remaining terms were obtained. The resulting projection is shown in Fig. 1 and is adequate for placing the atoms in the unit cell, with all the atoms, including the water molecule O_4 , being resolved with the exception of C_1 and O_2 (see Fig. 2).

A preliminary examination of the structure using y -co-ordinates derived by assuming probable bond-lengths for the glycyl-L-alanine molecule showed satisfactory hydrogen-bonding, the glycyl-L-alanine and water molecules forming spirals bound together laterally by N—H bonds. A detailed discussion of this aspect will, however, be postponed until the structure has been refined using the hydrochloride, which is isomorphous with the hydrobromide.

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¹ Bergmann, M., and Zervas, L., *Ber. Dtsch. Chem. Ges.*, **65**, 1192 (1932).

Formulation of the Rate Equation in Chemical Kinetics

ROBB¹ has recently pointed out that when the rate-constant for a reaction such as

is under discussion, it is necessary to state whether the rate referred to is the disappearance of A or of B , since the latter is half as fast as the former.

It is perhaps also worth pointing out that in the academic literature of reaction kinetics, rates are always written as rates of change of concentration in a closed system which is tacitly assumed to be at constant volume; for example:

$$-\frac{d}{dt}[A] = -2\frac{d}{dt}[B] = k[A]^2[B]. \quad (1)$$

This equation has only limited application to industrial processes. There are closed reaction systems, for example, in which the volume changes during the reaction, and open systems (such as continuous-flow tank and tubular reactors) in which the concentration is independent of time². The rate-equation is more generally useful when written in a less restricted form; for example:

$$-R_a = -2R_b = \frac{k}{V^2} \cdot a^2b. \quad (2)$$

The system to which this equation applies may be open or closed, but has a constant atomic content, and is assumed to be virtually uniform in composition and temperature. At a given instant it has volume V and contains a, b moles of A, B . $-R_a$, $-R_b$ are the rates of destruction of A, B by the reaction. k has the same significance and value as in equation (1).

In a closed system, $R_a = da/dt$; V may be a function of a, b, t . Equation (2) is then to be integrated accordingly. In a flow-system operating at steady state, V, a, b and R_a are constant, the latter being the difference between the rates of inflow and outflow of A . Other variants may also be encountered.

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¹ Robb, J. C., *Nature*, **172**, 1055 (1953).

² Denbigh, K. G., *J. App. Chem.*, **1**, 227 (1951).

A Competitive Method of determining Association Constants

THE method described by Benesi and Hildebrand¹ for determining the association constants of charge-transfer complexes involves optical measurements of a series of solutions at or near the wave-length of maximum absorption of the complex. A simple method for determining such constants which avoids these conditions has been devised.

Consider the two interactions:

involving two Lewis bases B' and B'' and a Lewis acid A (or vice versa). An equilibrium constant K may be defined as:

$$K = \frac{[AB]}{([A] - [AB])([B] - [AB])}, \quad (1)$$

where $[A]$ and $[B]$ are the initial concentrations of A and B . For simplicity, let $[B'] = [B''] = [B]$, say, then if $[B] \gg [A]$:

$$K' = \frac{[AB]}{[B]([A] - [AB] - [AB'])}, \quad (2)$$

$$\text{and} \quad K'' = \frac{[AB'']}{[B]([A] - [AB'] - [AB''])}. \quad (3)$$

Eliminating $[AB'']$ from equations (2) and (3):

$$[AB'] = \frac{K'[A][B]}{1 + K'[B] + K''[B]}. \quad (4)$$

A wave-length is selected at which the species A , B' , B'' and AB'' have negligible absorptions, but at which AB' absorbs (preferably at or near the maximum of the charge-transfer spectrum of this species). If the extinction coefficient of the species AB' at this wave-length is ϵ , then the optical density of a solution at this wave-length will be $D = \epsilon[AB']$.

The optical densities of two solutions, one containing A and B' at concentrations $[A]$ and $[B]$, the other containing A , B' and B'' at concentrations $[A]$, $[B]$ and $[B]$, are measured at this wave-length. If D_1 and D_2 are the two optical density readings so obtained, then applying equation (4):

$$\frac{D_2}{D_1} = \frac{1 + K'[B]}{1 + K'[B] + K''[B]}, \quad (5)$$

$$\text{or} \quad K'' = \frac{D_1 - D_2}{D_2} \left(K' + \frac{1}{[B]} \right). \quad (6)$$

Knowing K' , K'' may be determined.

Applying the method to the complex of N - n -butylaniline and s -trinitrobenzene by measuring the competition of the former with N - N - N' -tetramethyl p -phenylenediamine in *cyclohexane*, the following results were obtained:

$$[B] = 0.118 M; [A] \approx 10^{-4} M;$$

$$D_1 = 0.320 \text{ cm.}^{-1} \text{ and } D_2 = 0.255 \text{ cm.}^{-1} \text{ at } 650 \text{ m}\mu.$$

Using a value of $K = 20.4$ litres/mole for the association constant of N - N - N' - N'' -tetramethyl p -phenylenediamine with s -trinitrobenzene in *cyclohexane* (obtained by the method of Benesi and Hildebrand), a value of the association constant of N - n -butylaniline with s -trinitrobenzene in *cyclohexane* of 7.4 litres/mole is obtained. The value obtained by the method of Benesi and Hildebrand is 8.2 litres/mole.

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¹ Benesi and Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).