The Aqueous Solubilities of Nitrogen Trifluoride and Dinitrogen Tetrafluoride

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An apparatus has been designed for the measurement of very low gas solubilities (*ca.* 10^{-6} mol fraction), allowing fast equilibration between the solute and solvent. The solubilities of NF_3 (298—318 K) and of N_2F_4 (288—318 K) in water have been determined, and the enthalpies and entropies of solution derived.

GAS solubilities are relevant to the theoretical understanding of the liquid state and solutions, and to such practical applications as understanding the mechanism of the toxicology of inhaled gases. The anomalous solubility properties of fluorine compounds[1] have proved to be of great importance in the thermodynamic study of aqueous[2,3] and non-aqueous[4-6] solutions. Ashton *et al.*[3] have constructed an apparatus specifically designed to measure gas solubilities of the order of 10^{-6} mol fraction and they report the solubilities of CF_4, SF_6, and NF_3 in water between 275 and 323 K.

The aqueous solubilities of NF_3 and N_2F_4 are important in the understanding of their toxicity. Toxicological and other studies[7-11] have shown that inhalation results in methaemoglobin formation, though it is less certain how far this is a primary lethal factor. Kinetic experiments[11] have demonstrated the considerable oxidative capacity of these gases although in pure water NF_3 has been shown to be inert even at 406 K. N_2F_4, after long induction periods (several days at 333 K), undergoes hydrolysis with an exponential increase in reaction rate. However, exposure to a mixture of 1% (v/v) of NF_3 in air for 70 min, or to the same concentration of N_2F_4 for 25 min, was almost invariably lethal to rats.[8,10] Since the first stage of intoxication presumably is the dissolution of the gas, the aqueous solubility is clearly important.

An apparatus was designed for the measurement of gas solubilities of the order of 10^{-5}—10^{-6} mol fraction and since measurements of the solubility of N_2F_4 in water were expected to be complicated by its slow hydrolysis, the apparatus was designed so that gas-solvent equilibration was more rapid (*ca.* 3 h) than in the apparatus of Ashton *et al.*[3] (*ca.* 12 h).

EXPERIMENTAL

Part of the apparatus is shown in Figure 1. The gas-burette, of the usual form, was calibrated with weighed quantities of mercury. The glass solution vessel (Figure 2) was *ca.* 380 cm³ in volume and calibrated to give the volume between hairline (b) and stopcock (T), and to give the volume per unit length of the precision-bore tubing (C) below hairline (b). The base of the bulb (B) was flattened, the slope allowing drainage of solvent into tube (C). This arrangement permitted vigorous stirring by means of a polytetrafluoroethylene-encapsulated magnetic follower (F, 23 mm long) which caused intimate mixing of the vapour with the solvent. The follower was driven from below by a fully submersible magnetic stirrer motor. Tube (C) was used as the high-pressure arm of a mercury manometer and connected *via* a grease-free stopcock to the low-pressure arm (M). The mercury reservoir arm (R) was incorporated in order to maintain the level of mercury in the solution vessel within the tube (C). This system allowed pressures in the solution vessel of up to *ca.* 1300 mmHg † to be measured. The manometer tubes (C) and (M) were of 16 mm internal diameter in order to reduce 'capillary errors,'[12] and both arms were set vertical by use of a

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† mmHg = (101·325/760) kPa.

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spirit-level. A reference pressure of less than 10^{-3} mmHg was maintained above the mercury meniscus in the low-pressure arm of the manometer by pumping continuously during pressure measurements. Pressure measurements were made with a 2 m focal length cathetometer in conjunction with two steel rules, the latter placed between the arms of the manometer. The cathetometer was used only to interpolate between the scale divisions on the rule. Green transmitted light was used to illuminate the mercury menisci.[13] The solution vessel (B), the manometer (M), and the volume calibration vessel (D) were thermostatted at temperatures between 288 and 318 K by means of a water-bath controlled to $\pm 0{\cdot}01$ K.

