

**1312.** *The Kinetics of the Reactions Between the Methyl Halides and Potassium Cyanide in Aqueous Solution*

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Methyl fluoride, methyl chloride, and methyl bromide react with the cyanide ion in aqueous solution bimolecularly and irreversibly. In deriving the bimolecular velocity constant,  $k_2$ , allowance must be made for the hydrolysis of both reactants. The constants of the Arrhenius equation,  $k_2 = A \exp(-E_A/RT)$  are derived and discussed.

THE kinetic investigation of the reaction between methyl iodide and potassium cyanide has already been described.<sup>1</sup> This Paper deals with the kinetics of the reactions of potassium cyanide with the other methyl halides. Second-order rate constants for the reactions between the methyl halides and the cyanide ion have been derived by means of kinetic equations which allow for the equilibrium between the cyanide ion and hydrocyanic acid, and for the hydrolyses of the methyl halides by water and by the hydroxide ion. Equilibrium constants calculated for the reactions between the methyl halides and the cyanide ion confirm their effective irreversibility.

EXPERIMENTAL

*Reagents.*—AnalaR potassium cyanide was found to contain 95—96% of the theoretical amount of cyanide as estimated by the method of Liebig and Deniges.<sup>2</sup> A considerable amount of the impurity was absorbed water, which could not be removed by either heating or evacuation, owing to the weakness and volatility of hydrocyanic acid. Purifications by extraction with

<sup>1</sup> B. W. Marshall and E. A. Moelwyn-Hughes, *J.*, 1959, 2640.

<sup>2</sup> I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Interscience, New York, 2nd edn. 1947, vol. II, pp. 282—283.

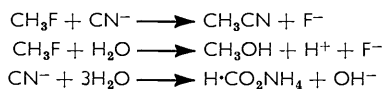
water-free ethanol, followed by washing with ether, and by fractional crystallisation<sup>3</sup> from liquid ammonia raised the cyanide assay to 98 and 99—99.5%, respectively. Kinetic runs carried out with these purified materials and with the untreated AnalaR salt showed no systematic difference in rate constants. The AnalaR reagent was, therefore, used without purification for the remaining kinetic investigations.

Methyl fluoride was prepared and purified by the method described by Farhat-Aziz and Moelwyn-Hughes.<sup>4</sup> Samples of methyl chloride and methyl bromide which had been purified by earlier workers in this Department were used without further purification. The water used as solvent was purified as previously described.<sup>1</sup> Solutions of the gaseous methyl halides were made by the use of a simple gas burette and solubility pipette. No attempt was made to estimate the concentration of methyl halide from the volume of gas dissolved, as it was more conveniently measured by determining the concentration of halide ion after samples had been allowed to react to completion.

*Methods of Analysis.*—The methods already described<sup>1</sup> were used to estimate the concentrations of free cyanide and of the halide ion in the runs on methyl chloride and methyl bromide. The technique advocated by Bullock and Kirk<sup>5</sup> was used to increase the sensitivity of the argentometric determination of the chloride ion with dichlorofluorescein as indicator.

The runs on the reaction between methyl fluoride and potassium cyanide were followed initially by the estimation of the cyanide ion by the method described earlier,<sup>1</sup> and by the determination of fluoride by titration with thorium nitrate.<sup>6</sup> The reproducibility of the latter analysis was found to be poor for solutions containing less than 10 mmoles/l. of fluoride ion, and an indirect analysis was used in later runs. The titration with thorium nitrate was used only for the estimation of the concentration of fluoride ion after reactions had been taken to completion in sealed ampoules in an oven at 100°. The indirect analysis estimated both cyanide ion and fluoride ion concentrations by a titration which measured both free cyanide and total alkali, including cyanide. The analysis, described by Kolthoff and Stenger,<sup>7</sup> depends on the weakness of hydrocyanic acid and the stability of undissociated mercuric cyanide in aqueous solution.

