.[10] The mean activity coefficient of free ions was evaluated from the Debye-Hückel equation.[11]

Table 1. Kinetic data for the exchange of ^{82}Br between lithium bromide and butyl bromide in acetone-methanol mixtures at 25.0 °C.

$b\times10^2$ M	$c\times10^4$ M	$R\times10^8$ M s^{-1}	$k\times10^4$ M^{-1} s^{-1}	α
0.10 wt-% CH_3OH				
5.087	76.64	56.570	14.51	0.2239
5.087	19.71	25.898	25.83	0.3693
5.046	9.975	14.869	29.54	0.4634
5.106	4.731	8.9862	37.20	0.5780
5.108	2.091	4.5126	42.25	0.7051
0.30 wt-% CH_3OH				
5.125	79.34	47.778	11.75	0.2493
5.132	39.18	29.336	14.59	0.3228
5.101	20.39	18.961	18.23	0.4046
5.136	9.841	11.721	23.19	0.5094
5.087	5.109	6.9964	26.92	0.6110
5.110	1.960	3.1830	31.78	0.7546
1.00 wt-% CH_3OH				
4.878	77.60	32.826	8.672	0.3133
5.089	39.41	18.598	9.273	0.3948
5.076	19.81	12.911	12.84	0.4900
5.106	4.608	4.5175	19.20	0.7097

Table 2. Kinetic data for the exchange of ^{82}Br between lithium bromide and butyl bromide in acetone-ethanol mixtures at 25.0 °C.

$b\times10^2$ M	$c\times10^4$ M	$R\times10^8$ M s^{-1}	$k\times10^4$ M^{-1} s^{-1}	α
0.30 wt-% C_2H_5OH				
5.047	65.55	49.261	14.89	0.2402
5.172	43.89	38.454	16.94	0.2793
5.067	22.19	25.017	22.25	0.3575
5.632	11.04	16.630	26.75	0.4523
5.163	5.538	9.4842	33.17	0.5571
5.077	2.273	4.5952	39.82	0.6962
0.60 wt-% C_2H_5OH				
5.317	45.63	30.812	12.70	0.2975
4.958	30.22	21.531	14.37	0.3448
5.692	14.98	16.550	19.41	0.4373
5.458	7.561	9.3266	22.60	0.5391
5.119	3.746	5.2753	27.51	0.6488
5.002	1.548	2.5560	33.01	0.7776
1.00 wt-% C_2H_5OH				
5.083	80.22	37.701	9.246	0.2603
5.140	42.64	29.807	13.60	0.3274
5.145	21.34	16.733	15.24	0.4148
5.153	10.59	9.8390	18.03	0.5162
5.032	5.323	5.9812	22.33	0.6225
5.200	2.115	3.0003	27.29	0.7594

Table 3. Permittivities and conductance parameters for lithium bromide in acetone-methanol [6] and acetone-ethanol [7] mixtures at 25 °C. The values of K_A for acetone-methanol as solvent have been reevaluated (see text) from conductance data in Ref. 6.

Hydroxylic conc. wt-%	ε	K_A M^{-1}	$r \times 10^{10}$ m
Methanol			
–	20.7	4160	13.54
0.10	20.6	3436	13.60
0.30	20.6	2664	13.60
1.00	20.7	1640	13.54
Ethanol			
0.30	20.6	3361	13.60
0.60	20.6	2830	13.60
1.00	20.6	2407	13.60

The ion-pair association constant, and hence the rate constants k_i and k_m, were found to be only slightly sensitive to the maximum center-to-center distance, r, between the ions in the ion-pair within the range $q/2 \leqslant r \leqslant q$, where q is the Bjerrum radius.[12] The association constants in Table 3, corresponding to $r = q$, were used in evaluating the α-values listed in Tables 1 – 2.

If the exchange of bromine between the organic and inorganic bromides is a mixed $S_N1 - S_N2$ reaction and if the contribution of ion-pairs of lithium bromide to the reaction rate is negligible, the latter may be expressed,

$$R = k_1 b + k_i b c \alpha \tag{2}$$

where k_1 is the first-order rate constant, k_i is the second-order rate constant for the exchange of free bromide ions, and α is the degree of dissociation of the ion-pairs.

