530. *The Kinetics of Certain Ionic Exchange Reactions of the Four Methyl Halides in Aqueous Solution.*

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The kinetics of six reactions of the type $CH_3X + Y^- \longrightarrow CH_3Y + X^-$, mostly involving fluorine, have been studied in aqueous solution. The apparent energies of activation have been compared with the energies estimated for partial de-solvation of the ion and the polar molecule. Many more data than we now possess are needed before a satisfactory theory of the kinetics of simple substitutions at the saturated carbon atom can be developed. This paper provides some new material, chiefly on the rates at which the fluoride ion attacks the other methyl halides in aqueous solution under vapour-free conditions.

Preparation and Purity of Reactants.—The commercial sample of methyl chloride used was found on analysis to be 99·8% pure. No impurities could be detected by infrared absorption spectroscopy. Methyl bromide was purified as described by Egan and Kemp.[1] Its vapour pressure at 0° was 664·55 mm. (cf. 660·4 mm. found by them). Methyl iodide was purified by Brown and Acree's method.[2] Its boiling point was 42·42° (cf. 42·36° recorded by Timmermans [3]). Methyl fluoride was prepared and purified as described by Glew and Moelwyn-Hughes.[4] Its vapour pressure was 754 mm. at the sublimation point of carbon dioxide (cf. the value of 756 mm. given by them). Water was purified by distillation and by passage through Amberlite ion-exchange resin No. MB3.

Methods of Analysis.—Hydrogen ion was determined by titration with standard potassium hydroxide solution, with nitrogen bubbling through to remove dissolved carbon dioxide. The end-point was determined either by using bromothymol blue as indicator, or by following the pH electrometrically. Iodide ion was determined by titration with standard potassium iodate, as described by Moelwyn-Hughes.[5] Fluoride ion was determined by Grant and Haendler's method [6] of titration with thorium nitrate and determining the position of the end-point by use of a high-frequency titrimeter.[7,8] The total concentration of ionic halide, excluding fluoride, was found by titration with standard silver nitrate, dichlorofluorescein being used as indicator. 5 ml. of a 2% solution of dextrin were added to the titration solution to prevent premature precipitation of the silver halide. It was found that this displaced the end-point slightly, by an amount for which quantitative correction was made. The correction is greater in the presence of fluoride ion.

Kinetic Procedure.—About 400 ml. of the solution of the potassium halide were sucked into a gas pipette and degassed by boiling at room temperature for a few minutes. An appropriate

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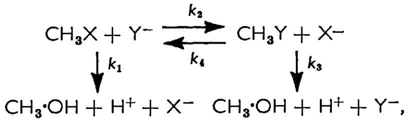
[1] Egan and Kemp, *J. Amer. Chem. Soc.*, 1938, **60**, 2097.
[2] Brown and Acree, *ibid.*, 1916, **35**, 2145.
[3] Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.
[4] Glew and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1952, *A*, **211**, 254.
[5] Moelwyn-Hughes, *ibid.*, 1953, *A*, **220**, 386.
[6] Grant and Haendler, *Ind. Eng. Chem. Anal.*, 1956, **28**, 415.
[7] Blaedel, Malmstadt, Petitjean, and Anderson, *ibid.*, 1952, **24**, 1240.
[8] Hall, *ibid.*, p. 1236.

amount of methyl halide was introduced either from a gas burette or from a graduated pipette and mixed by shaking. The mixture was then quickly sucked into a vapour-free reaction vessel of the type described by Fahim and Moelwyn-Hughes.[9] The time of starting the reaction was taken as the time when one half of the reaction mixture had entered the vessel. The vessel was kept in a water thermostat, maintained constant to within 0·03° by a mercury–toluene thermoregulator with a Sunvic relay. Temperatures were measured by a mercury-in-glass thermometer graduated in tenths of a degree and compared with a thermometer calibrated by the National Physical Laboratory. The absolute zero of temperature was taken as −273·16° c.