Consideration of the reaction scheme,



shows that the change in total alkali, including cyanide, is equivalent to the amount of fluoride ion liberated, so that the analysis estimates free cyanide, fluoride ion, and free alkali. The buffering actions of the fluoride and formate ions introduce a minor error in the titration of total alkali. Corrections were made for this error by calculating the amount of acid required to bring formate and fluoride solutions to pH 5, using values of the acid dissociation constants at 25° given by Robinson and Stokes.<sup>8</sup>

## RESULTS

*The Equilibria of the Methyl Halide-Cyanide Reactions.*—The heats of reaction and entropy changes of the reaction in aqueous solution between the methyl halides and the cyanide ion in hypothetical standard states of unit molality have been calculated from the thermodynamic properties of the reactants and products. The heats absorbed during the standard formation, and the entropies at hypothetical unit molality of the cyanide and halide ions have been provisionally accepted as those compiled by the National Bureau of Standards,<sup>9</sup> with the convention that the standard molar entropy,  $S^\circ$ , and heat  $\Delta H_f^\circ$  absorbed during formation of the hydrogen ion in aqueous solution at 25° are both zero. Long's calculated value of  $\Delta H_f^\circ$  for

<sup>3</sup> Hackspill and R. Grandadam, *Ann. Chim. (France)*, 1926, **5**, 218.

<sup>4</sup> Farhat-Aziz and E. A. Moelwyn-Hughes, *J.*, 1961, 1523.

<sup>5</sup> B. Bullock and P. L. Kirk, *Ind. Eng. Chem. Analyt.*, 1935, **7**, 178.

<sup>6</sup> A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, London, 2nd edn., 1951, 393.

<sup>7</sup> I. M. Kolthoff and V. A. Stenger, ref. 2, p. 204.

<sup>8</sup> R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959, pp. 390, 519.

<sup>9</sup> National Bureau of Standards, Circular 500, Washington D.C., 1952.

acetonitrile in the gaseous phase was used.<sup>10</sup> The difference between the value of 18°, the quoted temperature, and at 25° is negligible. Our calculated value of  $S^\circ$  for acetonitrile in the gaseous phase at 25° and atmospheric pressure confirms the value calculated by Thompson<sup>11</sup> using slightly different spectroscopic constants. The data of Hartley, Pritchard, and Skinner,<sup>12</sup> of Carson, Carson, and Wilmhurst,<sup>13</sup> and those cited by Bichowsky and Rossini<sup>14</sup> and by the National Bureau of Standards,<sup>9</sup> have been used to determine  $\Delta H_f^\circ$  for methyl chloride, methyl bromide, and methyl iodide in the gaseous state.

$\Delta H_f^\circ$  for methyl fluoride is not known, but an estimate may be computed from the known values of  $\Delta H_f^\circ$  for fluoroethanol, fluoroacetamide, fluoroacetic acid, and the corresponding unfluorinated compounds, on the assumption that the heat of dissociation of the C-F bond in the molecule, R-F, is independent of the nature of the aliphatic radical, R. The values of  $\Delta H_f^\circ$  (25°) calculated in this way for methyl fluoride are -59.5, -57.6, and -59.6 kcal./mole, respectively. We accept the value of  $\Delta H_f^\circ$  (25°) = -58.8 kcal./mole, which agrees well with that estimated by Luft<sup>15</sup> from electron impact measurements, and with the approximate value of -60 kcal./mole derived spectroscopically by Margrave.<sup>16</sup>

The heats of escape of the methyl halides from aqueous solutions at 25°, and the  $S^\circ$  values in solution in a standard state of hypothetical unit molality have been calculated by Glew and Moelwyn-Hughes<sup>17</sup> from measurements of their solubilities in water at various temperatures. The same properties have been calculated for acetonitrile in aqueous solution from the vapour pressure of pure acetonitrile and Griessbach-Vierk's<sup>18</sup> measurements on the vapour-liquid equilibria of the acetonitrile-water system.