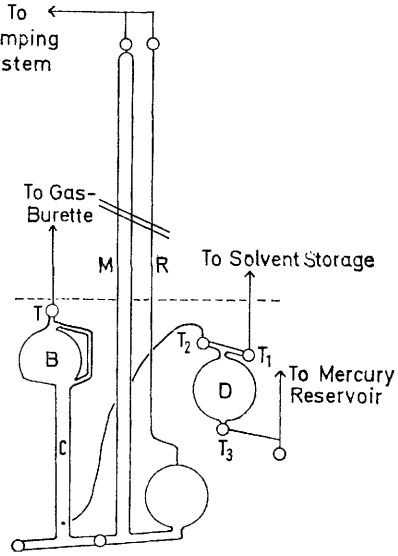

FIGURE 1 The gas-solubility vessel (B), the low-pressure manometer arm (M), the high-pressure manometer arm (C), the solvent-volume calibration vessel (D), and the compensating mercury manometer arm (R). Thermostatted to level indicated (- - - -)

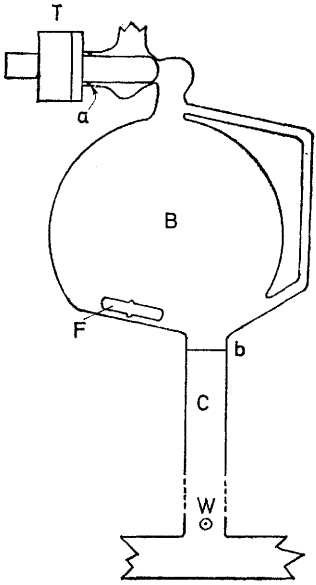

FIGURE 2 The solubility vessel (B), the isolating tap (T), the follower (F), the high-pressure manometer arm (C), and the solvent inlet (W)

Incomplete degassing of the solvent is probably the main source of error in determining gas solubilities.[13] Water obtained from the distillation of acidic potassium permanganate solution was degassed by high-vacuum trap-to-trap distillation with continuous pumping using U-tube traps designed to accommodate 250 cm^3 aliquot portions. Crushed solid carbon dioxide in acetone was used for condensing the water vapour. The water was distilled three times and during the final distillation the pressure of non-condensible vapours was maintained at the base-pressure of the pumping system (10^{-5}—10^{-6} mmHg) indicating satisfactory degassing. After distillation, the degassed water was siphoned out of the final trap into a storage vessel and sealed between stopcocks, the vapour pressure of the slightly warmed water being sufficient to initiate the siphon. An approximately measured quantity of gas was transferred from the gas-burette into the evacuated solution vessel. The accurate gas quantity was obtained from its measured pressure, the known volume of the solution vessel, the temperature, and an equation of state [14,15] (early experiments with use of the gas-burette as the accurate measure of quantity of gas were abandoned because of excessive fluctuations in atmosphere pressure). By addition of the gas before the solvent, it was possible to measure the gas in a dry state, *i.e.*, free from solvent vapour. It has been suggested that the commonly used 'wet' method can give rise to low values of gas solubilities.[3,16,17] The solvent was allowed to fill completely the solvent-calibration vessel (D) and the contents were thermostatted before stopcock (T_1) was closed, thus trapping a known fixed volume (*ca.* 300 cm^3) of solvent. The mercury level in the solution vessel was lowered to just below the solvent inlet (W in Figure 2). The solvent was then forced out through stopcock T_2 through a 0·5 mm capillary tube into the solution vessel by allowing mercury to enter the calibration vessel through stopcock T_3. When the mercury had forced all the solvent into the solution vessel, it was allowed to flow through the capillary tube until the mercury meniscus in tube (C) rose to above the solvent inlet. Three hours of fast stirring were found sufficient for equilibration and measurements of the positions of the mercury menisci, of the solvent meniscus, and of the hairline (b) were sufficient to define the pressure and volume of the residual gases (water vapour and undissolved solute). These results, in combination with the temperature of the solution vessel, permitted the amount of dissolved gas in a known volume of solvent to be calculated. This process was repeated at a series of temperatures and pressures (by adjustment of the manometer reservoir arm) without further transfer of gas. Grease-free high-vacuum stopcocks ('Uniform,' Glass Precision Engineering, Hemel Hempstead, polytetrafluoroethylene and Pyrex glass) were used throughout the apparatus but for use at sub-ambient temperatures (in the water-bath)

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they were modified by the addition of a 'Viton A' rubber O ring in the vacuum-to-atmosphere seal (a in Figure 2). Several corrections were applied in the calculation of the results.[18] The most important was that for the change in volume of the solution vessel due to pressure changes. Other corrections included those for the isothermal-compressibility of water and for the change in volume of the solvent due to evaporation. Following recommended practice,[16] full details of a typical calculation are given in ref. 18.