According to eqn. (2) a graph of R/b *vs.* $c\alpha$ should yield a straight line with intercept equal to k_1.

Graphs of this kind are shown in Figs. 2 – 3. All lines pass within experimental error through the origin indicating no significant S_N1 contribution to the reaction rate. Hence the exchange mechanism is considered to be of S_N2-type.

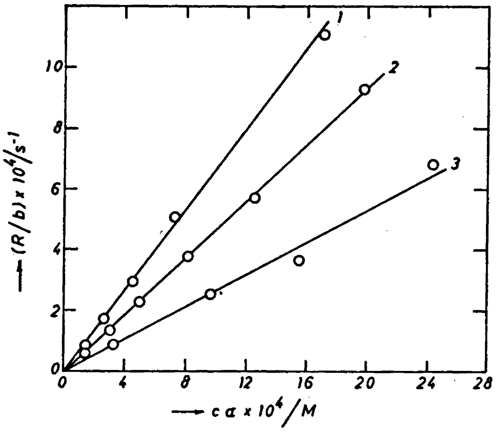

Fig. 2. Graphs of R/b *vs.* $c\alpha$ for the exchange of bromine between lithium bromide and butyl bromide in acetone-methanol mixtures at 25 °C. The curves 1 – 3 refer to solvent mixtures containing 0.1, 0.3 and 1.0 wt-% methanol, respectively.

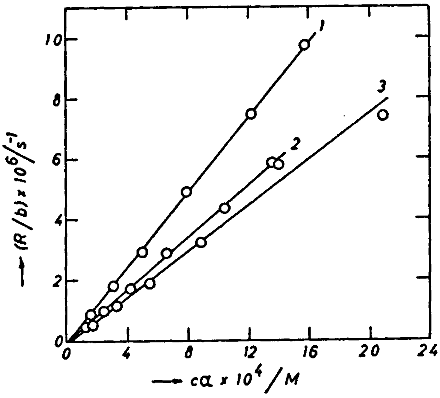

Fig. 3. Graphs of R/b *vs.* $c\alpha$ according to eqn. (2) for the same exchange reaction as in Fig. 2, in acetone-ethanol mixtures at 25 °C. The curves 1 – 3 refer to solvent mixtures containing 0.3, 0.6 and 1.0 wt-% ethanol, respectively.

If the ion-pairs contribute to the rate of exchange a term, $k_m bc(1-\alpha)$, where k_m is the second-order rate constant for the exchange of bromide between butyl bromide and lithium bromide ion-pairs, should be added to the right-hand side of eqn. (2). Combination of eqn. (1) with k_1 set equal to zero, and the extended form of eqn. (2) yields,

$$k/\alpha = k_i + k_m(1-\alpha)/\alpha \tag{3}$$

which is the Acree equation.[13]

Rate constants, k_i and k_m, derived from eqn. (3) by means of a relative deviation least squares treatment [14] of the kinetic data in

Table 4. Rate constants for reactions of ions and ion-pairs, k_i and k_m, respectively, for the same systems as in Tables 2 and 3.

Hydroxylic conc. wt-%	$k_i \times 10^4$ M^{-1} s^{-1}	$k_m \times 10^4$ M^{-1} s^{-1}
Methanol		
–	78.15 ± 0.40 [a]	1.0 ± 0.2 [a]
0.10	62.7 ± 2.9	1.2 ± 3.8
0.30	42.8 ± 0.7	1.4 ± 0.4
1.00	26.2 ± 2.5	-0.05 ± 1.73
Ethanol		
0.30	57.7 ± 1.0	1.5 ± 0.5
0.60	42.6 ± 0.8	0.03 ± 0.59
1.00	35.6 ± 1.9	0.8 ± 1.2

[a] Data from Ref. 2.

Tables 1–2, are summarized in Table 4 in which the corresponding rate constants for pure acetone as solvent medium are included. The errors listed in this table and elsewhere are standard deviations.

The rapid decrease in rate of exchange between the organic bromide and bromide ions with increasing concentration of methanol and ethanol, respectively, is illustrated in Fig. 4, where the corresponding graph for acetone-water solvent mixtures is included.

