

CXXXIII.—*The Behaviour of Hydrogen Chloride in Different Solvents.*

By W. F. KENRICK WYNNE-JONES.

HYDROGEN chloride when dissolved in water behaves as a very strong electrolyte, so strong, indeed, that it is usual to regard it as a completely ionised acid, since its solutions conform quite closely to the equations of the Debye-Hückel theory. The anhydrous compound, on the other hand, is a non-electrolyte, and it is generally considered that the hydrogen and chlorine atoms are so intimately bound that it requires considerable energy to separate them as ions. These facts have led to the hypothesis that the dissociation of the acid is occasioned by its combination with the solvent and that, according to Brönsted's definition of an acid and a base (*Rec. trav. chim.*, 1923, **42**, 718), the acid will be ionised only in a basic solvent. Thus in water, ammonia, and methyl alcohol we have the reaction schemes $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}'$; $\text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{Cl}'$; $\text{HCl} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OH}_2^+ + \text{Cl}'$.

This hypothesis makes a clear distinction between an electrolyte such as hydrochloric acid and other strong electrolytes such as salts, since, with the latter, dissociation is primarily determined by the dielectric constant, whereas with hydrochloric acid the chemical nature of the medium is the determining factor.

In order to test this hypothesis further, it was decided to examine the behaviour of hydrogen chloride in a solvent of no marked basic character but possessing a fairly high dielectric constant. For this purpose, nitrobenzene seemed admirably suited, since its dielectric constant is 34, and, from an acid-base standpoint, it might be expected to be inert; moreover its immiscibility with water made it possible to use the partition method for investigating the behaviour of hydrogen chloride.

This method has been employed by several investigators, and the work of Rothmund and Drucker (*Z. physikal. Chem.*, 1903, **46**, 827) and of Cavanagh (*Proc. Roy. Soc.*, 1924, *A*, **106**, 243), in particular, has proved the trustworthiness of the method for determining activities in one solvent when those in the other solvent are known. There has, however, been a certain amount of criticism of the method, owing partly to a misunderstanding of the nature of the results obtained by it, and partly to a misconception of its limitations. On the one hand, it is clear that the Nernst equation

$$K = C_1^n / C_2 \quad \dots \dots \dots (1)$$

where C_1 and C_2 refer to the concentrations in the two solvents and n is the degree of association in solvent 2, is only an approximation

and certainly cannot hold for electrolytes. A more precise method of treating the results is to write for solutions in one solvent

$$\mu = RT/n \cdot \log cf + k \quad . \quad . \quad . \quad . \quad (2)$$

where μ is the chemical potential of the solute, n the degree of association, f the activity coefficient of the associated molecules, and k a constant, the other symbols having the usual significance. If, for the other solvent, the values of μ are known, then these values may be substituted in the above equation. In a case such as that studied here, we may write for aqueous solutions

$$\mu_1 = RT \log p + k_1 \quad . \quad . \quad . \quad . \quad (2a)$$

while for solutions in nitrobenzene we have

$$\mu_2 = RT/n \cdot \log cf + k_2 \quad . \quad . \quad . \quad . \quad (2b)$$

whence, for equilibrium,

$$K = p^n/cf \quad . \quad . \quad . \quad . \quad (3)$$

p being the partial pressure.

The limitations of the method, on the other hand, must be clearly recognised. Evidently, the application of equation (2a) is only justifiable if the chemical potential of the solute is not markedly affected by the presence of the other solvent. Also the results for the second solvent will refer, not to the pure liquid, but to one saturated with the other solvent. The solubility of one solvent in the other, provided it remain constant, as at low concentration of the solute, will not invalidate the results; if, however, the solubility varies appreciably, then some uncertainty will be introduced dependent upon the manner in which the potential of the solute varies with the properties of the solvent.

E X P E R I M E N T A L.