Samples were removed from the vessel at measured intervals of time, chilled in ice-water, and analysed for inorganic halides. When the reaction was relatively fast, infinity values were found by following it until no further change took place. When this was not practicable, measured samples were sealed in glass ampoules with an equal volume of N-sodium hydroxide when the reaction was about three-quarters complete, and digested at 100° until the methyl halide was completely hydrolysed; the contents of the ampoule were then analysed for the appropriate halide ion. This method could not be used to determine the concentration of methyl fluoride, as the high concentration of hydroxide interferes with the estimation of fluoride ion. Therefore with reactions involving methyl fluoride, samples were sealed in glass ampoules without sodium hydroxide, and digested at 100° for long enough to ensure the complete hydrolysis of the methyl fluoride.

Kinetic Formulation.—The general scheme for the system of reactions here studied can be described as follows:



where X and Y represent halogen atoms.

There are three special cases to be considered.

(1) When both hydrolyses can be ignored, we have *

$$k_2 = \frac{1}{2(1-K)\beta t} \ln \left[\frac{1 - x/(\alpha + \beta)}{1 - x/(\alpha - \beta)}\right] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $K = k_4/k_2$, $\alpha = (a + b)/2(1 - K)$, and $\beta = [(a - b)^2 + 4Kab]^{\frac{1}{2}}/2(1 - K)$.

Here a and b are the initial concentrations of CH_3X and Y^-, respectively. This equation has been found applicable at temperatures below 350° K when X = Cl and Y = I.

(2) When $d[Y^-]/dt$ is zero, $d[X^-]/dt = d[H^+]/dt$,
and $[CH_3Y] = k_2[CH_3X][Y^-]/(k_3 + k_4[X^-])$.

The rate equation then becomes

$$\frac{dx}{dt} = k_1(a - x) + \frac{k_2(a - x)(b - x)}{1 + (k_4/k_3)x}$$

and the observed first-order constant is consequently

$$k = k_1 + \frac{k_2(b - x)}{1 + (k_4/k_3)x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

These simple conditions correspond very nearly to those found when X = F and Y = I.

(3) When the reverse reaction can be ignored, terms involving k_4 can be omitted, and the differential form of the rate equation is

$$dx/dt = k_1(a - x) + k_2(a - x)(b - x)$$

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* This equation is identical with eqn. 7 (p. 2644) except that, at the suggestion of a referee, we have used γ for α in the earlier equation.

[9] Fahim and Moelwyn-Hughes, *J.*, 1956, 1034.

which can be readily integrated. It has been shown that the first-order constant is

$$k = k_1 + k_2(b - x),$$

or, if $b \gg a$,

$$k = k_1 + k_2b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

These conditions tally with those found when X is Cl, Br, or I, and Y = F.

The Reactions between Methyl Chloride and Potassium Iodide and between Methyl Iodide and Potassium Chloride in Aqueous Solution.—The ratio $k_4/k_2 = K$ was first determined for this system by ascertaining the position of the minimum concentration of the halide ion originally present, for two runs started in opposite directions at the same temperature, as described by Moelwyn-Hughes.[10] Values of K thus found were constant to within ±10% while a/b was changed fourfold. The observed values of K at different temperatures in the region where this treatment is applicable are shown in Table 1, where they are compared with values calculated from the equation

TABLE 1.

T (°K)	323·11	333·04	343·70
K (obs.)	0·210	0·211	0·250
K (calc.)	0·205	0·224	0·245

$$K = 3{\cdot}89 \exp(-1900/\boldsymbol{R}T) . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The calculated values of K were used in determining k_2 and k_4 by means of eqn. (1), which yielded reliable results for reactions starting with methyl chloride and potassium iodide. In reactions started with methyl iodide and potassium chloride, hydrolysis is appreciable even in the early stages of the reaction. A typical run is shown in Table 2, the entries in the last column of which were calculated from the equation

TABLE 2.

$a = [CH_3Cl]_0 = 40{\cdot}47$ mmoles/l., $b = [KI]_0 = 80{\cdot}85$ mmoles/l., $T = 333{\cdot}04°$ K, $k_2 = 7{\cdot}55 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$, $k_4 = 1{\cdot}69 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$.

t (min.)	0	40	80	150·5	220	310	∞
x (obs.)	0	4·23	8·47	14·86	19·72	24·12	40·47
x (calc.)	0	4·58	8·90	14·47	19·48	29·40	40·47

$$x = ab/(1 - K)\{\alpha + \beta \coth[(k_2 - k_4)\beta t]\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

k_2 and k_4 were found to vary by ±3% at a given temperature while a/b was varied by a factor of 4. Values at different temperatures are shown in Table 3, together with those calculated from the equations

$$k_2 = 9{\cdot}55 \times 10^9 \exp(-20{,}020/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$k_4 = 4{\cdot}17 \times 10^{10} \exp(-21{,}970/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The standard deviation of the apparent activation energies is ±300 kcal./mole.

