

COMPONENTS:

1. Methanamine (methylamine); CH_5N ; [74-89-5]
N-Methylmethanamine (dimethylamine); $\text{C}_2\text{H}_7\text{N}$; [124-40-3]
N,N-Dimethylmethanamine (trimethylamine); $\text{C}_3\text{H}_9\text{N}$; [75-50-3]
2. Organic liquids

EVALUATOR:

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August 1983

CRITICAL EVALUATION:

The solubility of amines in organic liquids has been reviewed and assessed by Gerrard (1) and by Counsell, Ellender and Hicks (2). In the case of many systems only one series of measurements has been carried out and therefore the reliability of the data must then be judged by testing whether a particular set fits into a general pattern shown for closely related systems.

Methanamine

Mole fraction solubilities of methanamine show a similar pattern to those of ammonia in that values are higher when the solvent contains oxygen or nitrogen as compared with values for hydrocarbons.

Hydrocarbon solvents

Solubilities in hydrocarbons have been measured by Gerrard (1) and by Wolff *et al.* (3-6). Very detailed investigation of the systems with butane, hexane and nonane were made by Wolff and co-workers. The measurements on the system with butane (4) extended to temperatures above the boiling point of pure butane at 1 atm. Mole fraction solubilities at a partial pressure of 1 atm for these three hydrocarbons, calculated from measurements by Wolff *et al.*, show an appreciable decrease with increase in chain length at 273 K but insignificant change at 283 K and 293 K. However the mole fraction solubility in decane at 273 K and 1 atm partial pressure, as determined by Gerrard, is 0.413 compared with the value of 0.353 for nonane at this temperature and partial pressure, as determined by Wolff *et al.*

The solubility in benzene was measured by Gerrard (1) at 283 K and 1 atm partial pressure. The mole fraction solubility is about double that in *n*-alkanes under similar conditions but is smaller than the value corresponding to a reference line based upon the equation

$$x_1 = p_1 / p_1^{\circ}$$

where p_1 is the partial pressure of methanamine and p_1° is the vapor pressure of liquified methanamine at the temperature of measurement. Measurements by Gerrard indicate that substitution of methyl groups into benzene lowers the mole fraction solubility of methanamine. Ammonia shows a similar pattern of solubility behaviour in benzene and substituted benzenes and there is no reason to doubt the values reported by Gerrard.

Solvents containing oxygen

The solubilities of methanamine in numerous solvents containing oxygen have been reported by Gerrard (1) and may be accepted as tentative values. Mole fraction solubilities in alcohols are above the reference line values and higher than those in other solvents containing oxygen. Gerrard's measurements of the solubilities in 1,2-ethanediol and 1,2,3-propanetriol at 283 K indicate that mole fraction solubility increases with increase in the number of hydroxyl groups as is the case with ammonia. Measurements at 305 K and a partial pressure of methanamine of 1223 mmHg were made by Copley *et al.* (7) on 1,2-ethanediol, 2,2'-oxybisethanol and 1,2,3-propanetriol. In this case the reported mole fraction solubility in 1,2-ethanediol is greater than that in 1,2,3-propanetriol but these values may be less reliable than the values reported by Gerrard because of the nature of the apparatus used.

Cont.