NF_3 (Air Products and Chemicals, Inc., Pennsylvania, U.S.A.) was purified by high-vacuum trap-to-trap distillation through traps held at 113 and 77 K. The purity of the 77 K fraction was confirmed by pressure measurements on the vapour above liquid NF_3 held at 147 K before and after expansion of the vapour into an evacuated bulb.

TABLE 1

Solubility (in Keunen coefficients, k), enthalpies (ΔH), and entropies (ΔS) of solution for NF_3 in water (data from Ashton *et al.*[3] in parentheses)

T/K	n [d]	10^3k	T/K	$-\Delta H$ [b]/kcal mol^{-1}	$-\Delta S$ [b]/cal mol^{-1} K^{-1}
298·21	8	17·76 ± 0·24 [c] (17·78 ± 0·10)	278·15	4·7 [a](5·3)	38 [a](40)
298·26	1	17·25 (17·76 ± 0·10)	288·15	4·1 [a](4·6)	36 [a](38)
298·56	1	17·60 (17·66 ± 0·10)	298·15	3·5 (3·8)	34 (35)
308·29	5	14·82 ± 0·07 [c] (14·73 ± 0·10)	308·15	2·9 (3·1)	32 (32)
318·28	4	12·95 ± 0·07 [c] (12·84 ± 0·10)	318·15	2·3 (2·3)	30 (30)

Constants for equation (1): a = 4596·4 K (5785·95 K), b = 29·558 (38·2556), c = −93·404 (−118·9122).

[a] Extrapolated from equation (1). [b] 1 cal = 4·184 J. [c] Uncertainty quoted as ± $\bar{s}$. [d] n = no. of experiments.

The N_2F_4 (Research Grade: Air Products and Chemicals, Inc.) was initially pale mauve when condensed in the vacuum line from the cylinder. This colour has been attributed to the thermally unstable compound, NF_2NO.[19-21] High-vacuum trap-to-trap distillation through traps held at 113 K and 77 K failed to produce any appreciable fractionation. The impure N_2F_4 was therefore mixed with bromine in the vapour phase (to form NOBr) and then fractionated through traps at 193, 113, and 77 K. The 77 K fraction was initially a very pale mauve and was discarded, but after continued fractionation a clear fraction was obtained at 77 K. The identity and purity of this N_2F_4 were confirmed by gas-phase i.r. spectra and by vapour-pressure measurements with expansion (as for NF_3, see above).

RESULTS

The experimental results for the solubility of NF_3 in water at temperatures between 298 and 318 K are in Table 1. These are given as Kuenen coefficients, defined as the volume of gas in cm^3, corrected to 273·15 K and 760 mmHg pressure, which, at a partial pressure of 760 mmHg, will dissolve in 1 g of solvent. The results were fitted by the method of least-squares to an equation of the form (1) (x_2 = mol fraction of solute, T = temperature/K,

$$\log_{10} x_2 = a/T + b \log_{10} T + c \qquad (1)$$

and a, b, and c are constants) and the enthalpy and entropy changes for dissolution obtained according to Ashton *et al.*[3] Table 1 includes comparison with the data of Ashton *et al.* and the agreement is satisfactory over the common temperature range (298—318 K) but our extrapolated results are in less satisfactory agreement.

The results for the solubility of N_2F_4 in water are in Table 2. Analysis of the results indicated that a slow reaction had almost certainly occurred during measurements. This produced a slow increase in the calculated solubilities with time, equivalent to the removal of *ca.* $1{\cdot}8 \times 10^{-5}$ mol of N_2F_4 (0·4% of that originally added) during measurements. In order to compensate for this reaction, the exponential increase in reaction rate with time found by Hurst and Khayat[11] was assumed. Further assuming that the rate increased by a factor of two for each 10 K rise in temperature and that the reaction products were completely dissolved and did not interfere with the solubility of the remaining N_2F_4, we obtained the corrected solubilities, given in Table 2. Derived enthalpies and entropies of solution at 10 K intervals are in Table 3. Although several assumptions were involved, this correction was very small (*ca.* 2% in the Kuenen coefficient at 298 K), and thus even a fairly large error in the calculation of the extent of reaction would have a very small effect on the corrected solubility. At the end of the solubility run, the water was purged of N_2F_4 and analysed for ionic fluoride by use of a fluoride selective-ion electrode. This concentration ($2{\cdot}55 \times 10^{-4}$ mol dm^{-3}) indicated that $1{\cdot}96 \times 10^{-5}$ mol of N_2F_4 had reacted with the water in the solution