TABLE I

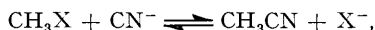
Thermodynamic properties of the reactants and resultants in the standard gaseous (hypothetical 1 atm.) and dissolved (hypothetical 1M) aqueous states at 25°. Heats in kcal./mole; entropies in cal./mole-degree

X	F	Cl	Br	I	CN
$\Delta H_f^\circ(\text{CH}_3\text{X}, \text{gas})$	-58.8	-19.9	-8.5	+4.9	+19.8
$\Delta H_{\text{escape}}(\text{CH}_3\text{X}, \text{aq} \longrightarrow \text{CH}_3\text{X}, \text{gas})$	4.4	5.67	6.28	6.36	6.37
$\Delta H_f^\circ(\text{CH}_3\text{X}, \text{aq})$	-63.2	-25.57	-14.78	-1.46	+13.43
$S^\circ(\text{CH}_3\text{X}, \text{aq})$	32.9	32.52	34.09	36.19	43.64
$\Delta H_f^\circ(\text{X}^-, \text{aq})$	-79.5	-40.02	-28.9	-13.37	+36.1
$S^\circ(\text{X}^-, \text{aq})$	-2.3	13.17	19.29	26.14	28.2

The thermodynamic properties of the reactants and products are summarised in Table 1. The equilibrium data calculated for the reactions between the methyl halides and the cyanide ion (Table 2) show that the reactions in water are highly exothermic and effectively irreversible.

TABLE 2

Calculated values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reactions,



in aqueous solutions at 25° in a standard state of hypothetical unit molality

$$K = [\text{CH}_3\text{CN}] [\text{X}^-] / [\text{CH}_3\text{X}] [\text{CN}^-]$$

X	$\Delta H^\circ$ (kcal./mole)	$\Delta S^\circ$ (cal. mole <sup>-1</sup> deg. <sup>-1</sup> )	$10^{-26}K$ at 25°
F	-38.97	-19.76	0.018
Cl	-37.12	-3.91	2.3
Br	-36.79	+0.64	13
I	-34.58	+5.39	3.5

<sup>10</sup> L. H. Long, *Proc. Roy. Soc.*, 1949, **A**, 198, 60.

<sup>11</sup> H. W. Thompson, *Trans. Faraday Soc.*, 1941, **37**, 344.

<sup>12</sup> K. Hartley, H. O. Pritchard, and H. A. Skinner, *Trans. Faraday Soc.*, 1950, **46**, 1019.

<sup>13</sup> A. S. Carson, E. M. Carson, and B. Wilmhurst, *Nature*, 1952, **170**, 320.

<sup>14</sup> F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold, New York, 1932.

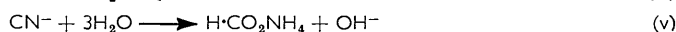
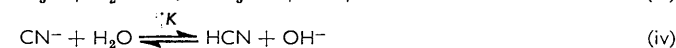
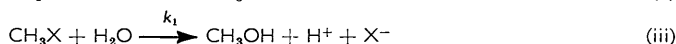
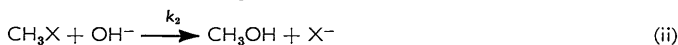
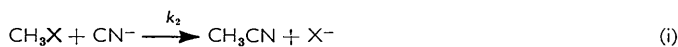
<sup>15</sup> N. W. Luft, *J. Chem. Phys.*, 1955, **23**, 973.

<sup>16</sup> J. L. Margrave, *J. Chem. Phys.*, 1956, **24**, 475.

<sup>17</sup> D. N. Glew and E. A. Moelwyn-Hughes, *Discuss. Faraday Soc.*, 1953, **15**, 150.

<sup>18</sup> A. L. Griessbach-Vierk, *Z. anorg. Chem.*, 1950, **261**, 279.

*Kinetic Scheme.*—It is assumed that the rate of reaction of the methyl halide with hydrocyanic acid is so much slower than that of the reaction with the cyanide ion that it may be ignored. This assumption may be justified by comparing these reactions with the hydrolyses of the methyl halides. The rates of reaction of the methyl halides with water and with the hydroxide ion indicate that at similar concentrations the anion reacts  $10^3$ – $10^4$  times as fast as the neutral molecule. The significant reactions are:



The formation of methyl isocyanide has been excluded from the scheme for reasons given earlier.<sup>4</sup> The rate constants of the hydrolyses of the methyl halides have been interpolated from the data of Moelwyn-Hughes,<sup>19</sup> of Glew and Moelwyn-Hughes,<sup>20</sup> and of Heppollette and Robertson.<sup>21</sup> The equilibrium (iv) was assumed to be maintained throughout any kinetic run. Values of the hydrolysis constant,  $K = [\text{HCN}][\text{OH}^-]/[\text{CN}^-]$ , calculated from the data of Madsen<sup>22</sup> and of Brown and Cranston,<sup>23</sup> could be fitted to the equation,  $\log_{10} K$  (moles/l.) =  $-2.274 - 757.2/T$  ( $^{\circ}\text{K}$ ).