<p>COMPONENTS:</p> <p>1. Methanamine (methylamine); CH_5N; [74-89-5] <i>N</i>-Methylmethanamine (dimethylamine); $\text{C}_2\text{H}_7\text{N}$; [124-40-3] <i>N,N</i>-Dimethylmethanamine (trimethylamine); $\text{C}_3\text{H}_9\text{N}$; [75-50-3]</p> <p>2. Organic liquids</p>	<p>EVALUATOR:</p> <p>P. G. T. Fogg, School of Chemistry, Polytechnic of North London, Holloway, London, U.K.</p> <p>August 1983</p>
<p>CRITICAL EVALUATION:</p> <p>Solvents containing oxygen (cont.)</p> <p>Values published by Gerrard (1) of the mole fraction solubilities in 1,1'-oxybis-pentane, 1,1'-oxybis-octane, ethoxybenzene and 1,4-dioxane fall below reference line values, i.e. show positive deviations from Raoult's law, but are greater than values for hydrocarbons, as expected by analogy with ammonia. There is a marked variation in the mole fraction solubility in 1,1'-oxybis-octane with change in temperature. At a partial pressure of methanamine of 1 atm the mole fraction solubility is 0.604 at 273 K and 0.388 at 283 K. The mole fraction solubility at a partial pressure of methanamine of 1 atm in <i>N,N</i>-dimethylformamide, also reported by Gerrard, shows a similar marked variation so there is no reason to question the values.</p> <p>Solvents containing nitrogen</p> <p>The solubilities of methanamine in a wide range of solvents containing nitrogen have been investigated by Gerrard (1). The methanamine and <i>N,N</i>-dimethylmethanamine system has also been studied by Wolff and Würtz (6) over the whole of the concentration range at temperatures from 223 K to 293 K. There are no obvious inconsistencies in any of these measurements which should be accepted as tentative.</p> <p>Measurements by Gerrard on benzenamine and <i>N</i>-substituted benzenamines give an interesting series of mole fraction solubilities at 283 K with the values in the order: benzenamine > <i>N</i>-methyl- > <i>N</i>-ethyl- > <i>N,N</i>-dimethyl- > <i>N,N</i>-diethyl-. He also found that the mole fraction solubility in quinoline and pyridine at 283 K and a partial pressure of 1 atm were greater than the value of the solubility in benzene under the same conditions. This is to be expected since other workers (see ammonia evaluation p.3) have found that the mole fraction solubility of ammonia in quinoline is greater than that in benzene at 291 K.</p> <p>Solvents containing halogens</p> <p>The equilibrium between methanamine and tetrachloromethane at 253 K, 273 K, and 293 K and the full composition range has been investigated by Wolff and Würtz (4). The mole fraction solubility of methanamine at 283 K and a total pressure of 1 atm was measured by Gerrard (1). The evaluator has estimated that this value agrees to about 1% with a corresponding value interpolated from the measurements reported by Wolff and Würtz. Unlike ammonia, methanamine has greater mole fraction solubility in tetrachloromethane than in hydrocarbons, at the same temperature and partial pressure.</p> <p>Gerrard also measured mole fraction solubilities in trichloromethane at 273 K and 283 K. Values are similar to ones reported by the same author for dissolution in long chain alcohols.</p> <p>Gerrard (1) measured solubilities in benzene and bromobenzene and found that introduction of a bromine atom into the benzene nucleus increases the mole fraction solubility of methanamine at 283 K. Ammonia shows a similar behaviour in benzene and chlorobenzene but the reported mole fraction solubility of ammonia in bromobenzene (9) is slightly less than that in benzene (10). Gerrard also found that the mole fraction solubilities in 1-methyl-3-bromobenzene were lower than those in bromobenzene at 283 K but close to those in 1-bromo-naphthalene. Again ammonia shows analogous behaviour in benzene and toluene. (See ammonia evaluation p.10 .) There is therefore no reason to doubt Gerrard's measurements.</p> <p style="text-align: right;">Cont.</p>	