In view of the fact that hydrogen chloride is much more soluble in water than in nitrobenzene, it was thought possible that errors might arise through traces of emulsification if the two liquids were brought into direct contact as is usual in partition measurements. In order to avoid this, an H form of apparatus was constructed and equilibrium between the two liquids was reached through the vapour phase; the attainment of equilibrium was accelerated by evacuating the apparatus through a tap on the connecting tube. Siphon tubes were introduced through rubber stoppers in the two upright tubes, and the apparatus was filled and emptied by means of these siphons. In most of the experiments the apparatus was left in a thermostat, electrically controlled at $25.00^\circ \pm 0.01^\circ$, for 2—5 days with occasional shaking; in a few of the later experiments a shaking apparatus was installed and equilibrium attained

in less than 24 hours. At the end of this time air was admitted to the apparatus, the ends of the siphons were broken, and suitable amounts of the two liquids run into flasks and weighed. Titrations were carried out with carbonate-free sodium hydroxide, bromocresol-purple being used as indicator. The ultimate standard was constant-boiling hydrochloric acid, prepared according to the directions of Foulk and Hollingsworth (*J. Amer. Chem. Soc.*, 1923, **45**, 1220).

In one experiment with nitrobenzene and all the experiments with benzene the two liquids were shaken together in stoppered bottles. The agreement of the nitrobenzene value thus obtained with the others is satisfactory evidence that either method can give correct results under proper conditions.

The solubility of hydrogen chloride in water and nitrobenzene was determined by passing the gas for several hours through the liquids contained in test tubes: the gas passed out through two guard tubes and was then absorbed in alkali. The hydrogen chloride was generated by dropping A.R. hydrochloric acid into concentrated sulphuric acid. As a check on this method, a few measurements were made with gas generated by the action of sulphuric acid on ammonium chloride, but no difference was detected.

The nitrobenzene was of "pure" quality. It was shaken with caustic soda and distilled twice under 20 mm. pressure, the second distillation being from phosphoric oxide. The final product was very pale yellow.

Results.—The results are summarised in Table I. In the first column are recorded the values (C_w) of the concentration in the

TABLE I.
Results for nitrobenzene at 25°.

C_w .	C_n .	$\alpha_{\text{HCl}} \times 10^{-5}$.	C_w .	C_n .	$\alpha_{\text{HCl}} \times 10^{-5}$.	C_w .	C_n .	$\alpha_{\text{HCl}} \times 10^{-5}$.
9.635	0.0027	0.0828	14.84	0.0707	2.37	18.05	0.335	11.9
9.766	0.0029	0.0912	14.93	0.0773	2.77	18.38	0.394	13.4
11.147	0.0080	0.242	15.21	0.0833	2.93	†19.33	0.556	18.8
*11.61	0.0109	0.331	16.46	0.164	5.70	19.52	0.603	20.5
12.84	0.0229	0.721	17.19	0.223	8.28	20.42	0.833	27.3
13.84	0.0396	1.33	17.76	0.292	10.6			

* This value was obtained from an experiment in a stoppered bottle.

† This value is obtained from the following determinations of the solubility of hydrogen chloride in the two solvents:

	p_{HCl} (mm. Hg).	C .	C (corr. to 760 mm.).
Water	747	19.29	19.34
	752	19.29	19.32
			Mean 19.33
Nitrobenzene (saturated with water)	742	0.535	0.548
	749	0.551	0.559
	760	0.561	0.561
			Mean 0.556

aqueous layer expressed in mols. per 1000 g. of water; in the 2nd, the concentrations (C_n) in the nitrobenzene similarly expressed; in the 3rd, the values of the activities in the aqueous layer calculated from the data of Randall and Young (*J. Amer. Chem. Soc.*, 1928, **50**, 989) up to a concentration of 16 molal, and, for higher concentrations, from the vapour pressures given in the International Critical Tables, Vol. III, p. 301.

Discussion of Results.

On comparing these results with those of Knight and Hinshelwood (J., 1927, 470) for the distribution of hydrogen chloride between benzene and water, we find two marked differences. In the first place, there is a difference in the general form of the curves representing the variation of the concentration in the non-aqueous phase with the concentration in the water. For, whereas in this work the curve rises continuously and is always concave towards the axis of the concentration in the water, Knight and Hinshelwood's curve has a point of inflexion and flattens out very considerably at high concentrations, where a constant value is actually obtained for the ratio of the concentrations in the two layers. Such a result is quite inexplicable on theoretical grounds and, moreover, is in conflict with the vapour-pressure data of a number of authors. That it is probably due to some experimental error is further shown by the fact that the value given by Knight and Hinshelwood for the solubility of hydrogen chloride in water at 20° differs considerably from the standard value. Thus, Roscoe and Dittmar (J., 1859, **12**, 128) found that 1 g. of water at 20° dissolves 0.721 g. of hydrogen chloride, whereas Knight and Hinshelwood found that 1 litre of the saturated solution contains 718.8 g. of hydrogen chloride; combining this with the density of the solution, *viz.*, 1.22, we obtain a value of 1.44 g. of hydrogen chloride per g. of water.