Observed and calculated values of  $K$  are given in Table 3.

TABLE 3  
 $K = [\text{HCN}][\text{OH}^-]/[\text{CN}^-]$  (moles/l.)

$T$ ( $^{\circ}\text{C}$ ) .....	10.3	15.00	16.20	25.05	41.80	42.50
$10^3 K$ (obs.) (moles/l.) .....	1.13	1.27	1.28	1.54	2.05	2.16
$10^3 K$ (calc.) (moles/l.) .....	1.13	1.25	1.29	1.55	2.10	2.12

It was found in the kinetic studies of the reactions of methyl bromide and iodide that the rates of liberation of halide ion and of consumption of cyanide were almost equal. Comparison of the rates of the hydrolyses of methyl bromide with the rates of the exchange reaction showed that only the neutral hydrolysis need be considered. The equation for the rate of production of halide ion may be formulated as follows;

$$d[\text{X}^-]/dt = k_2[\text{CH}_3\text{X}][\text{CN}^-] + k_1[\text{CH}_3\text{X}] \quad (1)$$

$$[\text{CH}_3\text{X}]_0 = a, [\text{CH}_3\text{X}]_t = a - x, [\text{X}^-]_t = x$$

$$[\text{KCN}]_0 = b, [\text{KCN}]_t \simeq b - x$$

$$[\text{HCN}]_t \simeq [\text{OH}^-]_t \simeq K^{\frac{1}{2}} \cdot [\text{CN}^-]^{\frac{1}{2}} \simeq K^{\frac{1}{2}} \cdot (b - x)^{\frac{1}{2}}$$

$$[\text{CN}^-]_t \simeq b - x - K^{\frac{1}{2}} \cdot (b - x)^{\frac{1}{2}}$$

Then 
$$dx/dt \simeq k_2 \cdot (a - x) [(b - x) + (k_1/k_2) - K^{\frac{1}{2}} \cdot (b - x)^{\frac{1}{2}}] \quad (2)$$

This equation may be simplified by substituting  $B - k_1/k_2$  for  $b$ , and by ignoring  $B - b$  in the correction term for the hydrolysis of the cyanide ion. This expedient is justified by the smallness of the correction term and of  $k_1/k_2$ . Then,  $dx/dt = k_2(a - x)[B - x - K^{\frac{1}{2}}(B - x)^{\frac{1}{2}}]$ , which may be integrated to give,

$$k_2 t = [1/(B - a - K^{\frac{1}{2}})] \{ \log_e [a/(a - x)] + 2 \cdot \log_e [(z - K^{\frac{1}{2}})/(z_0 - K^{\frac{1}{2}})] + [K/(B - a)]^{\frac{1}{2}} \cdot \log_e [(z_0 - z_{\infty}) \cdot (z + z_{\infty})/(z - z_{\infty}) \cdot (z_0 + z_{\infty})] \} \quad (3)$$

where  $z_0 = B^{\frac{1}{2}}$ ,  $z = (B - x)^{\frac{1}{2}}$ , and  $z_{\infty} = (B - a)^{\frac{1}{2}}$ .

<sup>19</sup> E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1949, *A*, **196**, 540.

<sup>20</sup> D. N. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1952, *A*, **211**, 254.

<sup>21</sup> R. L. Heppollette and R. E. Robertson, *Proc. Roy. Soc.*, 1959, *A*, **252**, 273.

<sup>22</sup> E. H. Madsen, *Z. phys. Chem.*, 1901, **36**, 290.

<sup>23</sup> H. F. Brown and J. A. Cranston, *J.*, 1940, **578**.