TABLE 3.

T (°K)	323·11	333·04	343·70	353·60	366·02
10^4k_2 (l. mole^{-1} sec.$^{-1}$), obs.	2·79	7·51	18·8	37·7	111
,, ,, calc.	2·75	6·92	17·8	40·7	107
10^4k_4 (l. mole^{-1} sec.$^{-1}$), obs.	0·57	1·68	4·60	9·97	31·9
,, ,, calc.	0·59	1·62	4·57	11·2	31·6

The Reaction of Methyl Fluoride with Potassium Iodide, and the Reactions of Potassium Fluoride with Methyl Chloride, Methyl Bromide, and Methyl Iodide in Aqueous Solution.—The reactions

$$CH_3F + I^- \longrightarrow CH_3I + F^-; \quad CH_3Cl + F^- \longrightarrow CH_3F + Cl^-;$$

$$CH_3Br + F^- \longrightarrow CH_3F + Br^-; \text{ and } CH_3I + F^- \longrightarrow CH_3F + I^-$$

were found to be of pseudo-first order. This is so for the first-mentioned reaction because the methyl iodide produced is hydrolysed rapidly enough to keep the concentration of the iodide ion

[10] Moelwyn-Hughes, *J.*, 1938, 779.

effectively constant. In the other three reactions it is necessary to use fluoride ion at a concentration about fifty times that of the methyl halide in order that the ionic exchange should not be masked by hydrolysis. Under these conditions, it is the concentration of fluoride ion which remains appreciably constant. The reaction $CH_3F + I^- \longrightarrow CH_3I + F^-$ was followed by estimation of the acid produced by hydrolysis, which, as is shown below, is approximately equal to the concentration of fluoride ion under the experimental conditions. This reaction showed the greatest deviation of the four from pseudo-first-order kinetics, and, in agreement with eqn. (2), the apparent first-order constant was found to decrease as the reaction proceeded. The results of a typical run for each of the four reactions are shown in Tables 4—7 in which k is the apparent first-order constant governing the production of halide or hydrogen ion.

TABLE 4.

$[CH_3F]_0 = 19{\cdot}2$ mmoles/l., $[KI]_0 = 80{\cdot}04$ mmoles/l., $T = 343{\cdot}54°$ K, $k = 5{\cdot}78 \times 10^{-7}$ sec.$^{-1}$

t (min.)	1,196	5,725	13,078	28,955	69,160
x (obs.)	0·60	3·73	6·79	12·17	15·56
x (calc.)	0·93	3·53	7·03	12·31	17·46

TABLE 5.

$[CH_3Cl]_0 = 16{\cdot}83$ mmoles/l., $[KF]_0 = 971$ mmoles/l., $T = 343{\cdot}74°$ K, $k = 1{\cdot}488 \times 10^{-5}$ sec.$^{-1}$

t (min.)	110	212	310	537	1,265	1,530	1,742
x (obs.)	1·28	2·56	3·72	6·20	11·17	12·46	13·19
x (calc.)	1·22	2·53	3·77	6·16	11·27	12·15	13·19

TABLE 6.

$[CH_3Br]_0 = 29{\cdot}16$ mmoles/l., $[KF]_0 = 971$ mmoles/l., $T = 313{\cdot}28°$ K, $k = 5{\cdot}67 \times 10^{-6}$ sec.$^{-1}$

t (min.)	122	406	1,150	1,380	1,545
x (obs.)	0·74	3·43	9·11	10·66	11·64
x (calc.)	0·76	3·38	9·12	10·64	11·64

TABLE 7.