<p>COMPONENTS:</p> <p>1. Methanamine (methylamine); CH_5N; [74-89-5] <i>N</i>-Methylmethanamine (dimethylamine); $\text{C}_2\text{H}_7\text{N}$; [124-40-3] <i>N,N</i>-Dimethylmethanamine (trimethyl- amine); $\text{C}_3\text{H}_9\text{N}$; [75-50-3]</p> <p>2. Organic liquids</p>	<p>EVALUATOR:</p> <p>P. G. T. Fogg, School of Chemistry, Polytechnic of North London, Holloway, London, U.K.</p> <p>August 1983</p>
<p>CRITICAL EVALUATION:</p> <p style="text-align: center;"><i>N</i>-Methylmethanamine</p> <p><i>N</i>-Methylmethanamine has a higher boiling point than methanamine and has therefore the greater tendency to condense. Relative mole fraction solubilities in different organic solvents are similar for the two gases.</p> <p>Hydrocarbon solvents</p> <p>As is the case with ammonia and methanamine, the mole fraction solubility is lower in hydrocarbons than in alcohols.</p> <p>The <i>N</i>-methylmethanamine and hexane system has been studied over the whole of the concentration range at temperatures from 223 K to 293 K by Wolff <i>et al.</i> (10,11). Gerrard (1) measured the mole fraction solubility in decane at various partial pressures and temperatures from 283 K to 298 K. The evaluator has calculated that Wolff's data indicate a mole fraction solubility of 0.473 at 293 K and a partial pressure of 1 atm when the solvent is hexane. This is close to the value of 0.501 given by Gerrard for the mole fraction solubility in decane under the same conditions of temperature and pressure.</p> <p>Gerrard (1) has also measured the solubility in benzene and methyl benzenes. As expected by analogy with the behaviour of ammonia and methanamine, the mole fraction solubility is greater in benzene than in alkanes. However he did not observe the regular change in mole fraction solubilities of <i>N</i>-methylmethanamine with increase in number of methyl groups substituted into the benzene nucleus which he had observed for methanamine.</p> <p>Solvents containing oxygen</p> <p>Mole fraction solubilities in methanol, ethanol and 1-propanol have been measured by Niepel <i>et al.</i> (12) and in 1-butanol and 1-octanol by Gerrard (1). Mole fraction solubilities tend to increase with increase in chain length but the solubility in methanol is greater than that in ethanol. Ammonia shows a similar pattern of behaviour with anomalous solubility in methanol and there is no reason to reject the values for <i>N</i>-methylmethanamine. Gerrard measured the mole fraction solubilities in 1,2-ethanediol and 1,2,3-propanetriol at 283 K. As with ammonia, increase in number of hydroxyl groups increases the mole fraction solubility. The solubility in 1,2,3-propanetriol was also measured by Copley <i>et al.</i> (7) but direct comparison with Gerrard's values is not possible because the temperature of measurement was 305 K.</p> <p>Gerrard measured the mole fraction solubilities in three ethers and in dioxane at 293 K. As expected by analogy with ammonia and methanamine, solubilities are higher than in the two alkanes which have been studied but lower than in alcohols. Gerrard showed that the mole fraction solubility in ethoxybenzene is higher than the solubility in benzene. Methanamine behaves in a similar way in these two solvents so the measurements fall into a consistent pattern. Gerrard's measurements indicate that the mole fraction solubilities at 293 K in 1-phenylethanol and in ethyl benzoate are similar to solubilities in the ethers which were studied. However the mole fraction solubility in 1-phenyl benzoate is slightly less than the solubility in methylbenzene under the same conditions. This differs from the pattern reported for methanamine.</p>	

Cont.

COMPONENTS:

1. Methanamine (methylamine); CH_3N ; [74-89-5]
N-Methylmethanamine (dimethylamine); $\text{C}_2\text{H}_7\text{N}$; [124-40-3]
N,N-Dimethylmethanamine (trimethylamine); $\text{C}_3\text{H}_9\text{N}$; [75-50-3]
2. Organic liquids

EVALUATOR:

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 Polytechnic of North London,
 Holloway,
 London, U.K.
 August 1983

CRITICAL EVALUATION:

Solvents containing nitrogen

The solubilities of *N*-methylmethanamine in a wide range of organic solvents containing nitrogen have been measured by Gerrard (1). There is no reason to doubt their reliability as values appear to fall into a consistent pattern but there are no measurements by other workers for direct comparison. Measurements on benzenamine and *N*-substituted benzenamines lead to a series of mole fraction solubilities at 293 K and 1 atm which is similar to the order of solubilities of methanamine at 283 K. Values are in the order: benzenamine > *N*-methyl- > *N*-ethyl- > *N,N*-diethyl- > *N,N*-dimethyl-. The two last mentioned compounds are in the reverse order in the case of the solubilities of methanamine. As in the case of methanamine however, the mole fraction solubility in benzylamine is less than the solubility in benzenamine. The mole fraction solubility in pyridine was found to be higher than that in quinoline at 293 K. Gerrard found that methanamine behaved in the same way at 283 K.