The earlier work on methyl iodide<sup>1</sup> was re-interpreted on the assumption that the first-order hydrolysis of this molecule was negligible, and equation (3) was used with  $B$  replaced by  $b$ . The complete equation was used to interpret the work on methyl bromide. The first approximate estimate of  $k_2$ , necessary for estimating  $B$ , was found by fitting the experimental results to the ordinary integrated form of the second-order rate equation.

$$k_2 t = [1/(b - a)] \cdot \log_e [a(b - x)/b(a - x)] \quad (4)$$

The interpretation of the results of the kinetic studies on methyl chloride allowed for both reactions (ii) and (iii). The difference between the estimated amounts of chloride ion liberated and cyanide consumed seldom exceeded 0.5 mmole/l., which is about 5% of the total halide concentration, and a correction was applied to equation (3) to allow for the effect of reaction (iii). The rate of hydrolysis of methyl chloride was described by the equation,

$$\begin{aligned} d[\text{CH}_3\text{OH}]/dt &= k_1 [\text{CH}_3\text{Cl}] + k_2' [\text{CH}_3\text{Cl}] [\text{OH}^-], \\ &= (k_1 + k_2' [\text{OH}^-]) \cdot [\text{CH}_3\text{Cl}] \end{aligned} \quad (5)$$

The change in hydroxide ion concentration in the course of a run was small and a pseudo-first-order rate constant was calculated from equation (5),

$$k_1' \simeq k_1 + k_2' [\text{OH}^-]_{\text{mean}}$$

This constant was used to replace  $k_1$  in equation (4).

The differential form of the rate equation,

$$d[\text{X}^-]/dt = k_2 [\text{CH}_3\text{X}] [\text{CN}^-] + k_1 [\text{CH}_3\text{X}] + k_2' [\text{CH}_3\text{X}] [\text{OH}^-] \quad (6)$$

was used to determine the rate constant for the reaction between methyl fluoride and the cyanide ion. In this case the integrated form of the rate equation could not be used since reaction (v) became significant, and led to substantial differences between the rates of consumption of cyanide ion and of liberation of fluoride ion. Graphs of the halide ion concentration were plotted against time and tangents were drawn to estimate  $d[\text{X}^-]/dt$ . Values of the concentrations of cyanide ion and hydroxide ion were estimated from the measured concentrations of potassium cyanide and fluoride ion.

Rate constants were calculated from equation 4 by a linear plot of the right-hand side of this equation against time. Typical results are given in Tables 4—6. The results at various temperatures fitted to the Arrhenius equation by the method of least squares are summarised in Tables 7—10, where errors are stated as standard deviations.

TABLE 4  
CH<sub>3</sub>F and KCN  
 $T = 343.40^\circ\text{K}$

$$10^7 k_1 = 2.75 \text{ sec.}^{-1}; \quad 10^5 k_2' = 7.2 \text{ l. mole}^{-1} \text{ sec.}^{-1}.$$

$10^3 d[\text{F}^-]/dt$ (mmoles l. <sup>-1</sup> min. <sup>-1</sup> )	$[\text{CH}_3\text{F}]$	$[\text{CN}^-]$ (mmoles/l.)	$[\text{OH}^-]$	$10^4 k_2$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )
6.45	11.42	32.44	2.30	2.76
4.14	8.32	27.88	4.20	2.76
2.71	6.28	24.38	5.74	2.66
2.23	5.30	22.51	6.64	2.78
			Mean	2.74

$k_2$  (uncorr. for solvent expansion) =  $2.74 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>;  $k_2$  (corr. for solvent expansion) =  $2.80 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. The correction for solvent expansion is applied to allow for the difference between concentrations measured at 20° and actual concentrations at a reaction temperature.

TABLE 5  
CH<sub>3</sub>Cl and KCN  
T = 328.23°K

$[\text{HCN}]_{\text{mean}} = 1.14$  mmoles/l. =  $[\text{OH}^-]_{\text{mean}}$ .  $10^6 k_1 = 1.4$  sec.<sup>-1</sup>;  $10^4 k_2' = 2.8$  l./mole<sup>-1</sup> sec.<sup>-1</sup>.  $[\text{KCN}]_0 = b = 66.40$  mmoles/l.;  $B' = 66.55$  mmoles/l.

All concentrations in mmoles/l. at 20°.