$[CH_3I]_0 = 19{\cdot}12$ mmoles/l., $[KF]_0 = 942$ mmoles/l., $T = 363{\cdot}86°$K, $k = 4{\cdot}33 \times 10^{-4}$ sec.$^{-1}$

t (min.)	10	20	30	40	50	60	80	215
x (obs.)	2·30	6·50	8·96	11·52	13·02	14·60	16·34	18·86
x (calc.)	2·33	6·17	9·15	11·41	13·19	14·54	16·40	18·90

Values of k, k_1, $[X^-]$, and k_2 for various temperatures are given in Tables 8—11. Values of k_1 in Table 8 were taken from Glew and Moelwyn-Hughes,[4] and in Tables 9—11 from Moelwyn-Hughes.[5] The Arrhenius equations for the variation of k_2 with respect to temperature, and the

TABLE 8. $CH_3F + I^- \longrightarrow CH_3I + F^-$.

T (°K)	10^7k	10^7k_1 (sec.$^{-1}$)	$[I^-]$ (moles/l.)	10^6k_2 (l. mole^{-1} sec.$^{-1}$) obs.	calc.
333·3	13·2	1·24	1·025	1·16	1·25
343·5	5·78	2·59	0·080	4·0	3·52
353·8	99	7·04	1·002	9·2	9·33
363·7	38	18·8	0·080	24	22·8
363·8	228	18·8	1·008	21	23·1

$$k_2 = 1{\cdot}65 \times 10^9 \exp\,(-23{,}060/\boldsymbol{R}T)$$

TABLE 9. $CH_3Cl + F^- \longrightarrow CH_3F + Cl^-$.

T (°K)	10^6k	10^6k_1 (sec.$^{-1}$)	$[F^-]$ (moles/l.)	10^6k_2 (l. mole^{-1} sec.$^{-1}$) obs.	calc.
323·32	13·43	8·60	0·981	4·92	5·25
343·74	148·8	80·6	0·971	70·2	67·6
366·25	1472	765	1·001	707	776

$$k_2 = 7{\cdot}36 \times 10^{11} \exp\,(-26{,}900/\boldsymbol{R}T)$$

TABLE 10. $CH_3Br + F^- \longrightarrow CH_3F + Br^-$.

T (°K)	10^7k	10^7k_1 (sec.$^{-1}$)	$[F^-]$ (moles/l.)	10^7k_2 (l. mole^{-1} sec.$^{-1}$) obs.	calc.
313·28	5·67	3·43	0·971	2·31	2·69
333·14	62·7	35·2	0·915	30·1	27·5
353·53	480	271	0·910	229	263
366·18	1755	903	0·994	857	851

$$k_2 = 9{\cdot}12 \times 10^{11} \exp\,(-25{,}200/\boldsymbol{R}T)$$

values of k_2 at the experimental temperatures calculated therefrom, are also given in Tables 8—11.

TABLE 11. $CH_3I + F^- \longrightarrow CH_3F + I^-$.

T (°K)	10^6k (sec.$^{-1}$)	10^6k_1 (sec.$^{-1}$)	[F$^-$] (moles/l.)	10^6k_2 (l. mole^{-1} sec.$^{-1}$) obs.	calc.
323·74	4·81	2·92	0·863	2·04	2·19
343·74	43·6	27·3	0·842	20·9	19·5
363·86	433	279	0·942	162	163

$k_2 = 2{\cdot}09 \times 10^{11} \exp(-25{,}200/\boldsymbol{R}T)$

TABLE 12. *Constants of the Arrhenius equation* $\log_{10}k_2$ (*l. mole*$^{-1}$ *sec.*$^{-1}$) $= \log_{10} A - E_A/2{\cdot}303\boldsymbol{R}T$ *for substitutions of the methyl halides in water, and calculated values of the energies of activation.*