According to Fig. 4 the effectiveness of the protic component as inhibitor for the exchange reaction decreases in the following order:

Methanol > ethanol > water

The order between ethanol and water is the same as that found by Leary and Kahn,[15] who investigated the effect of various protic components in acetone on the kinetics of the exchange of radioiodine between potassium iodide and benzyl iodides. The order between methanol and ethanol indicates that the ionic reactant is more strongly solvated by methanol than by ethanol. The same order has been reported by Becker,[16] who investigated hydrogen-bonding in several alcohol-base systems by means of infrared spectroscopy.

Free energies of formation of 1:1 hydrogen-bonded complexes between acetone-methanol and acetone-ethanol were found to be −1.5 and −0,5 kJ mol^{-1}, respectively.

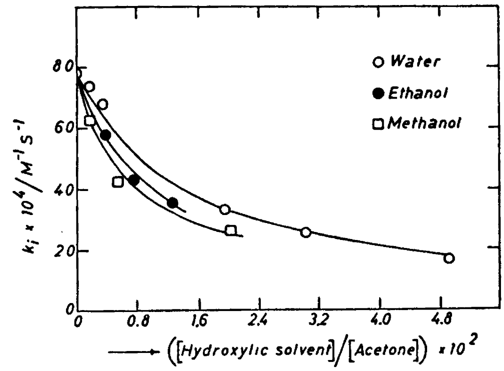

Fig. 4. The variation of k_i with solvent composition as calculated from eqn. (8).

The decrease in rate of the exchange reaction with increasing concentration of the protic component may be qualitatively explained by the ability of the hydroxylic constituent to form hydrogen bonds. This would result in a decrease in Gibbs' free energy of activation for the exchange reaction, in the following order:

Acetone-methanol > acetone-ethanol > acetone-water > acetone

If we assume that unpaired bromide ions in a solution of acetone containing a protic component of low concentration are solvated by either n molecules of acetone ("A") or by $(n-m)$ molecules of acetone and m molecules of protic component ("P"), we are concerned with the solvation equilibrium (I), *cf.* Ref. 2.

$$Br^-A_n + mP \rightleftharpoons Br^-A_{n-m}P_m + mA \tag{I}$$

Following the derivation in Ref. 2, the overall equilibrium constant, K, for the equilibrium (I) may be written as eqn. (4), and the rate of

$$K = \frac{[Br^-A_{n-m}P_m][A]^m}{[Br^-A_n][P]^m} \tag{4}$$

exchange may be expressed as eqn. (5), where

$$R = k_A b[Br^-A_n] + k_{AP} b[Br^-A_{n-m}P_m] \tag{5}$$

k_A is the rate constant for exchange of bromine between Br^-A_n and butyl bromide and k_{AP} is the rate constant for the corresponding exchange reaction involving $Br^-A_{n-m}P_m$.

Using the results of eqns. (2 – 3), which indicate that the terms containing k_1 and k_m may be omitted, together with the stoichiometric condition for bromide ions [eqn. (6)],

$$[\mathrm{Br}^-]_{\mathrm{tot}} = [\mathrm{Br}^-\mathrm{A}_n] + [\mathrm{Br}^-\mathrm{A}_{n-m}\mathrm{P}_m] \tag{6}$$

we obtain upon combining eqns. (4 – 6) eqn. (7).

$$\lg \frac{k_\mathrm{A} - k_\mathrm{i}}{k_\mathrm{i} k_\mathrm{A}} = \mathrm{m} \lg \frac{[\mathrm{P}]}{[\mathrm{A}]} + \lg \frac{K}{k_\mathrm{A}} \tag{7}$$

A condition for eqn. (7) to be valid is that the concentration of the protic component in the solvent mixtures is sufficiently low to keep $k_\mathrm{i} \gg k_\mathrm{AP}$.

