443. *The Heat of Solution of Water Vapour in Various Solvents.*

By Ronald P. Bell.

Heats of solution (or, more generally, heats of transfer between two phases) are of great importance in experimental tests of theories of solution. In many cases the heat of solution cannot conveniently be measured directly, but is more readily accessible through the equation

$$d(\log_e c_1/c_2)/dT = -Q/RT^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c_1 and c_2 are the concentrations in the phases 1 and 2 at equilibrium, and Q is the heat of transfer at constant volume (which differs by a work term from the value obtained by direct measurement at constant pressure). This equation is valid for small values of c_1 and c_2.

The method described (preceding paper) for the quantitative determination of water in solution makes it possible to determine the heat of solution of water vapour in various solvents by this indirect method. The distribution coefficient of water between the solution and the vapour phase was determined by measuring the water concentration in equilibrium with a salt hydrate pair of known vapour pressure. This determination was carried out at various temperatures, and Q then calculated from equation (1). It would, of course, be possible to use liquid water in place of the hydrate pair, but this would introduce difficulties of filtering, and the possibility that the water might dissolve appreciable amounts of the other phase and thus alter its vapour pressure.

EXPERIMENTAL.

Unless otherwise stated, the solvents used were " Z. Analyse " preparations from Merck or Kahlbaum which were redistilled before use, only the middle fraction being retained. C_2Cl_4 was obtained by fractionating a commercial product three times; b. p. 124—125°. Di*iso*amyl ether was prepared from pure *iso*amyl alcohol and H_2SO_4; it was shaken with dil. NaOH aq., dried over anhyd. K_2CO_3, and twice distilled; b. p. 172—173°.

The salt hydrate pair used was $Na_2SO_4,10H_2O + Na_2SO_4$; this was chosen because it has a high v. p. which is known accurately over a convenient temp. range. The decahydrate was a guaranteed preparation of Merck, and it was mixed with an approx. equal amount of the dehydrated salt.

In carrying out a determination, 50 c.c. of solvent were rotated with about 10 g. of the hydrate mixture in a thermostat. Three temps. were used, 15°, 20°, and 25°, the control being in each case ± 0·02°. The first sample was taken after *ca.* 12 hrs.' rotation, which was found to suffice for the attainment of equilibrium. The determination was in all cases repeated after a further period of rotation, with concordant results (see Table I). A few comparative expts. with C_6H_6 showed that in this case equil. was reached after 1 hr.'s rotation, starting either with dry C_6H_6 or with C_6H_6 satd. with H_2O at room temp. The samples were withdrawn in a 10-c.c. pipette with a small filter of cotton-wool. Suction was applied through a $CaCl_2$ tube. The pipette was kept in an enclosure in the thermostat, and was calibrated by wt. for each solvent used.

The amount of H_2O in the sample was determined by the method described in the preceding paper. The HCl was titrated with 0·02*N*-NaOH (methyl-orange); 2—4 successive determinations were carried out with each solvent, using the same α-naphthoxydichlorophosphine. For volatile solvents, the current of air was satd. with solvent vapour before entering the drying tubes.

The correction necessary for the v. p. of the α-naphthoxydichlorophosphine varied between 1% and 8%. The final values for the equil. concns. of H_2O are given in the last col. of Table I. In calculating the values of Q (see Table II), equation (1) was used in the form

$$\log_{10} c_1T/p = Q/2{\cdot}303RT + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

where c_1 = concn. of H_2O in solution; p = partial pressure of H_2O vapour; B = integration const. This equation assumes that Q is independent of T in the range considered; and when $\log_{10} c_1T/p$ was plotted against $1/T$, a straight line was obtained in every case within the limits of experimental error.

The values of p (the v. p.'s of the salt hydrate pair at the three temps.) were taken from the work of Baxter and Lansing (*J. Amer. Chem. Soc.*, 1920, **42**, 419), whose value at 25° (19·19 mm.) agrees well with that obtained by Wilson (19·22 mm.; *ibid.*, 1921, **43**, 705) by a different method.

The values of c_1 can be used to calculate the solubility of H_2O in the various solvents at 15°, 20°, and 25° by assuming that the v. p. of H_2O in these solutions is proportional to its concn. over the small range involved: this is probably not quite correct, on account of the interaction between the water dipoles.

TABLE I.

(c_1 is given as g. per 1000 c.c. of solvent.)