Solvents containing halogens

The *N*-methylmethanamine and tetrachloromethane system was studied by Wolff and Höppel (10) at 253 K to 293 K over the whole of the concentration range. Gerrard measured the mole fraction solubility of *N*-methylmethanamine in tetrachloromethane and in several other halogenated solvents at 293 K (1).

Gerrard reported that the mole fraction solubility in tetrachloromethane at a total pressure of 1 atm and 293 K was 0.596. The evaluator has estimated that this corresponds to a mole fraction solubility of 0.624 at a partial pressure of *N*-methylamine of 1 atm. This is close to the value of 0.604 which the evaluator has calculated from measurements reported by Wolff and Höppel. The mole fraction solubility in this solvent is higher than that in hydrocarbons but lower than that in alcohols under the same conditions. The behaviour of methanamine is similar.

Gerrard also found that the mole fraction solubility in trichloromethane was higher than that in tetrachloromethane at 293 K and a total pressure of 1 atm. This is again similar to the behaviour of methanamine at 283 K.

The mole fraction solubility of *N*-methymethanamine in chloro-, bromo- and iodobenzene (1) was found to be higher than the solubility in benzene at 293 K at a total pressure of 1 atm just as the solubility of methanamine in chlorobenzene was found to be higher than that in benzene.

N,N-Dimethylmethanamine

N,N-dimethylmethanamine has a boiling point, and hence a tendency to condense, in between that of methanamine and that of *N*-methylmethanamine. However replacement of all three hydrogen atoms in ammonia by methyl groups causes significant differences in behaviour from that of the primary or secondary amine.

Hydrocarbon solvents

Solubilities in hydrocarbons have been measured by Gerrard (1), by Halban (13) and by Wheeler and Levy (14). Wolff and Würtz (5) have investigated the *N,N*-dimethylmethanamine and hexane system at 223 K to 293 K over the whole of the concentration range. The evaluator has calculated from data given by Wolff and Würtz that the mole fraction solubility in hexane is 0.024 at 298 K and a partial pressure of *N,N*-dimethylmethanamine of 42 mmHg. The value given by Halban for the mole fraction solubility under these conditions is 0.022. Although the Halban value is likely to be the less accurate it gives support to the work by Wolff and Würtz.