Eqn. (7) was fitted to the kinetic data in Table 4 according to the method of least squares. The equation of the straight lines yielded the overall values $m = 0.90 \pm 0.11$ and $m = 1.02 \pm 0.15$ for the bromide ion in acetone containing methanol and ethanol, respectively. For the solvation equilibrium involving bromide ions in acetone-water mixtures[2] at 25 °C, the value of m is 1.09 ± 0.06. According to these calculations the overall number of hydroxylic molecules associated with each bromide ion is close to one for the range of concentrations of hydroxylic compound investigated.

If m is set equal to one, eqn. (7) may conveniently be rewritten [eqn. (8)].

$$\frac{1}{k_\mathrm{i}} = \frac{1}{k_\mathrm{A}} + \frac{K}{k_\mathrm{A}} \frac{[\mathrm{P}]}{[\mathrm{A}]} \tag{8}$$

To evaluate K, eqn. (8) was fitted to values of $1/k_\mathrm{i}$ *vs.* [P]/[A] using the relative deviation least squares method. For the acetone-methanol and acetone-ethanol systems this procedure yielded $K = 110$ and $K = 98$, respectively. Compare these values with the figure, $K = 73$, for the corresponding equilibrium in acetone-water.[1]

If the hydroxylic compound as a hydrogen-bond donor solvates the bromide ion much more strongly than acetone, the solvation equilibrium (II) may be used to calculate m and K. The numerical values of m

$$\mathrm{Br}^- + m\mathrm{P} \rightleftharpoons \mathrm{Br}^-\mathrm{P}_m \tag{II}$$

calculated on this assumption are the same as those calculated for equilibrium (I). With $m = 1$ equilibrium (II) yields $K = 7.3$ and 8.2 for the acetone-ethanol and acetone-methanol systems, respectively.

In a previous paper[2] transfer activity coefficients were used to obtain information about changes in ion-pair solvation when small amounts of water were added to anhydrous acetone.

The transfer activity coefficient is defined[17–18] in eqn. (9), where $(\mu_\mathrm{i}^0)_\mathrm{S}$ stands for the standard

$$(\mu_\mathrm{i}^0)_\mathrm{S} = (\mu_\mathrm{i}^0)_\mathrm{R} + RT \ln \gamma_{t,\mathrm{i}} \tag{9}$$

chemical potential of a solute, "i", in any solvent, "S", $(\mu_\mathrm{i}^0)_\mathrm{R}$ is the corresponding quantity in the selected reference solvent, "R". R is the gas constant, T is the absolute temperature, and $\gamma_{t,\mathrm{i}}$ is the transfer activity coefficient.

Following the derivation in Ref. 2, the effect of solvent on the rate of the exchange reaction concerned may be written as eqn. (10), where

$$\frac{(k_\mathrm{i})_\mathrm{P}}{(k_\mathrm{i})_\mathrm{A}} = \frac{(\gamma_{t,\mathrm{Br}-})(\gamma_{t,\mathrm{BuBr}})}{\gamma_{t,\ddagger}} \tag{10}$$

"P" and "A" denote solvent mixture and pure acetone, respectively, and ‡ stands for the activated complex. According to the theory of absolute reaction rate,[19–21]

$$(\Delta G_t^0{}^\ddagger)_{\mathrm{A}\to\mathrm{P}} = -RT \ln [(k_\mathrm{i})_\mathrm{P}/(k_\mathrm{i})_\mathrm{A}] \tag{11}$$

where $(\Delta G^0{}^\ddagger)_{\mathrm{A}\to\mathrm{P}}$ is the difference in Gibbs' free energy of activation for the exchange reaction in pure acetone and in acetone containing a protic component.

On the reasonable assumption that $\gamma_{t,\mathrm{BuBr}} \geq \gamma_{t,\ddagger}$ a comparison of eqns. (10) and (11) reveals that

$$\gamma_{t,\mathrm{Br}^-} \leq (k_\mathrm{i})_\mathrm{P}/(k_\mathrm{i})_\mathrm{A} \tag{12}$$

Application of a thermodynamic cycle to the association equilibrium (III) in pure acetone

$$\mathrm{Li}^+ + \mathrm{Br}^- \rightleftharpoons \mathrm{LiBr} \tag{III}$$

and in the corresponding protic-aprotic solvent mixture and use of the relation $\Delta G^0 = -RT \ln K$, yields eqn. (13),

$$\frac{(K_\mathrm{A})_\mathrm{P}}{(K_\mathrm{A})_\mathrm{A}} = \frac{(\gamma_{t,\mathrm{Li}^+})(\gamma_{t,\mathrm{Br}-})}{\gamma_{t,\mathrm{LiBr}}} \tag{13}$$

where $(K_\mathrm{A})_\mathrm{A}$ is the ion-pair association constants of lithium bromide in pure acetone and $(K_\mathrm{A})_\mathrm{P}$

Table 5. Transfer activity coefficients at 25 °C according to eqns. (12) and (13).

