CXXVIII.—*A Method for the Determination of the Equilibrium in Aqueous Solutions of Amines, Pseudo-acids and -bases, and Lactones.*

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THE substances mentioned in the title of this paper resemble each other in that their aqueous solutions contain, in addition to ions, two non-ionised forms. Thus a pseudo-acid of which the ketonic form is $\text{H}\cdot\text{X}\cdot\text{O}$ gives ions $\text{X}\cdot\text{O}'$ and H' which correspond with the enolic form $\text{X}\cdot\text{O}\cdot\text{H}$. The relations are expressed by the equations :

and similar equations apply to pseudo-bases.

Ammonia, the amines, the lactones, and carbon dioxide differ from

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pseudo-acids and bases in that the form directly in equilibrium with the ions is formed from the non-ionising part by union with water, so that for an amine the equations are

But when the law of mass-action is applied to these equations, the distinction between ammonia, amines, &c., on the one hand, and pseudo-acids and bases, on the other, disappears. For if x be in each case the concentration of the non-ionising part (e.g. NH_3 , $H \cdot X \cdot O$), y the concentration of the ionising part (e.g. $NH_4 \cdot OH$, $X \cdot OH$), and z the concentration of the ionised part (e.g. NH_4' , $X \cdot O'$):

$$k_1 y = z^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{and } y = k_2 x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k_1 and k_2 are constants for each particular substance.* The constants k_1 and k_2 are of considerable theoretical importance, for k_1 is the "true" ionisation constant of the substance and k_2 expresses the relation between the ionising and the non-ionising parts. But so far their values have been determined in only a few particular cases (compare Hantzsch, *Ber.*, 1899, 32, 576, and subsequent papers; Dimroth, *Annalen*, 1904, 335, 1; and Chanlaroff, *Annalen*, 1884, 226, 333), and the properties of the greater number of pseudo-acids and bases and of all the amines are such that the methods used in these cases are not generally applicable.

Hantzsch and Sebaldt (*Zeitsch. physikal. Chem.*, 1899, 30, 258) and Hantzsch and Vagt (*Zeitsch. physikal. Chem.*, 1901, 38, 703), from experiments on the variation with temperature of the partition ratios of amines between water and a second solvent, drew conclusions as to the extent of the combination of amine with water in certain cases. These conclusions are, however, of a qualitative nature, and do not give any idea of the relative magnitudes of k_1 and k_2 for different substances.

In the present paper it is shown that the actual values of these two constants can be calculated by combining the results of experiments on the partition of a substance between two solvents, at different temperatures, with the values of the "apparent" ionisation constants (see p. 1377) at the same temperatures.

If two substances, X and Y , are shaken up with two immiscible solvents, such as benzene and water, the relations between the concentrations in the two solutions when equilibrium has been attained are

$$x = P_1 x' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$y = P_2 y' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

Equation (1) applies to such substances as form only two ions. The equations developed in this paper would therefore not apply directly to carbon dioxide.

where x and y are the concentrations in the aqueous solution, x' and y' are the concentrations in the benzene solution, and P_1 and P_2 are constants.

If X and Y are the non-ionising and ionising parts respectively of an amine or pseudo-acid or lactone, we cannot, in general, determine any of the quantities in these equations, but we can determine the total concentration $x' + y'$ in the non-aqueous solution.

$$\text{Now } x' + y' = \frac{x}{P_1} + \frac{y}{P_2} = [\text{from equation (2)}] \quad x \left\{ \frac{1}{P_1} + \frac{k_2}{P_2} \right\} = Mx,$$

where M is a constant for any particular temperature. Thus the total concentration in the non-aqueous solution is proportional to the concentration of the non-ionising part in the aqueous solution even when both the non-ionising and the ionising parts are soluble in the second solvent.

If now we take two aqueous solutions at the same temperature, giving x , y , and z their previous meanings and putting α for the total concentrations in the aqueous solution, we have

$$x_1 + y_1 = \alpha_1 - z_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$x_2 + y_2 = \alpha_2 - z_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the value of z may be calculated from the electrical conductivity. If these solutions are in equilibrium with two benzene solutions in which the total concentrations are c and c_2 respectively, then

$$\frac{x_1}{x_2} = \frac{c_1}{c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

$$\text{And from equation (2): } \frac{x_1}{x_2} = \frac{y_1}{y_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a).$$

We have then four equations containing four unknown quantities, x_1 , x_2 , y_1 , y_2 ; yet the unknown quantities cannot be found, for on substituting from equations (6) and (6a) in equations (4) and (5), the latter become of the same form. The difficulty disappears only if the conditions are so altered that equation (6a) is no longer true. This shows that the essential condition for the solution of the problem is that the solutions under consideration shall be at different temperatures.