TABLE II.

Knight and Hinshelwood's results at 20°.

C_w , g./l.	C_b , g./l.	p_{HCl} .	p_{HCl}/C_b .
165.9	0.100	0.0343	0.343
212.0	0.252	0.162	0.643
236.1	0.382	0.351	0.92
249.0	0.449	0.538	1.20
259.0	0.532	0.742	1.40
289.3	0.706	1.905	2.70
312.0	0.929	3.91	4.21

A further peculiarity about the results of these authors is that the concentrations in the benzene layer are not even approximately proportional to the partial pressures of the aqueous solutions. This is shown in Table II where a few of the data are tabulated.

The concentrations are expressed as g. of acid per litre of solution; the vapour pressures have been interpolated from the data in the International Critical Tables (*loc. cit.*) and are expressed in mm. of mercury.

In order to determine whether this deviation from normality had any real existence, it was decided to carry out a few experiments with benzene. The results are summarised in Table III, in which the concentrations are expressed as mols. per 1000 g. of solvent.

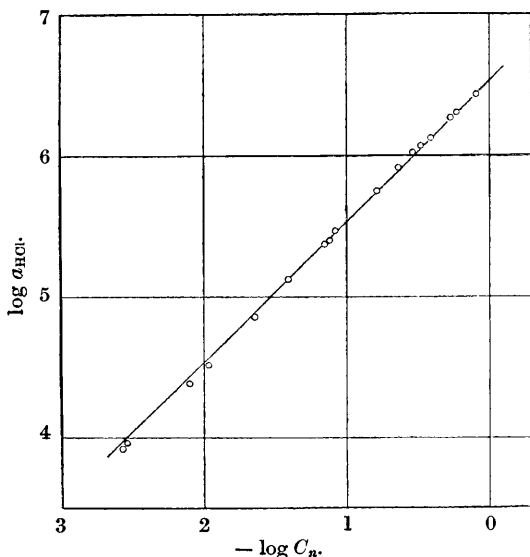
TABLE III.

Results with benzene at 25°.

C_w .	C_b .	p_{HCl} .	$p_{\text{HCl}}/C_b \times 10^3$.
9.603	0.00213	2.95	1.39
10.215	0.00340	4.67	1.37
10.508	0.00423	5.72	1.35
11.43	0.00768	10.74	1.40
11.99	0.0110	15.6	1.42
12.93	0.0216	28.1	1.30

It is clear that the behaviour of hydrogen chloride in benzene is quite normal.

FIG. 1.



That hydrogen chloride is a normal solute in nitrobenzene also is shown most clearly in Fig. 1, where the logarithm of the activity is plotted against the logarithm of the concentration in the solvent; the straight line has been drawn with a slope of unity and it is

evident that over the whole range the activity is proportional to the concentration.

As previously mentioned, the activities were obtained by combining Randall and Young's results with the vapour-pressure data in the International Critical Tables. If Randall and Young's values of $\log \gamma$ are plotted against \sqrt{M} (where M = molality) a linear relationship holds over the range 9—16*M*, but it is not possible to use this for extrapolation, since the values thus obtained diverge considerably from the values calculated from the vapour pressures by means of the equation

$$\log \gamma - 1.718 = \log \sqrt{p}/M.$$

That there is no serious error in the vapour pressures is shown by the fact that the interpolated value for the concentration of the saturated solution (under a pressure of 760 mm. of Hg) is 19.33*M*, in exact agreement with the figure obtained in this work. It is also quite justifiable to calculate activities from the vapour pressures, since Gray and Burt (J., 1909, 95, 1633) have shown that at 0° and a pressure of 1 atm. the deviation of hydrogen chloride vapour from the gas laws is less than 1%. Since there are no published values for the activity coefficients of hydrochloric acid at concentrations above 16*M*, Table IV has been compiled from the vapour-pressure data.

TABLE IV.

Activity coefficients of hydrochloric acid at 25°.

