

### 333. Kinetics of Slow Reactions, and their Entropy Changes.

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THE marked solvent effect on the rates of certain reactions has been associated with the contrast in the polar nature of the reagents and products (Richardson and Soper, *J.*, 1929, 1873; Soper and Williams, *ibid.*, 1931, 2297; *Proc. Roy. Soc.*, 1933, *A*, 140, 58; Roberts and Soper, *ibid.*, p. 71; Jones and Soper, *ibid.*, 1934, *A*, 144, 643), and the idea has been advanced that the solvent may exert this effect by causing an alteration in the fraction of critical complexes which break down to form the reaction products.

When the phase changes of metastable substances were considered by Robinson (*J. Physical Chem.*, 1930, **34**, 208), a rule was found governing which of alternative products appears first. This was that the substance changes into the form of highest thermodynamic probability, *i.e.*, of highest entropy content—a conclusion of interest in connexion with the decomposition of the critical complex. On the hypothesis that the decomposition of the critical complex into the products is proportional to the relative thermodynamic probabilities,  $W_x$  and  $W_2$ , of the two states, the rate of decomposition will vary as  $W_2/W_x = e^{(S_2^0 - S_x)/R}$ , since  $R \log_e W = S$ . Here  $S_2^0$  refers to the entropy of the products at unit concentration. The corresponding rate of decomposition of the critical complex into the reagents will be given by  $e^{(S_1^0 - S_x)/R}$ . Hence the fraction of critical complexes which break up to form the products is given by

$$\frac{e^{(S_2^0 - S_x)/R}}{e^{(S_2^0 - S_x)/R} + e^{(S_1^0 - S_x)/R}} = \frac{e^{S_2^0/R}}{e^{S_2^0/R} + e^{S_1^0/R}}$$

and the velocity coefficient of formation of products by the product of this factor and the rate of activation, *i.e.*, by

$$k_1 = C e^{(H_1 - H_x)/RT} e^{S_2^0/R} (e^{S_2^0/R} + e^{S_1^0/R})$$

where  $H$  represents heat content. This equation is of correct thermodynamic form, although it does not include an entropy of activation (Scheffer and Konstamm, *Verslag. Akad. Wetensch. Amsterdam*, 1911, **19**, 878; La Mer, *J. Chem. Phys.*, 1933, **1**, 289). This may be demonstrated by writing the analogous equation for the reverse reaction:

$$k_2 = C e^{(H_2 - H_x)/RT} e^{S_1^0/R} / (e^{S_1^0/R} + e^{S_2^0/R})$$

whence the equilibrium constant  $K = k_1/k_2 = e^{[(H_1 - TS_1^0) - (H_2 - TS_2^0)]/RT} = e^{(F_1^0 - F_2^0)/RT}$ , where  $F^0$  refers to molar free energies at unit concentration.

The result of the introduction of this break-up factor into the velocity equation is that the latter assumes two forms according as the reaction is attended by an entropy increase or decrease. If the reaction is of the first type,  $S_2^0 > S_1^0$ , and the expression  $e^{S_2^0/R} / (e^{S_2^0/R} + e^{S_1^0/R})$  is close to unity and has little effect on the calculated rate of reaction. If, however, it is of the second type, the expression becomes approximately  $e^{(S_2^0 - S_1^0)/R}$  and may be several powers of ten less than unity. The introduction of this factor will therefore affect only those reactions attended by an entropy decrease. It is thus possible to test the hypothesis concerning the break-up of the critical complex by examining the entropy changes of normal and of slow reactions.

*Quaternary ammonium salt formations.* These reactions are abnormal in the sense that  $P$ , in the equation  $k = PZ e^{-E/RT}$ , is of the order  $10^{-4}$  to  $10^{-9}$ . They are typical slow reactions. The entropy changes are unknown except for the interaction of dimethylaniline

and methyl iodide (Essex and Gelormini, *J. Amer. Chem. Soc.*, 1926, **48**, 882), where the equilibrium constant was measured at two temperatures. These measurements give  $\Delta H$  and  $\Delta F$  and an entropy decrease of 37 units for the formation of the salt. The value of the proposed factor is  $e^{S_2^{\circ}/R}/(e^{S_2^{\circ}/R} + e^{S_1^{\circ}/R}) = e^{-37/R} = 0.9 \times 10^{-8}$ .  $P$  has been determined for this reaction (Moelwyn-Hughes, "Kinetics of Reaction in Solution," Oxford, 1933, 111) and equals  $0.5 \times 10^{-7}$ . The value assigned to the entropy decrease depends, however, on only two values of the equilibrium constant.