A difference in temperature between the two solutions causes difficulty in that the partition coefficient may, and k_1 certainly does, alter with temperature. It becomes necessary to consider three solutions at temperatures t_1 , t_2 , t_3 , such that $t_2 - t_1 = t_3 - t_2$. For then, if k_1' , k_1'' , k_1''' are the values of k_1 corresponding to t_1 , t_2 , t_3 respectively and q is the heat absorbed on ionisation, we have

$$\log_e \frac{k_1''}{k_1'} = \frac{q}{R} \frac{t_2 - t_1}{(273 + t_1)(273 + t_2)} = \frac{q}{R} \frac{t_2 - t_1}{(273 + t_2)^2} \text{ when } t_1 \text{ and } t_2 \text{ are near together.}$$

$$\text{Similarly, } \log \frac{k_1'''}{k_1''} = \frac{q}{R} \frac{t_3 - t_2}{(273 + t_2)^2}.$$

$$\therefore \frac{k_1'''}{k_1''} = \frac{k_1'''}{k_1''} = l \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

if q is constant over the range of temperature t_1 to t_3 .

For the variation of k_2 with temperature we have in the same way :

$$\frac{k_2''}{k_2'} = \frac{k_2'''}{k_2''} = \frac{1}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8).$$

If the ionising part of the substance is insoluble in the second solvent, we have similarly for the partition coefficient :

$$\frac{M''}{M'} = \frac{M'''}{M''} = n \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

If the solubility of the ionising part in the second solvent is considerable, equation (9) will be no longer strictly true, since M then involves three constants, P_1 , P_2 , and k_2 . But, as may be seen from the calculations in the paper following this, small variations in n may at present be neglected.

Then if x_1, y_1, z_1, a_1 , and c_1 , are concentrations corresponding to t_1
 „ x_2, y_2, z_2, a_2 „ c_2 „ „ t_2
 „ x_3, y_3, z_3, a_3 „ c_3 „ „ t_3

where x = conc. of non-ionising part in aqueous sol. (*e.g.* NH_3)

„ y = „ ionising „ (*e.g.* $\text{NH}_4 \cdot \text{OH}$)

„ z = „ ionised „ (*e.g.* NH_4^+)

„ a = total concentration in aqueous solution = $x + y + z$

„ c = „ non-aqueous solution ;

and, further, putting

$$\frac{c_1}{c_2} = r_1, \quad \frac{c_2}{c_3} = r_2, \quad \frac{t_1^2}{t_2^2} = s_1, \quad \frac{t_2^2}{t_3^2} = s_2;$$

we have :

$$x_1 + y_1 = a_1 - z_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10).$$

$$x_2 + y_2 = a_2 - z_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (11).$$

$$x_3 + y_3 = a_3 - z_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

And

$$\frac{x_1}{x_2} = \frac{c_1}{c_2} \cdot \frac{M''}{M'} = r_1 n \quad . \quad . \quad . \quad . \quad . \quad . \quad (13).$$

$$\frac{x_2}{x_3} = \frac{c_2}{c_3} \cdot \frac{M'''}{M''} = r_2 n \quad . \quad . \quad . \quad . \quad . \quad . \quad (14).$$

From equation (1) :

$$\therefore \frac{y_1}{y_2} = \frac{t_1^2}{t_2^2} \cdot \frac{k_1''}{k_1'} = s_1 l \quad . \quad . \quad . \quad . \quad . \quad . \quad (15).$$

$$\text{and, similarly, } \frac{y_2}{y_3} = s_2 l \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Of these quantities, the values a and c are determined experimentally, and the values of z are determined from the "apparent" ionisation constants. So that r_1, r_2, s_1, s_2 are known.