Reactants	$\log_{10} A$	E_A	E	Reactants	$\log_{10} A$	E_A	E
$CH_3Cl + F^-$	11·9	26·9	25·9	$CH_3F + I^-$	9·1	22·9	17·70
$CH_3Br + F^-$	12·0	25·2	25·8	$CH_3Cl + I^-$	9·9	20·0	17·8
$CH_3I + F^-$	11·3	25·2	25·6	$CH_3Br + I^-$	10·2	18·3 [10]	17·7
				$CH_3I + I^-$	9·5	17·7 [13]	17·5
$CH_3F + Cl^-$	7·7	22·2 [11]	23·7				
$CH_3Br + Cl^-$	12·8	24·7 [12]	23·7	$CH_3F + OH^-$	9·6	21·6 [4]	22·5
$CH_3I + Cl^-$...............	10·6	22·0	23·5	$CH_3Cl + OH^-$.........	12·6	24·3 [14]	22·6
				$CH_3Br + OH^-$	13·0	23·0 [14]	22·6
$CH_3Cl + Br^-$	14·1	27·8 [12]	21·2	$CH_3I + OH^-$	12·1	22·2 [14]	22·3
$CH_3I + Br^-$	9·8	19·3 [10]	20·9				

Discussion.—Reference can be made here to but a few theories. Ogg and Polanyi,[15] in adapting to reactions between ions and polar molecules in solution the theory of Heitler and London [16] for reactions between atoms and non-polar molecules in gases, naturally allowed for the work required to de-solvate the ion, and estimated the energy of activation by finding the point of intersection of the potential energy curves of the systems $CH_3X + Y^-$ and $CH_3Y + X^-$. Their conclusion, which numerically has been confirmed,[17] is that the energy of activation is expended in increasing the bond length of the molecule and in overcoming its intrinsic repulsion to the ion. The idea that activation in these reactions corresponds roughly with the critical interaction energy of an ion-dipole pair has since been more directly expressed,[14] and statistical allowance has been made for the effect of the axially symmetrical field of the dipole on approach of the ion.[18] Despite simplification and improvement, however, and the ease with which steric hindrance effects can be ascribed to additional repulsions, Ogg and Polanyi's theory leads to energies of activations which are far too large, and reflect a dependence on bond energies which is not supported by experiment.

Hurst and Moelwyn-Hughes [19] base their treatment of the gaseous reaction $CH_3X + Y^- \longrightarrow CH_3Y + X^-$ on Born and Heisenberg's theory of polar diatomic molecules.[20] The reacting molecule and ion are regarded as a tripole $[X{\cdot}CH_3{\cdot}Y]^-$, and the reaction as the gradual transference of the electronic charge from X to Y. As in the theories of Heitler and London and of Ogg and Polanyi, only linear combinations are considered. Repulsions are ascribed in part to Coulombic forces, but mainly to intrinsic interactions of closed shells of electrons. Attractions are attributed to Coulombic and polarisation

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[11] Fahim, *Dissertation*, Cambridge, 1955.

[12] Holland, *Dissertation*, Cambridge, 1954.

[13] Swart and LeRoux, *J.*, 1956, 2110.

[14] Moelwyn-Hughes, *Proc. Roy. Soc.*, 1949, *A*, **196**, 540.

[15] Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604.

[16] Heitler and London, *Z. Physik*, 1927, **44**, 457.

[17] Moelwyn-Hughes, *Acta Physicochim. U.S.S.R.*, 1936, **4**, 173.

[18] Kacser, *J. Phys. Chem.*, 1952, **56**, 1101.

[19] 2° *Corso di Chimica, Varenna, Ed. Accademia dei Lincei*, 1957; Hurst, Dissertation, Cambridge, 1948.

[20] Born and Heisenberg, *Ann. Physik*, 1916, **49**, 229.

forces. Numerical constants governing the repulsions and attractions exerted between the three ionic pairs are derived from the polarisabilities and the energies of ionisation of the ions and the dipole moments of the molecules. According to this treatment, no energy of activation is necessary, in the gas, for symmetrical reactions of the type $CH_3X + X^- \longrightarrow CH_3X + X^-$, because the intermediate complex $[X{\cdot}CH_3{\cdot}X]^-$ has less energy, and is therefore more stable, than the isolated pair $X{\cdot}CH_3$ and X^-. If the theory is sound and the numerical constants reliable, it follows, for example, that the replacement $CH_3F + F^- \longrightarrow CH_3F + F^-$ in the gas should take place at every collision, since the critical intermediate $[F{\cdot}CH_3{\cdot}F]^-$ is stable (cf. the stability of the ion $[F{\cdot}H{\cdot}F]^-$). Only highly endothermic substitutions would require an energy of activation. How is it, then, that these reactions in solution are, on the basis of one chemical change for one collision, so slow? It would appear that the rôle of the solvent in reactions between ions and polar molecules is to impede the reaction, and to render measurable in solution a rate which would be immeasurably fast in the gas. This conclusion concerning reactions between ions and polar molecules is sharply contrasted with that reached by Hinshelwood [21] and Moelwyn-Hughes [22] in the many bimolecular reactions which they investigated between electrically uncharged molecules in the gaseous phase and in non-polar solvents.