*Saponification of esters.* Essex and Clark (*J. Amer. Chem. Soc.*, 1932, **54**, 1290) give for the reaction  $\text{AcOEt} + \text{H}_2\text{O} = \text{AcOH} + \text{EtOH}$  (all liquid),  $\Delta H = -4795.0$ . From the changes in heat content on solution in water (I.C.T., **5**, 148),  $\Delta H = 4,513$  cal. for the reaction in aqueous solution. The gaseous equilibrium has been investigated, but the free energies of solution of the components in water are not known. The value, 0.25, for the equilibrium constant in the mixed liquids has therefore been taken, giving  $\Delta F = 822$  cal. and  $\Delta S = -17.9$  units. The entropy changes on ionisation of water and of acetic acid are calculated as  $-23.5$  and  $-20.7$  units respectively, and hence the entropy change for the saponification of ethyl acetate,  $\text{CH}_3\cdot\text{CO}_2\text{Et} + \text{OH}' = \text{CH}_3\cdot\text{CO}_2' + \text{EtOH}$ , is  $-15.1$  units, corresponding to a break-up factor of  $5 \times 10^{-4}$ .  $P$  for this reaction (Moelwyn-Hughes, *op. cit.*, p. 57) is approximately  $2 \times 10^{-5}$ .

*Interaction of chlorine and phenolic ethers.* The rates and critical increments of a large number of these reactions have been measured in acetic acid by Bradfield and Jones (*J.*, 1928, 1006, 3073; 1931, 2903, 2907), and the velocity coefficients may be expressed by  $k = 2.7 \times 10^6 \cdot e^{-E/RT}$ . The velocity coefficient depends only on changes in the energy of activation. Roberts and Soper (*loc. cit.*) have suggested that the constancy of the non-exponential term may be due to a constant degree of resolution of critical complexes into the products, determined by the fact that the substances of contrasted physical properties, *viz.*, hydrogen chloride and chlorine, are common to all chlorinations. No data exist for the relative entropies of a phenolic ether and of its chloro-derivative, but the entropies of chlorine and hydrogen chloride are known, and it is plausible that the entropy change of the group of reactions is mainly determined by the entropies of these latter. The entropies of gaseous chlorine and hydrogen chloride (I.C.T., **5**, 88; **7**, 233) are 52.6 and 45.8 respectively at 25°. Unpublished work on the solubilities and heats of solution of these gases in acetic acid (containing 1% water) gives for the entropies at unit concentration in solution:  $S_{\text{Cl}_2} = 35.3$ ;  $S_{\text{HCl}} = 14.1$ . The entropy decrease for the reaction on the above assumption is 21.2 units, corresponding to a break-up factor of  $2.2 \times 10^{-5}$ . The value of  $Z$ , the collision frequency, is calculated as  $1.75 \times 10^{11}$ , whence  $P = 1.5 \times 10^{-5}$ .

*Interaction of sodium arsenite and sodium tellurate.* This has been studied by Stroup and Meloche (*J. Amer. Chem. Soc.*, 1931, **53**, 3331) and  $P$  is approximately  $10^{-5}$ .  $\Delta F$  for the reaction at 90° is  $-5,620$  cal. The heats of formation of  $\text{K}_2\text{TeO}_3$  aq. and  $\text{K}_2\text{TeO}_4$  aq. are known (I.C.T., **5**, 205) but not those for the normal arsenite and arsenate. In default of these values, the heats of formation of the potassium monohydrogen arsenite and arsenate have been used, giving for the reaction,  $\text{HAsO}_3'' + \text{TeO}_4'' = \text{HAsO}_4'' + \text{TeO}_3''$ ,  $\Delta H = -23,910$  cal. Assuming that the difference in the heats of tertiary ionisation of arsenic and arsenious acids can be neglected, the entropy change for the arsenite-tellurate reaction is a decrease of 50 units corresponding to a factor of  $10^{-11}$ .

*Interaction of ethyl sulphide and ethyl bromide.* The equilibrium constant of this reaction and its change with temperature have been measured by Corran (*Trans. Faraday Soc.*, 1927, **23**, 605), and the combination is attended by an entropy decrease. The velocity coefficient of combination deduced from the equilibrium constant and the rate of decomposition of the sulphonium bromide is approximately 40 times greater than the calculated rate of activation. Preliminary experiments on the equilibrium constant of this reaction in alcoholic solutions show that other reactions, besides the decomposition of the salt, occur. The bromide titre of a solution of the salt first decreases owing to the normal decomposition but later increases. The heat of dissociation calculated from values of the equilibrium constants may thus be in error.