Time (min.)	0.0	32.9	53.0	80.0	125	160	200	280	364
$a - x$	35.58	30.40	27.52	23.94	20.35	17.76	15.31	11.40	8.93
$a - x$ (calc.)		30.33	27.57	24.49	20.41	17.75	15.30	11.61	8.80

$k_2$  (uncorr.) =  $1.298 \times 10^{-3}$  l./mole<sup>-1</sup> sec.<sup>-1</sup>.  $k_2$  (corr. for solvent expansion) =  $1.315$  l. mole<sup>-1</sup> sec.

TABLE 6

$10^5 K = 1.96$  moles/l.;  $T = 311.14^\circ K$ ;  $k_1 = 2.61 \times 10^{-6}$  sec.<sup>-1</sup>.

Time (min.)	0.00	42.05	62.20	84.95	108.0	130.3	151.0	171	196
$a - x$	12.26	8.16	6.76	5.57	4.47	3.79	3.16	2.71	2.11
$a - x$ (calc.)		8.14	6.74	5.46	4.55	3.75	3.16	2.68	2.23

$k_2$  (equation 3, corr. for solvent expansion) =  $5.51 \times 10^{-3}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

TABLE 7

Reaction between methyl fluoride and the cyanide ion

$\log_{10} k_2$  l. mole<sup>-1</sup> sec.<sup>-1</sup> =  $11.05 \pm 0.63 - (23 \pm 1.0) \times 10^3/2.303RT$

T (°K)	343.40	353.36	360.99	366.28
$10^4 k_2$ (obs.)	2.72	6.09	14.7	21.8
$10^4 k_2$ (calc.)	2.66	6.85	13.7	21.8

TABLE 8

Reaction between methyl chloride and the cyanide ion

$\log_{10} k_2$  (l. mole<sup>-1</sup> sec.<sup>-1</sup>) =  $11.50 \pm 0.19 - (21.56 \pm 0.3) \times 10^3/2.303RT$

T (°K)	307.77	317.36	322.58	328.23	334.97	340.44	348.50
$10^4 k_2$ (obs.)	1.64	4.49	7.60	13.33	25.9	46.7	97.6
$10^4 k_2$ (calc.)	1.54	4.46	7.75	13.85	26.9	45.3	97.0

TABLE 9

Reaction between methyl bromide and the cyanide ion

$\log_{10} k_2$  (l. mole<sup>-1</sup> sec.<sup>-1</sup>) =  $12.27 \pm 0.17 - (20.7 \pm 0.23) \times 10^3/2.303RT$

T (°K)	279.59	284.38	291.46	298.61	307.30	311.14	313.48	320.56
$10^3 k_2$ (obs.)	0.120	0.223	0.601	1.37	3.76	5.54	7.35	13.7
$10^3 k_2$ (calc.)	0.124	0.233	0.567	1.335	3.58	5.44	6.98	14.5

TABLE 10

The reaction between methyl iodide and the cyanide ion

$\log_{10} k_2$  (l. mole<sup>-1</sup> sec.<sup>-1</sup>) =  $11.78 \pm 0.08 - (20.47 \pm 0.12)/2.303RT$

T (°K)	293.26	300.05	305.32	309.87	314.40	318.46	323.00	327.43
$10^4 k_2$ (obs.)	3.33	7.26	13.9	22.4	35.0	52.7	86.2	133.7
$10^4 k_2$ (calc.)	3.33	7.46	13.5	22.1	35.5	53.9	84.8	130.3

## DISCUSSION

The Arrhenius energies of activation of the reactions between the methyl halides and the cyanide ion vary in the same direction as the bond strengths of the molecules, CH<sub>3</sub>F > CH<sub>3</sub>Cl > CH<sub>3</sub>Br > CH<sub>3</sub>I, but the variation is very small. The present result and those of certain other kinetic studies are summarised in Table 11.