The theory can be applied without much conjecture or computation.

Each ion in solution, as in crystalline hydrates, is surrounded by solvent molecules, of number c, to which it adheres with a known tenacity. If the chemical reaction of such a solvated ion with a molecule in solution necessitates its partial exposure, it must rid itself of at least one of the solvent molecules forming its sheath, and present itself to the molecule it seeks to attack with only $c - 1$ solvent molecules around it. The ratio of the concentration, n^*, of such partly de-solvated ions to the concentration, n, of completely solvated ions is proportional to the Boltzmann factor $\exp(-\psi^*/\boldsymbol{k}T)/\exp(-\psi/\boldsymbol{k}T) = \exp[-(\psi^* - \psi)/\boldsymbol{k}T]$, where ψ and ψ^* respectively are the energies of interaction of the normal and the activated ion with its solvent neighbours. If c and c^* denote the corresponding co-ordination numbers, and D the energy required to remove one solvent molecule to infinity from its equilibrium position around the ion, then n^*/n is proportional to $\exp[-(c - c^*)D/\boldsymbol{k}T]$. A similar expression holds for the ratio of the concentration of partly de-solvated solute molecules to the total concentration. The rate of reaction is $dn/dt = Zn^*_1n^*_2 = Zn_1n_2\exp\{-[(c_1 - c_1^*)D_1 + (c_2 - c_2^*)D_2]/\boldsymbol{k}T\}$, where Z is proportional to the collision frequency (and is not to be confused with $\boldsymbol{k}T/\boldsymbol{h}$ or any other frequency term which may be applicable to unimolecular reactions). The bimolecular velocity coefficient is then $k_2 = (dn/dt)/n_1n_2 = Z\{\exp - [(c_1 - c_1^*)D_1 + (c_2 - c_2^*)D_2]/\boldsymbol{k}T\}$ and, details being omitted, the true energy of activation, E, becomes

$$E = (c_1 - c^*_1)D_1 + (c_2 - c^*_2)D_2$$

The energy required to deprive an ion of one of its sheath molecules is E_s/c_1, where E_s is the gain in energy when the ion is removed from solution. The values adopted for E_s, in kcals./g.-ion, are 98·6 (F), 66·9 (Cl^-), 58·1 (Br^-), 48·9 (I^-), and 84·4 (OH^-). They have been obtained from recent data published by the National Bureau of Standards,[23] supplemented by the electron affinity of the hydroxyl ion given by Page.[24] We shall assume that only one molecule of solvent need be removed from the sheath about the solute molecule, *i.e.* that $c_2 - c^*_2 = 1$. Then

$$E_1 = E_s(c_1 - c_1^*)/c_1$$

Following Glew and Moelwyn-Hughes,[4] it has been assumed that c^*_1 is 4 when c_1 is 6, and 3

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[21] Hinshelwood, " The Kinetics of Chemical Change in Gaseous Systems," Oxford, 1933, pp. 233—241.

[22] Moelwyn-Hughes, " The Kinetics of Reactions in Solution," Oxford, 1933, pp. 51—73.

[23] National Bureau of Standards Circular 500, Washington D.C., 1952.

[24] Page, *Discuss. Faraday Soc.*, 1955, **19**, 87.

when c_1 is 4. The energy term D_2 can be estimated[4] from the dipole moments of the solute and solvent molecules and the dielectric constant of the solvent:

$$D_2 = 2\left[\mu_l\mu_s\left(\frac{D+2}{9D}\right)\right]^{\frac{3}{2}} . \, A^{-\frac{1}{2}}$$

where $A = 1{\cdot}66 \times 10^{-82}$ erg. cm.[9] Table 12 gives a comparison of observed energies of activation (E_A), in kcal./mole, with those calculated in this way.

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