Temp.	c_1.	Mean.	Temp.	c_1.	Mean.
	Nitrobenzene.			*Carbon tetrachloride.*	
15°	0·995, 1·010	1·00	15°	0·0620, 0·0650	0·0635
20	1·245, 1·225	1·23	20	0·0801, 0·0747, 0·0751	0·0767
25	1·480, 1·480	1·48	25	0·0945, 0·0925	0·0935
	Chlorobenzene.			*Bromobenzene.*	
15	0·262, 0·265, 0·265	0·264	15	0·251, 0·247	0·249
20	0·305, 0·300, 0·310	0·305	20	0·306, 0·300, 0·314	0·306
25	0·353, 0·356	0·354	25	0·378, 0·371	0·374
	Tetrachloroethylene			*Ethylene bromide.*	
15	0·0638, 0·0663	0·0650	15	1·03, 1·05	1·04
20	0·0871, 0·0850, 0·0815	0·0845	20	1·28, 1·32	1·30
25	0·108, 0·108	0·108	25	1·61, 1·61	1·61
	Toluene.			*Diisoamyl ether.*	
15	0·239, 0·241, 0·231, 0·237	0·237	15	0·572, 0·564	0·568
20	0·296, 0·300	0·298	20	0·691, 0·698	0·695
25	0·376, 0·364	0·370	25	0·839, 0·851	0·845

DISCUSSION OF RESULTS.

Except in the case of ions, very few attempts have been made to treat theoretically the energy changes connected with the transference of a molecule from one medium to another. The problem is in general very complex, but the author has previously pointed out (J., 1931, 1371; *Trans. Faraday Soc.*, 1931, **27**, 797) that for certain molecules (notably H_2O and NH_3) the change in the electrostatic energy of the dipole may be expected to be one of the chief factors. It was shown that, by taking a simple model for a dipole molecule and treating the solvent as a continuous dielectric, the following expression is obtained for the free energy of transferring 1 mol. at constant volume from a vacuum to a medium of dielectric constant D,

$$(N_0\mu^2/3a^3)[(D-1)/(2D+1)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where N_0 = number of molecules in 1 mol.; μ = dipole moment; a = radius of dipole molecule.

The corresponding expression for the heat of transference at constant volume is therefore

$$Q = A - T\frac{\partial A}{\partial T} = \frac{N_0\mu^2}{3a^3}\left\{\frac{D-1}{2D+1} - \frac{3T}{(2D+1)^2}\cdot\frac{\partial D}{\partial T}\right\}$$

which we shall write as

$$\left.\begin{aligned} Q &= \frac{N_0\mu^2}{3a^3}\phi(D) \\ \text{where} \quad \phi(D) &= \frac{D-1}{2D+1} - \frac{3T}{(2D+1)^2}\cdot\frac{\partial D}{\partial T} \end{aligned}\right\} \quad . \quad . \quad . \quad (3)$$

In the second paper quoted above, it was shown that equation (1) is in semi-quantitative agreement with the experimental results for the solubilities of water and ammonia in various solvents. The data given above for the heat of solution of water provide another test of the theory.

The magnitude of the discrepancies to be expected may be estimated by examining the data for the heats of solution of non-polar gases (cf., *e.g.*, Lannung, *J. Amer. Chem. Soc.*, 1930, **52**, 68), which should be zero according to the present treatment. They show a variation of about ± 1 kg.-cal. per mol., so that only molecules having a dipole energy change considerably larger than this can be expected to show any agreement with equation (3).

Table II contains the values of Q (in kg.-cal.) calculated from the results in Table I, and in addition values for other solvents (marked *) calculated from the solubility of water in these solvents at different temperatures. The data have been taken from "International Critical Tables," only those cases being used in which the mutual solubility is low. The values of Q were calculated according to equation (1a), p being in this case the vapour pressure of water. In each case Q was found to be constant over the whole temperature range.

The values of D and $\partial D/\partial T$ are from "International Critical Tables," except for di*iso*amyl ether, where the results of Estermann

(*Z. physikal. Chem.*, 1927, *B*, **1**, 152) are taken. In many cases the true values of $\partial D/\partial T$ are considerably in doubt, which causes some uncertainty in the values of $\phi(D)$, especially for low values of D. $\partial D/\partial T$ for tetrachloroethylene has not been experimentally determined, and the value given is based on analogy with carbon tetrachloride.

TABLE II.