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<p>COMPONENTS:</p> <p>1. Methanamine (methylanine); CH_5N; [74-89-5] <i>N</i>-Methylmethanamine (dimethylamine); $\text{C}_2\text{H}_7\text{N}$; [124-40-3] <i>N,N</i>-Dimethylmethanamine (trimethyl- amine); $\text{C}_3\text{H}_9\text{N}$; [75-50-3]</p> <p>2. Organic liquids</p>	<p>EVALUATOR:</p> <p>P. G. T. Fogg, School of Chemistry, Polytechnic of North London, Holloway, London, U.K.</p> <p>August 1983</p>
<p>CRITICAL EVALUATION:</p> <p>Hydrocarbon solvents (cont.)</p> <p>Direct comparison cannot be made between solubilities in benzene measured by Gerrard and those measured by Halban because they were made at different temperatures. However in each case the mole fraction solubility is less than the mole fraction solubility in hexane under the same conditions as may be calculated from the data given by Wolff. This contrasts with the behaviour of ammonia, methanamine and of <i>N</i>-methylmethanamine which have greater mole fraction solubilities in benzene than in alkanes at temperatures between 273 K and 293 K.</p> <p>Wheeler and Levy (14) apparently calculated the Henry's law constant for heptane at 233 K from a linear variation of mole fraction solubility with variation of pressure to about 70 mmHg. In the same way the Henry's law constant for 273 K was calculated from a linear variation of mole fraction solubility to about 140 mmHg. The evaluator has calculated that the corresponding mole fraction solubility at 233 K and 70 mmHg is 0.473 and that at 273 K and 140 mmHg is 0.162. These may be compared with values for hexane which the evaluator has calculated from data provided by Wolff and Würtz. At 233 K and 70 mmHg the mole fraction solubility in hexane is 0.653 and at 273 K and 140 mmHg the value is 0.189. The study carried out by Wolff and Würtz covers the whole of the concentration range and, in the opinion of the evaluator, is more reliable than that carried out by Wheeler and Levy. In the light of the comparison of apparent solubilities in hexane and heptane the values for heptane should be used with caution.</p> <p>Gerrard (1) measured the mole fraction solubilities in decane at 283 K. The value which was reported for a pressure of 1 atm is 0.786. This value compares favourably with the value of 0.771 for mole fraction solubility in hexane under the same conditions, which the evaluator has calculated from data given by Wolff and Würtz.</p> <p>Solvents containing oxygen</p> <p>The solubility in a number of alcohols has been measured by Gerrard (1) at pressures to 1 atm and by Halban (13) at low pressures. There is no reason to question the general pattern of solubilities.</p> <p>Benzenemethanol is the only alcohol studied by both workers. For this solvent the evaluator has plotted Gerrard's values of mole fraction solubilities against pressure for 298 K and pressures from 100 mmHg to 760 mmHg. (Fig. 1) On the same graph he has plotted values calculated from data given by Halban for the same temperature but for pressures from 1 mmHg to 25 mmHg. All experimental points may be joined by a smooth curve passing through the origin indicating that there is no inconsistency between the two sets of measurements for this solvent. A linear extrapolation of Halban's solubility data to give solubilities for a pressure of 1 atm is clearly not justified in the case of this solvent and is likely to lead to errors in the case of other solvents studied by Halban. This has been discussed in more detail by Gerrard (1).</p> <p>Mole fraction solubilities in straight chain aliphatic alcohols show a small increase with increase in chain length, although Halban's measurements indicate that mole fraction solubilities in methanol are greater than those in ethanol at 298 K and pressures less than 10 mmHg. No measurements of solubilities in these two solvents have been made at higher pressures. The solubilities of ammonia, methanamine and <i>N</i>-methylmethanamine in alcohols show a similar pattern of behaviour.</p> <p style="text-align: right;">Cont.</p>	

COMPONENTS:

1. Methanamine (methanamine); CH_5N ;
[74-89-5]
N-Methylmethanamine (dimethylamine);
 $\text{C}_2\text{H}_7\text{N}$; [124-40-3]
N,N-Dimethylmethanamine (trimethyl-
amine); $\text{C}_3\text{H}_9\text{N}$; [75-50-3]
2. Organic liquids

EVALUATOR:

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August, 1983

CRITICAL EVALUATION:

Solvents containing oxygen (cont.)

Gerrard found that the mole fraction solubilities in 1,2-ethanediol and in 1,2,3-propanetriol at 283 K and 298 K were less than in the aliphatic monohydric alcohols which he had studied. This is in contrast to the behaviour of ammonia, methanamine and *N*-methylmethanamine. Gerrard attributed this difference to a greatly reduced tendency to form hydrogen bonds with the solvent when all the hydrogen atoms in ammonia are replaced by methyl groups.

He also found that the mole fraction solubilities in 2,2,2-trichloroethanol were greater than in other alcohols. This is similar to the behaviour found for ammonia, methanamine and *N*-methylmethanamine.

Gerrard (1) measured the mole fraction solubilities in three ethers. There is no reason to doubt the reliability of these measurements. Solubilities in ethoxybenzene were measured at 283 K and at pressures from 100 mmHg to 760 mmHg. Values are close to those obtained for methylbenzene at the same temperature. Solubilities in 1,1'-oxybisoctane were measured at 293 K and 298 K and pressures from 100 mmHg to 760 mmHg. Mole fraction solubilities are close to values for 1-octanol. Extrapolation of mole fraction solubilities to 283 K gives values which are close to those for decane indicating that the presence of the ether linkage may have little influence on the solubility.