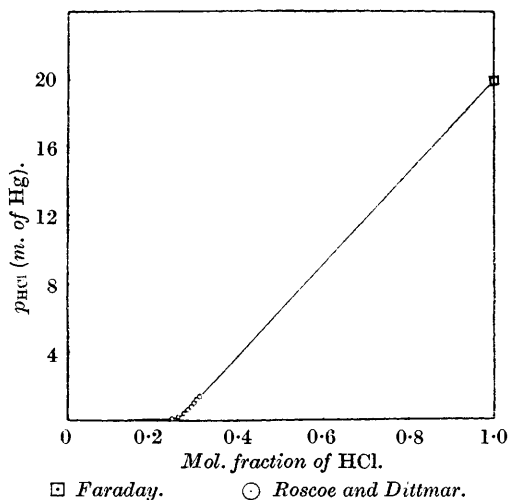
<i>M</i> (mols./1000 g.) ...	16	17	18	19	20
$\log \gamma$	1.628	1.708	1.776	1.836	1.890
<i>p</i> (mm. Hg)	169.1	276	423	623	884

The value of $\log \gamma$ at 16*M* is that given by Randall and Young and may be somewhat in error, but further investigation is required to decide this.

The results presented in this paper clearly support the theoretical considerations outlined in the introduction: in the three solvents water, nitrobenzene, and benzene, with dielectric constants 79, 34, and 2.2, respectively, the behaviour of hydrogen chloride is conditioned, not by the dielectric constant of the medium, but by its capacity to combine with it. That hydrogen chloride probably forms a compound with water has long been postulated, but it is interesting to note that vapour-pressure data lend considerable support to this view and also enable us, on the basis of a simple assumption, approximately to evaluate the extent of combination. Roscoe and Dittmar have measured the vapour pressures of hydrochloric acid solutions at 0° up to a pressure of 1300 mm.; in addition, Faraday (*Phil. Trans.*, 1845, 135, 155) determined the vapour

pressure of pure hydrogen chloride at the same temperature. These results are combined in Fig. 2, where the vapour pressure is plotted against the mol fraction of hydrogen chloride, which is calculated on the assumption that the molecular weights of hydrogen chloride and of water are normal. Although there is a large range for which no data are available, it is very striking that a linear extrapolation of Roscoe and Dittmar's results comes very close to Faraday's value for pure hydrogen chloride. The whole form of the curve strongly suggests that at mol fractions of less than 0.25 practically all the hydrogen chloride has combined with the water and exerts a negligible vapour pressure, whereas above that value any additional hydrogen chloride added to the solution is uncombined and is able

FIG. 2.



to exert its full vapour pressure. This can be simply explained if each molecule of hydrogen chloride is combined with 3 molecules of water.

If we now assume that the partial pressure of hydrochloric acid is always proportional to the mol fraction of the uncombined acid, it is possible to calculate its amount. Thus, the partial pressure of a molal solution at 0° is 2×10^{-8} atm., while the vapour pressure of pure hydrogen chloride is 26.2 atm.; hence the mol fraction of uncombined hydrochloric acid is $2 \times 10^{-8}/26.2$, and its molality is $55 \times 2 \times 10^{-8}/26.2 = 4 \times 10^{-8}$. On the assumption that all the combined hydrogen chloride is ionised, the dissociation constant of hydrochloric acid is $K = 1/4 \times 10^{-8} = 2.5 \times 10^7$. This value agrees well with the previous estimates of Schreiner (*Z. physikal.*

Chem., 1924, **111**, 419) and of Ebert (*Naturwiss.*, 1925, **13**, 393), both based on quite different considerations.

Summary.

The partition of hydrogen chloride between nitrobenzene and water has been determined, and the results indicate that in nitrobenzene it behaves as a normal undissociated solute. A few measurements on the system benzene-water lead to a similar conclusion. These results support the view that the behaviour of an acid is primarily determined by the basic character, and not by the dielectric constant, of the solvent.

Consideration of the vapour-pressure data shows that a molecule of hydrogen chloride in aqueous solution is probably associated with 3 molecules of water, and it is estimated that the dissociation constant of hydrochloric acid is 2.5×10^7 .

I wish to express my thanks for a grant from the Research Fund of the Chemical Society which has helped to defray the cost of this work.

THE UNIVERSITY, READING.

[Received, March 10th, 1930.]
