# LXVIII.—*The Partition of Hydrogen Chloride between Water and Benzene.*

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THE well-known method of determining the state of substances in solution by partition experiments can be utilised to throw light upon the state of strong electrolytes dissolved in water.

Debye and Hückel have shown that when the apparent degree of dissociation of such an electrolyte is corrected for the effect of the inter-ionic forces on the conductivity and on the osmotic pressure, the result is nearly unity for solutions of moderate concentration. This is referred to as complete dissociation. The result does not prove the absolute non-existence of un-ionised molecules, but simply shows that their concentration, if they do exist, is very much smaller than was supposed before the proper corrections were introduced.

There is, on the other hand, positive evidence for the existence of un-ionised molecules, if only in extremely small concentration, wherever there is a definite partition between water and some non-polar solvent. Little work has been done on the partition of strong electrolytes, because it is difficult to find one having a sufficiently great solubility in a suitable non-polar solvent, a fact which itself indicates the reluctance with which un-ionised molecules are formed. Among the most important papers bearing on the subject are those of Hill (*J. Amer. Chem. Soc.*, 1921, **43**, 254), on the partition of silver perchlorate between water and benzene, Rothmund and Drucker (*Z. physikal. Chem.*, 1903, **46**, 827), on picric acid and the same two solvents, and Cavanagh (*Proc. Roy. Soc.*, 1924, [*A*], **106**, 243), on the partition of lithium chloride between water and amyl alcohol.

At sufficiently high concentrations aqueous solutions of hydrogen chloride have a considerable partial pressure of gaseous hydrogen chloride, showing that un-ionised molecules must exist in solution. It seemed likely that further information would be obtained by studying the partition of hydrogen chloride between water and benzene up to concentrations as high as possible. The work now described does not aim at establishing standard values for the various solubilities, but only at showing the general nature of the partition relationships. Nevertheless, it seems to show quite clearly that there is a definite equilibrium in water between ionised and un-ionised hydrogen chloride. Up to a concentration of about 10*N* there is only a very small proportion of un-ionised molecules, in accordance with the results of Debye and Hückel, a fact which can also be seen from the vapour-pressure results. Above about 15*N*, however, the proportion of un-ionised molecules becomes very considerable, and in the region 15—20*N* there is a roughly constant partition coefficient, indicating that the state of the greater part of the hydrogen chloride in the water is the same as its state in the benzene.

No information could be found about the solubility of hydrogen chloride in benzene. This was therefore determined. The solubility in water is given in most standard works, but all data appear to rest upon the original determination of Roscoe and Dittmar (J., 1860, **12**, 128). The value was therefore re-determined at 20° by a different method.

The benzene was prepared from the purest " Analytical Reagent." It was first extracted with pure concentrated sulphuric acid, after which it showed no trace of the indophenin reaction. It was then fractionated through a 6-foot column and collected in large flasks provided with syphons, all corks used being covered with pure tinfoil. It was subsequently twice purified by freezing. The final m. p.'s of four portions were 5·48°, 5·48°, 5·47°, and 5·47° (correct to 0·02°). (Sidgwick, J., 1920, **117**, 1340, gives 5·49° for pure benzene.)

The hydrogen chloride was made by the action of pure sulphuric acid, free from nitrate (diphenylamine reaction), on fused ammonium chloride, free from carbonate and nitrate. The gas was passed through two towers tightly packed with glass wool and was frequently tested for sulphuric acid spray; none was detected.

Pipettes and burettes were standardised by weight.

For experiments in which the concentration was so low that there was no fuming, 400-c.c. glass bottles with ground stoppers and special caps were used. About 80 c.c. each of benzene and distilled water were placed in a bottle and hydrogen chloride was bubbled in for the requisite time. The bottle was then placed in a rocker in a thermostat at 20·00° for 6 hours, the contents were allowed to settle during a further 3 hours, and the two layers were removed by syphons. The aqueous layer was titrated with baryta. The hydrogen chloride in the benzene layer was determined by extracting 10 c.c. with 50 c.c. of boiled-out water, and estimating the hydrogen-ion concentration of the extract by means of " universal indicator " and suitable standards. The results are given in Table III. They show the order of magnitude only, but it is evident that up to a concentration in the water of about 100 g./litre the amount passing into the benzene is very small indeed. Some of that even will be due to the water dissolved in the benzene, so that the values at these very low concentrations are not suitable for such purposes as the calculation of " activities."

FIG. 1A.