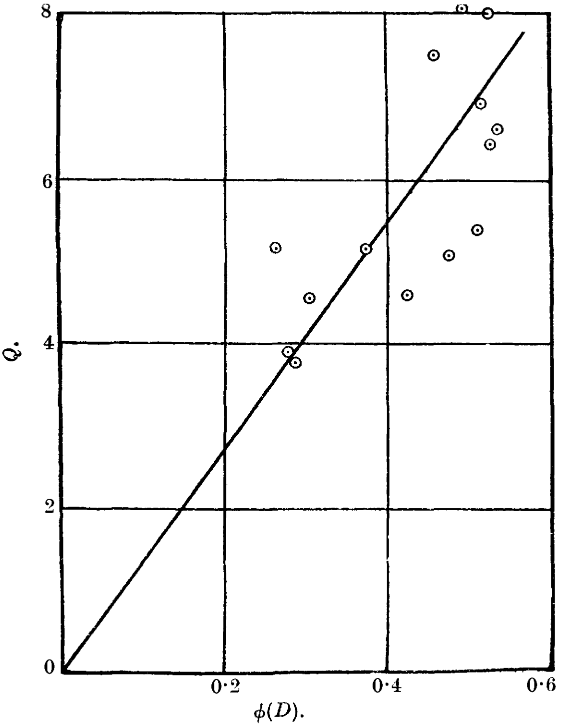
Solvent.	D.	$-100\partial D/\partial T$.	$\phi(D)$.	Q.
Carbon tetrachloride	2·24	0·14	0·266	5·16
Tetrachloroethylene	2·46	0·14	0·281	3·76
Benzene	2·28	0·19	0·285	3·77*
Toluene	2·39	0·23	0·301	4·58
Di*iso*amyl ether	2·82	0·52	0·376	5·13
Ethylene bromide	4·86	0·8	0·424	4·58
Ethyl acetate	6·4	1·5	0·459	7·55*
Bromobenzene	5·40	1·6	0·474	5·05
Aniline	7·25	2·5	0·495	8·10*
Nitrobenzene	36	18	0·510	5·36
Furfural	42	25	0·513	6·92*
Diethyl ether	4·34	1·9	0·524	8·00*
Paraldehyde	14·5	7·7	0·525	6·40*
Chlorobenzene	5·94	2·4	0·530	6·58

In the figure the experimental values of Q have been plotted against $\phi(D)$. The straight line represents equation (3), with the values $\mu = 1{\cdot}85 \times 10^{-18}$, $a = 1{\cdot}03 \times 10^{-8}$. The deviations of the experimental points are of the order of magnitude expected, *ca.* ± 1 kg.-cal. per mol. It therefore seems probable that the assumption of a spherical molecule and a continuous dielectric gives at least approximate values for the dipole contribution to the energies of transference, a reasonable value being used for the radius of the molecule. In the absence of any reliable theory for the transference energy of non-polar molecules, and of accurate data for $\partial D/\partial T$, it is impossible to make any stricter test.

Equation (1) is based on purely thermodynamical reasoning, and is strictly true for small values of c_1 and c_2. In previous papers (*loc. cit.*) the author has used the equation

$$A = RT \log_e c_1/c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for testing equation (2), expressing c_1 and c_2 as volume concentrations. Equation (4) has previously been employed extensively by other authors (see, *e.g.*, Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 2098; Bjerrum and Larsson, *Z. physikal. Chem.*, 1927, *A*, **127**, 358; Bjerrum, *Trans. Faraday Soc.*, 1927, **23**, 445; Tammann, *Z. anorg. Chem.*, 1928, **159**, 17; Brönsted, *Chem. Rev.*, 1928, **5**, 296; *Z. physikal. Chem.*, 1929, *A*, **143**, 301). It should, however, be emphasised that equation (4) has no thermodynamic basis when c_1 and c_2 refer to different media. It has, in fact, been pointed out by Scatchard (*loc. cit.*) that the use of volume concentrations in the above expression is inconsistent with the theory of perfect solutions. Scatchard therefore employs the mole-fraction as unit, but the expression still lacks any strict theoretical basis except for two perfect solutions in equilibrium, for which $c_1 = c_2$ (in mole-fractions) and A is zero. In any case it is obviously impossible to apply this version of the equation to a system in which one phase is a gas under varying pressure.



Boltzmann's theorem leads to an expression of the same form as equation (4), but it has been shown by Herzfeld (Müller–Pouillet, " Handbuch der Physik," section on kinetic theory) that in a strict statistical treatment c_1 and c_2 are concentrations expressed in terms of " free volume," *i.e.*, the space between the solvent molecules. This concept of " free volume " is not directly accessible to experiment, and we may doubt if it corresponds to any real property of the liquid.

It would thus appear that equation (4) has no strict theoretical basis in any concentration scale (except when c_1 and c_2 refer to the same medium). While it probably has a qualitative significance when A is very large, it is certainly preferable to employ equation (1) in testing any theory of energies of transfer.

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