The constants in Table 12 have been derived from the data of Table 2. The energies of activation for the reactions of methyl chloride, bromide, and iodide with any given anion seem to vary in such a way as to suggest that the energy of activation contains a term specific to the methyl halide. No such regularity is found in the reactions of methyl fluoride. Though its reactions are very much slower than those of the other methyl halides, the present work and that of Bathgate and Moelwyn-Hughes<sup>24</sup> indicate that this

TABLE 11

$$\log_{10} k_2 \text{ (l. mole}^{-1} \text{ sec.}^{-1}\text{)} = \log_{10} A - E_A/2.303RT$$

Reactants	Ref.	$\log_{10} A$	$E$ (kcal./mole)	$10^6 k_2$ (25°)
CH <sub>3</sub> F + CN <sup>-</sup> .....	This work	11.05 ± 0.63	23 ± 1	1.6 ± 0.37
CH <sub>3</sub> Cl + CN <sup>-</sup> .....	This work	11.50 ± 0.19	21.56 ± 0.3	49 ± 3
CH <sub>3</sub> Br + CN <sup>-</sup> .....	This work	12.27 ± 0.17	20.7 ± 0.23	1,260 ± 50
CH <sub>3</sub> I + CN <sup>-</sup> .....		11.78 ± 0.08	20.47 ± 0.12	590 ± 12
$10^7 k_2$ (25°)				
CH <sub>3</sub> Cl + F <sup>-</sup> .....	24	11.87 ± 0.31	26.9 ± 0.5	0.125 ± 0.017
CH <sub>3</sub> Br + F <sup>-</sup> .....	24	11.96 ± 0.32	25.2 ± 0.5	2.74 ± 0.23
CH <sub>3</sub> I + F <sup>-</sup> .....	24	11.32 ± 0.32	25.2 ± 0.5	0.69 ± 0.06
$10^8 k_2$ (25°)				
CH <sub>3</sub> F + Cl <sup>-</sup> .....	25	7.7 ± 1.1	22.2 ± 2	0.3
CH <sub>3</sub> Br + Cl <sup>-</sup> .....	26	11.8 ± 1.4	24.7 ± 1.9	470
CH <sub>3</sub> I + Cl <sup>-</sup> .....	24	10.62 ± 0.22	21.97 ± 0.34	312
CH <sub>3</sub> Cl + Br <sup>-</sup> .....	26	14.1 ± 1.3	27.8 ± 2.2	0.5
CH <sub>3</sub> I + Br <sup>-</sup> .....	27	9.78 ± 0.3	19.31 ± 0.5	43
CH <sub>3</sub> F + I <sup>-</sup> .....	24	9.07 ± 0.19	22.86 ± 0.3	0.02
CH <sub>3</sub> Cl + I <sup>-</sup> .....	24	9.98 ± 0.22	20.02 ± 0.34	20
CH <sub>3</sub> Br + I <sup>-</sup> .....	27	10.23 ± 0.1	18.26 ± 0.13	690
CH <sub>3</sub> I + I <sup>-</sup> .....	28	9.97 ± 0.15	18.1 ± 0.2	485
CH <sub>3</sub> F + OH <sup>-</sup> .....	20	9.61	21.6 ± 0.1	0.6
CH <sub>3</sub> Cl + OH <sup>-</sup> .....	19	12.61	24.28 ± 0.12	7.0
CH <sub>3</sub> Br + OH <sup>-</sup> .....	19	13.02	2.3.0 ± 0.15	150
CH <sub>3</sub> I + OH <sup>-</sup> .....	19	12.09	22.22 ± 0.23	67

TABLE 12

Reactants	$\log_{10} A$	$E$	$10^{30} k_{25}$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )
CH <sub>3</sub> CN + F <sup>-</sup> .....	15.37	62.0	5.4
CH <sub>3</sub> CN + Cl <sup>-</sup> .....	12.35	58.7	1.0
CH <sub>3</sub> CN + Br <sup>-</sup> .....	12.13	57.5	4.3
CH <sub>3</sub> CN + I <sup>-</sup> .....	10.60	55.1	6.6

appears to be due to a higher activation energy, whilst the data of Glew and Moelwyn-Hughes<sup>20</sup> and of Fahim<sup>25</sup> suggest that the slowness of the reactions of methyl fluoride with the chloride and hydroxide ions is due to an abnormally low pre-exponential term.