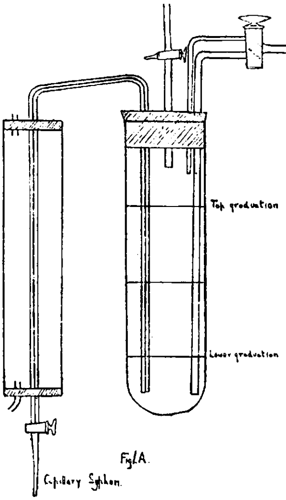
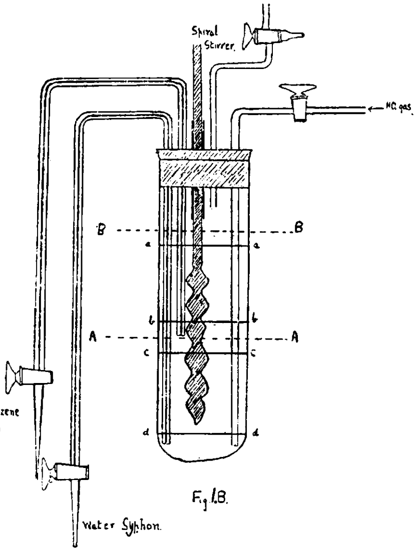


FIG. 1B.



The next determinations made were the solubilities of hydrogen chloride in (1) dry benzene; (2) water; (3) benzene saturated with water before saturation with hydrogen chloride; and (4) benzene saturated with water and hydrogen chloride simultaneously.

For measuring the solubility in dry benzene, the saturator used is shown in Fig. 1A. It was graduated, with all tubes in position, to deliver two amounts of 50 c.c. by means of a capillary syphon. The calibrations were found to be correct at 20°, to within about 0·01 c.c., by weighing water. Two inlet tubes for the hydrogen chloride were provided, one reaching below the lower graduation and the other just entering the vessel so that a stream of gas could be passed over the surface of the liquid when necessary. The gas escaped at atmospheric pressure. The syphon by which the liquid was removed was surrounded by a jacket kept filled with water at 20°. The saturator was placed in a thermostat and filled to just above the top graduation with benzene; and dry hydrogen chloride, after passing through a glass coil immersed in the thermostat, was bubbled through for many hours. The benzene was then run out as far as the top graduation, a stream of gas being passed over the surface all the time. The syphon was thus filled with saturated benzene. 50 C.c. were then run slowly into standard alkali, the jet of the syphon being kept below the surface of the liquid. The excess of alkali was titrated, phenolphthalein being used as indicator, since methyl-red is too soluble in benzene.

The results are summarised in Table I for 20·00°.

TABLE I.

| Expt. | Duration of saturation (hrs.). | Pressure (mm.). | Solubility (g./litre of solution). |
|---|---|---|---|
| 1 | 60 | 760·4 | 16·80 |
| 2 | 60 | 761·0 | 16·76 |
| 3 | 60 | 760·4 | 16·82 |
| 4 | 60 | 762·0 | 16·74 |
| 5 | 60 | 761·4 | 16·79 |
| 6 | 72 | 760·8 | 16·81 |
| 7 | 90 | 759·9 | 16·80 |
| | | Mean at 760 mm. | 16·80 |

For determining the solubility in water at 20·00° (Table II), a smaller saturator delivering 10 c.c. was used, and 24 hours were sufficient for saturation.

TABLE II.

| Expt. | Duration of saturation (hrs.). | Pressure (mm.). | Solubility (g./litre of solution). |
|---|---|---|---|
| 1 | 24 | 760·0 | 718·8 |
| 2 | 24 | 766·1 | 717·9 |
| 3 | 24 | 762·4 | 718·8 |
| 4 | 24 | 762·3 | 718·5 |
| 5 | 36 | 760·1 | 718·8 |
| | | Mean at 760 mm. | 718·8 |

The solubility in benzene previously saturated with water was found to be somewhat higher than in dry benzene: at 20·00° and atmospheric pressure, the results obtained were 18·28, 18·28, 18·32, 18·32, and 18·32 g. per litre.

This value cannot be used in conjunction with the solubility in water to determine the partition ratio at the saturation point, since when the wet benzene becomes saturated with hydrogen chloride it may take up a further amount of water and consequently still more hydrogen chloride. Accordingly, water was introduced into the saturator so that it covered the end of the long hydrogen chloride inlet tube but did not reach to the bottom of the syphon. The results for the solubility under these conditions were 18·47, 18·50, 18·50, and 18·50 g. HCl per litre.

We thus have at 20·0° and 760 mm. :

| | | |
|---|---|---|
| Solubility of hydrogen chloride in water ..................... | 718·8· | g. per litre. |
| Solubility of hydrogen chloride in dry benzene ........... | 16·80 | ,, ,, |
| Solubility of hydrogen chloride in benzene previously saturated with water ........................................ | 18·31 | ,, ,, |
| Solubility of hydrogen chloride in benzene simultaneously saturated with water and hydrogen chloride ........... | 18·50 | ,, ,, |