Halban measured the solubility in 1,1'-oxybisethane at 298 K and pressures to 47 mmHg. Extrapolation of these values to 760 mmHg is unreliable because such systems deviate markedly from Henry's law and reliable comparison cannot be made with systems studied at higher pressures.

Gerrard (1) also measured the mole fraction solubility in 1,4-dioxane at 283 K and a total pressure of 1 atm.

The solubilities in ethyl benzoate were measured by Gerrard (1) at 293 K and 298 K and pressures from 100 mmHg to 760 mmHg. Halban (13) made measurements on this compound at 298 K and pressures of 38 mmHg and 39 mmHg. Extrapolation of Gerrard's mole fraction solubilities at 298 K to the pressures at which Halban worked leads to solubilities which are about 10% lower than Halban's values. Halban also measured solubilities in ethyl acetate at 298 K and pressures to 59 mmHg but again extrapolation of these measurements to 760 mmHg would be unreliable. Comparisons may be made, however, with solubilities in other solvents at low pressures which have been measured by Halban or found by extrapolation of Gerrard's data. (See below.)

Gerrard measured the solubility in 1-phenylethanone at 298 K and pressures from 100 mmHg to 760 mmHg. Extrapolation of these results to 40 mmHg give values which again differ by about 10% from mole fraction solubilities calculated from data given by Halban (see below). There is no reason to doubt, however, the general pattern of solubilities of *N,N*-dimethylmethanamine in solvents containing oxygen which has been presented by Gerrard.

Estimated mole fraction solubilities 298K; 40 mmHg

ethyl acetate	0.017
ethyl benzoate	0.023 (Halban), 0.020 (Gerrard)
1,1'-bisoxyethane	0.012
2-propanone	0.012
1-phenylethanone	0.014 (Halban), 0.016 (Gerrard)

Cont.