TABLE 2

Experimental, corrected, and calculated solubilities (in Keunen coefficients, k) for N_2F_4 in water

T/K	10^3k (exptl.)	10^3k (corr.)	10^3k (calc.) [a]
288·15	27·32	26·42	26·22
289·15	25·59	24·77	25·33
289·15	26·26	25·53	
289·97	25·43	24·69	24·64
298·11	19·96	19·07	19·21
298·11	20·14	19·21	
298·11	20·19	19·21	
298·16	19·15	19·10	19·18
298·16	19·42	19·32	
298·16	19·67	19·55	
298·26	19·15	19·08	19·13
308·09	15·46	14·88	15·07
308·09	15·79	15·11	
318·18	12·88	12·55	12·56
318·18	12·95	12·55	
318·18	13·14	12·61	

[a] Calculated from equation (1) obtained by fitting the corrected solubility results to the equation: a = 6936·9, b = 45·345, and c = −140·28.

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vessel, in close agreement with the assumed extent of reaction (calculated as described above) of $2{\cdot}02 \times 10^{-5}$ mol N_2F_4 at the time of purging the liquid phase.

TABLE 3

Corrected (see text) Keunen coefficients (k), enthalpies (ΔH), and entropies (ΔS) of solution for N_2F_4 in H_2O at 10 K intervals

T/K	$10^3k_{\text{corr.}}$ [c]	$-\Delta H$ [b]/kcal mol^{-1}	$-\Delta S$ [b]/cal mol^{-1} K^{-1}
278·15	38·78 [a]	6·7 [a]	45 [a]
288·15	26·22	5·8	41
298·15	19·19	4·9	38
308·15	15·06	4·0	35
319·15	12·56	3·1	33

[a] Extrapolated by use of equation (1). [b] 1 cal = 4·184 J. [c] Precision *ca.* ±1%.

DISCUSSION

Enthalpies and entropies of solution for gases in water at room temperature are significantly different from the corresponding quantities for the same gases dissolved in non-polar solvents. Attempts to rationalize this fact have included postulating [22] an ordered water layer (or 'iceberg') around the dissolved gas molecules and the development [23] of a cavity model. In addition there are numerous empirical and semiempirical relationships between the thermodynamic solution functions and other properties of the solute. Of these, the Barclay–Butler rule [22,24] is perhaps the most widely used and its theoretical foundation has been examined.[25] Fluorinated species appear to deviate from this rule and the data of Ashton *et al.*[3] for CF_4, SF_6, and NF_3 together with our results for NF_3 and N_2F_4 are shown on a Barclay–Butler plot in Figure 3. Ashton *et al.* have shown (see their Figure 4 in ref. 3) that entropies of solution in water at 298·15 K for spherically-symmetric molecules (including fluorinated compounds) are linearly related to the molar volume of the liquid solute at its b.p., a relationship first suggested by Powell and Latimer.[26] Spherically asymmetric species (*e.g.*, hydrocarbons other than methane) appear to form a parallel correlation and our results show that N_2F_4 fits satisfactorily into the latter correlation.

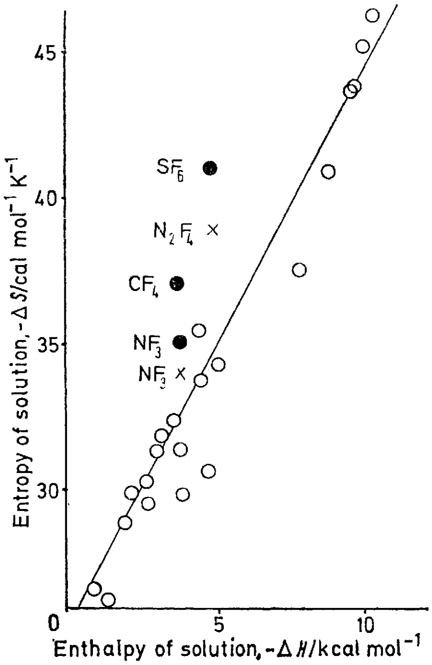

FIGURE 3 Barclay–Butler plot for non-polar gases at 298·15 K in water (points ○, taken from ref. 22 and H. F. G. Herington, *J. Amer. Chem. Soc.*, 1951, **73**, 5883; points ● from Ashton *et al.*;[3] points ×, this work)

We thank the Medical Research Council for financial support.

[3/1348 *Received*, 26*th June*, 1973]

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