From equations (10), (11), (13), (15):

$$y_2(s_1l - r_1n) = a_1 - z_1 - r_1n(a_2 - z_2) \quad \dots \quad (17).$$

Similarly,

$$y_3(s_2l - r_2n) = a_2 - z_2 - r_2n(a_3 - z_3) \quad \dots \quad (18).$$

Hence,

$$s_2l \frac{s_1l - r_1n}{s_2l - r_2n} = \frac{a_1 - z_1 - r_1n(a_2 - z_2)}{a_2 - z_2 - r_2n(a_3 - z_3)} \quad \dots \quad (19).$$

Further, by applying equation (2) to the solutions at t_1 and t_2 , we get

$$\frac{y_1}{y_2} = \frac{k_2'}{k_2''} \frac{x_1}{x_2}$$

$$\therefore \frac{s_1}{r_1} = \frac{mn}{l} \quad \dots \quad (20a).$$

Similarly,

$$\frac{s_2}{r_2} = \frac{mn}{l} \quad \dots \quad (20b).$$

Again, if the observed values of the electrical conductivity for a substance which exists in two non-ionised forms are substituted in the equation for the ionisation constant of an ordinary binary electrolyte,

$$K = \frac{\lambda_v^2}{v\lambda_a(\lambda_a - \lambda_v)},$$

K is found to be a constant and is generally called the ionisation constant, although, as we have seen, the "true" ionisation constant for such a substance is the quantity we have called k_1 . Kauffman (*Zeitsch. physikal. Chem.*, 1904, **47**, 618), has shown that the constant K , which we shall call the "apparent" ionisation constant, is connected with the constants k_1 and k_2 by the relation

$$K(1 + k_2) = k_1k_2.$$

Applying this equation to solutions at t_1 and t_2 , we get

$$\frac{K'}{K''} \cdot \frac{1 + k_2'}{1 + k_2''} = \frac{k_1'}{k_1''} \cdot \frac{k_2'}{k_2''} = \frac{m}{l} \quad \dots \quad (21a).$$

Similarly,

$$\frac{K''}{K'''} \cdot \frac{1 + k_2''}{1 + k_2'''} = \frac{m}{l} \quad \dots \quad (21b).$$

Eliminating k_2' , k_2'' and k_2''' between equations (8), (21a), and (21b), we get a quadratic in m of which the two roots are

$$m = 1 \text{ and } m = \frac{lA_1(lA_2 - 1)}{lA_1 - 1} \quad \dots \quad (22)$$

where $\frac{K'}{K''} = A_1$ and $\frac{K''}{K'''} = A_2$.

The root $m = 1$ is impossible, since on substitution in the above

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equations it gives a negative value for k_2 . The root required therefore is given by equation (22).

We now have nine equations (10 to 16 and 20 and 22) containing nine unknown quantities ($x_1, x_2, x_3, y_1, y_2, y_3, l, m$, and n), all of which may therefore be determined. The most convenient method is to take the three equations, (19), (20), and (22), from which values of l, m , and n may be obtained; y_1, y_2, y_3 , &c., may then be calculated from equations (17) and (18).

From equations (20*a*) and (20*b*) we see that if the temperature coefficients remain constant over the range of temperature $t_1 - t_3$, then

$$\frac{s_1}{r_1} = \frac{s_2}{r_2},$$

so that if the assumption that q is constant (p. 1376) is justified, this relation will be fulfilled, and, although the converse statement is not necessarily true, it is extremely probable. So that if in any particular case the values of $\frac{s}{r}$ are found to be constant, we may conclude that

l, m , and n are constant over the range of experiment.

Since the values of the temperature coefficients l, m , and n are given by the equations, the heat changes corresponding with the transition of the ketonic to the enolic form of a pseudo-acid or base, or to the hydration of an amine and to the ionisation, may be calculated. From these quantities the heat of neutralisation may be found, and the comparison of the result so obtained with the result of experiment gives a means of checking the accuracy of the method.

No account has been taken of the variation of the partition coefficient with concentration, although such a variation has been found by Hantzsch and Vagt (*loc. cit.*) and by Dawson and McCrae (*Trans.*, 1901, 79, 496, 1072, and 1906, 89, 1666). But when the laws governing this variation are known, it should not be difficult to introduce a correction into the above equations. And it should further be stated that the method of calculation does not deal with the question of the existence of non-ionising hydrates (which may be written, for example, $\text{NH}_3 \cdot \text{H}_2\text{O}$) as distinct from ionising hydroxides (for example, $\text{NH}_4 \cdot \text{OH}$). Such compounds may, of course, be present in aqueous solutions, and would with the non-hydrated compound (for example, NH_3) form what has been called in this paper the non-ionising part.

Examples of the application of these equations are given in the following paper, and the author is proceeding with the further experimental investigation of the subject.

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