For partition experiments at high concentrations the apparatus in Fig. 1 B was used. It consisted of a glass tube with four etched graduations *aa*, *bb*, *cc*, and *dd*. The volume contained between *aa* and *bb* and between *cc* and *dd* was 50 c.c. The apparatus was calibrated with the tubes in position and with the stirrer lowered to the bottom of the vessel. Two syphons were provided; that to take off the top layer extended for 1 cm. below *bb*, while the other, to take off the bottom layer, extended for 1 cm. below *dd*. Both were made of capillary tubing and were lagged with cotton wool. The apparatus was placed in the thermostat, filled to AA with pure water and then to BB with benzene. Hydrogen chloride was passed in for periods varying from 1 to 48 hours, according to the concentration required. The spiral stirrer was very efficient, breaking up the benzene into tiny globules and distributing these throughout the aqueous layer. After the gas had been allowed to pass for the requisite time, it was turned off, and the stirring was continued for another 2 hours. The stirrer was then disconnected and lowered to the bottom, since the apparatus had been calibrated with it in this position. The two layers were allowed to separate. The benzene was then run down to the graduation *aa*, thereby filling the syphon with solution of the same concentration as that in the bulk of the apparatus. This procedure also served to remove the top layer, which might have gained or lost a little hydrogen chloride during the settling. 50 C.c. of the benzene layer were then run out into standard alkali and titrated. The whole procedure was immediately repeated with the aqueous layer.

The results (Table III) are expressed as g./litre, $C_w$ and $C_B$ representing the concentrations in the water and benzene phases, respectively.

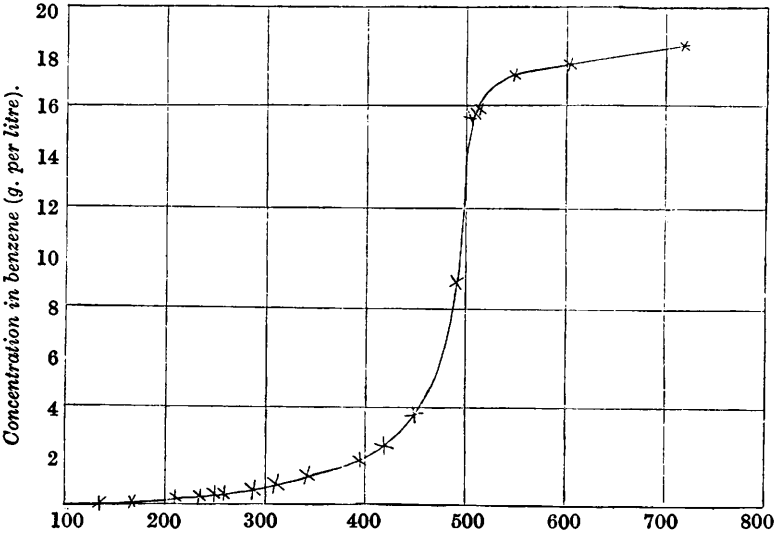
TABLE III.

*Partition of Hydrogen Chloride between Water and Benzene at 20·0°.*

| $C_w$. | $C_B$. | $C_w/C_B$. | $C_w$. | $C_B$. | $C_w/C_B$. | $C_w$. | $C_B$. | $C_w/C_B$. |
|---|---|---|---|---|---|---|---|---|
| 718·8 | 18·50 | 38·85 | 397·3 | 1·85 | 196·0 | 165·9 | 0·100 | 1660 |
| 604·0 | 17·7 | 34·1 | 379·8 | 1·818 | 208·9 | 134·6 | 0·059* | $2{\cdot}3\times10^3$ |
| 549·3 | 17·4 | 31·6 | 343·3 | 1·264 | 272 | 94·8 | 0·028 | $3{\cdot}4\times10^3$ |
| 513·3 | 15·99 | 32·1 | 312·0 | 0·929 | 336 | 71·9 | $1{\cdot}5\times10^{-2}$ | $4{\cdot}7\times10^3$ |
| 509·0 | 15·71 | 32·4 | 289·3 | 0·706 | 410 | 43·3 | $3{\cdot}6\times10^{-3}$ | $1{\cdot}2\times10^4$ |
| 504·6 | 15·62 | 34·2 | 259·0 | 0·532 | 504 | 34·5 | $1{\cdot}8\times10^{-3}$ | $2\times10^4$ |
| 492·5 | 8·96 | 55·0 | 249·0 | 0·449 | 554 | 19·5 | $2\times10^{-4}$ | $10^5$ |
| 448·5 | 3·72 | 120·7 | 236·1 | 0·382 | 619 | 12·3 | $10^{-4}$ | $1{\cdot}3\times10^5$ |
| 420·2 | 2·47 | 170·0 | 212·0 | 0·252 | 840 | | | |

* The figures for $C_B$ at and below this point are obtained from colorimetric estimations of hydrogen-ion concentration only; the others are based on volumetric titrations.

FIG. 2.



*Distribution of hydrogen chloride between benzene and water at 20°.*

It is evident from Fig. 2 that, at concentrations between 400 and 550 g./litre in the aqueous layer, there is a rapid passage from the polar to the non-polar form. When this is complete, there is a more or less constant partition ratio as shown by the table. If we regard the concentration in benzene as a measure of the amount of un-ionised hydrogen chloride in the water, then the shape of the curve in Fig. 2 is quite characteristic of an equilibrium between the ionised and un-ionised forms, the change from one to the other being about half complete at a concentration of about 490 g./litre.

According to uncorrected conductivity and osmotic data, this half-way point would come at much lower concentrations, where the Debye–Hückel theory shows ionisation to be still practically complete. The partition method reveals more nearly the true state of affairs.

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