Hydroxylic conc. wt-%	$(\gamma_{t,\mathrm{Br^-}})_{\mathrm{A\to P}}$	$(K_\mathrm{A})_\mathrm{P}/(K_\mathrm{A})_\mathrm{A}$	$(\gamma_{t,\mathrm{Li^+}})_{\mathrm{A\to P}}/(\gamma_{t,\mathrm{LiBr}})_{\mathrm{A\to P}}$
Methanol			
0.10	0.80	0.83	1
0.30	0.55	0.64	1.2
1.00	0.33	0.39	1.2
Ethanol			
0.30	0.74	0.81	1.1
0.60	0.54	0.68	1.3
1.00	0.46	0.58	1.3

is the corresponding quantity referring to the solvent mixture.

Using the values of K_A and k_i at 25 °C in Tables 3 and 4 the figures listed in Table 5 were derived from eqns. (12) and (13).

According to these data there is a tendency for the activity coefficient ratio $(\gamma_{t,\mathrm{Li^+}})_{\mathrm{A\to P}}/(\gamma_{t,\mathrm{LiBr}})_{\mathrm{A\to P}}$ to increase with increasing concentration of the protic component. This may be due to increasing solvation of the lithium bromide ion-pairs. If the solvation of the lithium ion increases with the concentration of the protic component, the values listed in the last column of Table 5 would be an underestimation of the effect of solvation on the ion-pairs.

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REFERENCES

1. Holmgren, A. and Beronius, P. *Acta Chem. Scand. 26* (1972) 3881.
2. Holmgren, A. *Acta Chem. Scand. A 31* (1977) 539.
3. Beronius, P. *Acta Chem. Scand. 15* (1961) 1151.
4. Beronius, P., Isacsson, U. and Nilsson, A.-M. *Acta Chem. Scand. 24* (1970) 189.
5. McKay, H. A. C. *J. Am. Chem. Soc. 65* (1943) 702.
6. Nilsson, A.-M. *Acta Chem. Scand. 27* (1973) 2722.
7. Beronius, P. *Unpublished.*
8. Fuoss, R. M. and Hsia, K.-L. *Proc. Natl. Acad. Sci. U.S.A. 57* (1967) 1550.
9. Fuoss, R. M. and Hsia, K.-L. *Proc. Natl. Acad. Sci. U.S.A. 58* (1968) 1818.
10. Fernández-Prini, R. *Trans. Faraday Soc. 65* (1969) 3311.
11. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1965, p. 229.
12. Bjerrum, N. *K. Dan. Vidensk. Selsk. Mat. Fys. Medd. 7* (1926) No. 9.
13. Acree, S. F. *Am. Chem. J. 48* (1912) 352.
14. Hald, A. *Statistical Theory with Engineering Applications*, Wiley, New York 1965, p. 551.
15. Leary, J. A. and Kahn, M. *J. Am. Chem. Soc. 81* (1959) 4173.
16. Becker, E. D. *Spectrochim. Acta 17* (1961) 436.
17. Trémillon, B. *Chemistry in Non-Aqueous Solvents*, D. Reidel Publishing Company, Dordrecht, Holland 1974, Chapter 5.
18. Parker, A. J. *J. Chem. Soc. A* (1966) 220.
19. Eyring, H. *J. Chem. Phys. 3* (1935) 107.
20. Evans, M. G. and Polanyi, M. *Trans. Faraday Soc. 31* (1935) 875.
21. Glasstone, S., Laidler, K. J. and Eyring, H. *The Theory of Rate Processes*, McGraw Hill, New York 1941.

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