A complete theory of ionic exchange reactions in solution requires detailed knowledge of the influence of solvation on the energies of the reactants and the critically activated complex. Ogg and Polanyi<sup>29</sup> have calculated energies of activation for the reactions of the methyl halides in acetone solution on the assumption that the influence of solvation is small. Hurst and Moelwyn-Hughes,<sup>30</sup> in a more detailed set of calculations, found that the ion, Y<sup>-</sup> ··· CH<sub>3</sub><sup>+</sup> ··· X<sup>-</sup>, was stable with respect to the isolated methyl halide and anion in the gaseous phase. This led to the suggestion that the energies of activation of the ionic exchange reactions of the methyl halides in aqueous solution were closely related to, if not completely dependent on, the solvation energies of the reactants. The direct calculation of energies of activation from experimental heats of solvation has been shown by Bathgate and Moelwyn-Hughes<sup>24</sup> to lead to reasonable agreement between the observed and calculated activation energies for the reactions of the methyl halides with the halide ions. This agreement, however, must be regarded as fortuitous, since the application of

<sup>24</sup> R. H. Bathgate and E. A. Moelwyn-Hughes, *J.*, 1959, 2647.

<sup>25</sup> R. B. Fahim, Thesis, Cambridge, 1954.

<sup>26</sup> H. G. Holland, Thesis, Cambridge, 1954.

<sup>27</sup> E. A. Moelwyn-Hughes, *J.*, 1938, 779.

<sup>28</sup> E. R. Swart and L. J. LeRoux, *J.*, 1957, 409.

<sup>29</sup> R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604.

<sup>30</sup> R. Hurst and E. A. Moelwyn-Hughes, *Accademia Nazionale dei Lincei*, 11° Corso Estivodi Chimica, Varenna, 1957, 85.

their method to the reactions  $\text{CH}_3\text{CN} + \text{X}^- \longrightarrow \text{CH}_3\text{X} + \text{CN}^-$ , would lead to energies of activation of approximately 20 kcal./mole, which is only one-third of the experimental value (Table 12). By taking account of the heats of reaction it is possible to remove this inconsistency, since the desolvated state of highest energy may be regarded as the critically activated state. Energies of activation calculated in this way differ but slightly from the values calculated by Bathgate and Moelwyn-Hughes.

From the data of Table 1 and the heats of escape of the ions from water to the gas phase, the difference between  $\Delta H$  for the reactions  $\text{CH}_3\text{X} + \text{Y}^- \rightleftharpoons \text{CH}_3\text{Y} + \text{X}^-$  may be found (column 5 of Table 13). Recent assignments of the heats of escape by Halliwell and Nyburg<sup>31</sup> are considerably higher than those used here, but the difference between the heats of escape of a pair of ions is not greatly altered. The values of  $\Delta H_{\text{gas}}$  (column 7) estimated here are, with the exception of the first entry, about 10 kcal. less than those

TABLE 13

$\Delta H^\circ$  (kcal./mole) for the reactions  $\text{CH}_3\text{X} + \text{Y}^- \rightleftharpoons \text{CH}_3\text{Y} + \text{X}^-$  in aqueous solution and in the gas phase

X <sup>-</sup>	Y <sup>-</sup>	$\Delta H_{\text{escape}}$		$\Delta H^\circ_{\text{gas}} - \Delta H_{\text{aq.}}$	$\Delta H^\circ_{\text{aq.}}$	$\Delta H^\circ_{\text{gas}}$
		X <sup>-</sup>	Y <sup>-</sup>			
F	CN	109	67.5	43.5	-39.0	4.5
Cl	CN	77	67.5	10.2	-37.1	-27.0
Br	CN	69	67.5	1.7	-36.8	-35.1
I	CN	60	67.5	-7.5	-34.6	-42.1
Cl	F	77	109	-33.3	+1.9	-31.4
Br	F	69	109	-41.9	2.2	-39.7
I	F	60	109	-51.0	4.4	-55.4
Br	Cl	69	77	-8.6	0.3	-8.3
I	Cl	60	77	-17.7	2.5	-15.2
I	Br	60	69	-9.1	2.2	-6.9

found by using the bond energies and electron affinities adopted elsewhere.<sup>32</sup> The fifth column shows the very considerable difference between  $\Delta H$  for these reactions in the gas phase and in solution. Comparable differences are to be expected in the energies of activation, but, though solvation is a significant factor, it seems at present impossible to decide what fraction of the activation energy is to be attributed to the energy required for partial desolvation of the reactants.

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<sup>31</sup> H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, 1963, **59**, 1126.

<sup>32</sup> E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon, 2nd Revised edn., 1964.