*Conversion of ammonium cyanate into urea.* Here there is satisfactory agreement between calculated and observed rates (Moelwyn-Hughes, *op. cit.*, p. 79). In water,  $\Delta F$

at 100° is  $-5,820$  cal. (I.C.T., 7, 245) and  $\Delta H$  is  $-7,500$ , giving an entropy decrease of 4.5 units. This corresponds to a factor of 0.1 and does not greatly alter the agreement between calculated and observed rates.

*Interaction of chloride ion and iodoacetic acid* (Wagner, *Z. physikal. Chem.*, 1925, 115, 121). Both the forward and the reverse reaction  $\text{Cl}^- + \text{CH}_2\text{I}\cdot\text{CO}_2\text{H} \rightleftharpoons \text{I}^- + \text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  have been investigated. The entropies of the acids are not known, but the entropy of the chloride ion (relative to hydrogen ion) is 15.6, and that of the iodide ion is 27 (Butler, "Chemical Thermodynamics," Vol. 2, London, 1934, 190). If the difference in the entropies of the ions dominates, the forward reaction is attended by an entropy increase and the reverse reaction by an entropy decrease. The value for  $P$  for the forward reaction is 3, and for the reverse reaction 0.09 (Moelwyn-Hughes, *op. cit.*, p. 79).

*Interaction of hydroxyl and iodoacetate ions* (Wagner, *loc. cit.*). The entropies of hydroxyl and iodide ions are  $-2$  and 27 units respectively. If this difference dominates, the reaction is attended by an entropy increase. The reaction shows agreement between calculated and observed rates ( $P = 2$ ).

*Gaseous homogeneous reactions.* In a number of these, dissociation occurs, and owing to the increase in the number of molecules, there is an increase of entropy. For the bimolecular reaction,  $\text{N}_2\text{O} = \text{N}_2 + \frac{1}{2}\text{O}_2$  (Kassel, *J. Amer. Chem. Soc.*, 1934, 56, 1839),  $K = 1.46 \times 10^{18}$ , and  $\Delta H = -19,620$  cal. Hence  $\Delta S$  for the dissociation is 17.4 units, and the break-up factor is unity.

*Decomposition of hydrogen iodide.* Here  $K = 0.18e^{-2.940/RT}$ , whence at 393°,  $\Delta S = -3.4$ . This gives a break-up factor of 0.15, and  $P = 0.47$ .

*Combination of ethylene and hydrogen to form ethane* (Pease, *ibid.*, 1932, 54, 1876). From Pease and Durgan's equilibrium measurements, the entropy change is calculated as  $-28.9$  units, which would correspond to a break-up factor of  $10^{-6}$ . Actually  $P$  is found to be 0.05. Velocity constants for the packed vessel were double those for the unpacked vessel, and whether this fact would account for the discrepancy is conjectural.

The data are summarised in the following table; reference to the ionic reactions, where the entropies of the various components are only partially known, is omitted.

Reaction.	$P$ .	Thermodynamic break-up factor.
Dimethylaniline + methyl iodide .....	$0.5 \times 10^{-7}$	$0.9 \times 10^{-8}$
Saponification of ethyl acetate.....	$2.0 \times 10^{-5}$	$5 \times 10^{-4}$
Chlorine + phenolic ethers .....	$1.5 \times 10^{-5}$	$2.2 \times 10^{-5}$
Sodium arsenite + tellurate.....	$10^{-5}$	$10^{-11}$
Ammonium cyanate $\rightarrow$ urea .....	unity	0.1
Gaseous dissociations, <i>e.g.</i> , of nitrous oxide .....	unity	unity
Decomposition of hydrogen iodide .....	0.47	0.15
Combination of hydrogen and ethylene .....	0.05	$10^{-6}$

#### SUMMARY.

1. A factor representing the fraction of critical complexes which break up to form the reaction products has been introduced into the reaction-velocity equation. The modified equation reduces to the simple form  $k = Ze^{-E/RT}$  when the reaction is attended by an entropy increase, but gives diminished rates when the reaction is associated with an entropy decrease.

2. The division between normal and slow reactions coincides satisfactorily (except in one case) with that according to the sign of the entropy change. When the entropy decrease is slight, as in the hydrogen-iodine reaction and in the formation of urea, the factor does not appreciably alter the existing agreement between observed and calculated rates.