<p>COMPONENTS:</p> <p>1. Methanamine (methylamine); CH_5N; [74-89-5] <i>N</i>-Methylmethanamine (dimethylamine); $\text{C}_2\text{H}_7\text{N}$; [124-40-3] <i>N,N</i>-Dimethylmethanamine (trimethylamine); $\text{C}_3\text{H}_9\text{N}$; [75-50-3]</p> <p>2. Organic liquids</p>	<p>EVALUATOR:</p> <p>P. G. T. Fogg, School of Chemistry, Polytechnic of North London, Holloway, London, U.K. August, 1983</p>										
<p>CRITICAL EVALUATION:</p> <p>Solvents containing nitrogen</p> <p>Gerrard (1) measured the solubilities in benzeneamine and several <i>N</i>-substituted benzeneamines. The measurements show that substitution of the first hydrogen atom has little effect on the mole fraction solubilities but substitution of the second hydrogen atom causes a decrease in solubilities. The solubility in 1-octamine was also reported to be close to that in benzeneamine. That in benzenemethanamine was reported to be less than those in benzeneamine. The mole fraction solubilities, at 283 K, in pyridine and in quinoline were less than in benzeneamine at the same pressure, with solubilities in pyridine greater than those in quinoline. Methanamine and <i>N</i>-methylmethanamine were reported to behave in a similar way in these two solvents. There is no reason to doubt the reliability of any of the solubility data for nitrogen bases reported by Gerrard.</p> <p>Gerrard also measured mole fraction solubilities in nitrobenzene at 283 K and 298 K and in 1-methyl-2-nitrobenzene at 278 K to 298 K and pressures from 100 mmHg to 760 mmHg. There was little difference in solubilities in the two solvents when conditions were the same. Halban (13) also made measurements of solubilities in these two solvents at 298 K and lower pressures. Mole fraction solubilities from Halban's data, (H), are lower than values obtained by extrapolation of Gerrard's measurements (G).</p> <p>i.e.</p> <table border="0" data-bbox="241 1008 1155 1209"> <tr> <td style="padding-right: 20px;">nitrobenzene;</td> <td>63 mmHg; $x_1 = 0.018$ (H), 0.020 (G)</td> </tr> <tr> <td></td> <td>82 mmHg; $x_1 = 0.024$ (H), 0.026 (G)</td> </tr> <tr> <td></td> <td>94 mmHg; $x_1 = 0.027$ (H), 0.030 (G)</td> </tr> <tr> <td style="padding-right: 20px;">1-methyl-2-nitrobenzene;</td> <td>87 mmHg; $x_1 = 0.029$ (H), 0.035 (G)</td> </tr> <tr> <td></td> <td>85 mmHg; $x_1 = 0.029$ (H), 0.034 (G)</td> </tr> </table> <p>Halban also measured solubilities in nitromethane at 298 K and pressures to 56 mmHg. The mole fraction solubilities are low compared with values for aromatic nitro compounds.</p> <p>Gerrard (1) measured the solubility in benzonitrile at 283 K and pressures from 100 mmHg to 760 mmHg. Mole fraction solubilities are less than reference values based upon the equation:</p> $x_1 = p_1/p_1^0$ <p>Halban measured solubilities in acetonitrile at 298 K and pressures to 47 mmHg. Mole fraction solubilities based upon these data are also less than the reference line values but the difference is even more marked than in the case of benzonitrile. This is in line with the observed difference between the behaviour of nitromethane and aromatic nitro compounds.</p> <p>Solubilities in <i>N,N</i>-dimethylformamide at 278 K, 283 K and 298 K and pressures from 100 mmHg to 760 mmHg were measured by Gerrard (1). Solubilities were found to be very low in this solvent compared with the reference line and with other solvents which were studied. The solubilities in water are also low and, in both cases, there may be little tendency for the gas to break up the hydrogen bonded structure of the solvent. As mentioned above, a similar explanation has been put forward for the relatively low solubility in 1,2-ethanediol and in 1,2,3-propanetriol. The values reported for <i>N,N</i>-dimethylformamide are therefore in accord with those for other solvents and are likely to be reliable.</p> <p style="text-align: right;">Cont.</p>		nitrobenzene;	63 mmHg; $x_1 = 0.018$ (H), 0.020 (G)		82 mmHg; $x_1 = 0.024$ (H), 0.026 (G)		94 mmHg; $x_1 = 0.027$ (H), 0.030 (G)	1-methyl-2-nitrobenzene;	87 mmHg; $x_1 = 0.029$ (H), 0.035 (G)		85 mmHg; $x_1 = 0.029$ (H), 0.034 (G)
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	85 mmHg; $x_1 = 0.029$ (H), 0.034 (G)										

<p>COMPONENTS:</p> <p>1. Methanamine (methylamine); CH_5N; [74-89-5] <i>N</i>-Methylmethanamine (dimethylamine); $\text{C}_2\text{H}_7\text{N}$; [124-40-3] <i>N,N</i>-Dimethylmethanamine (trimethylamine); $\text{C}_3\text{H}_9\text{N}$; [75-50-3]</p> <p>2. Organic liquids</p>	<p>EVALUATOR:</p> <p>P. G. T. Fogg, School of Chemistry, Polytechnic of North London, Holloway, London, U.K. August 1983</p>						
<p>CRITICAL EVALUATION:</p> <p>Solvents containing halogens</p> <p>The <i>N,N</i>- dimethylmethanamine and tetrachloromethane system has been studied at 253 K, 273 K and 293 K over the whole of the concentration range. This work (5), and other studies of amine systems carried out by Wolff <i>et al.</i>, seems to the evaluator to be of very high standard. Solubilities in several other solvents containing halogens have been measured by Gerrard (1) and by Halban (13).</p> <p>Gerrard found that the mole fraction solubility in trichloromethane at 298 K and a total pressure of 1 atm was 0.554. The evaluator has estimated that this corresponds to a mole fraction solubility of 0.62 at a partial pressure of <i>N,N</i>-dimethylmethanamine of 1 atm. This may be compared with the reference line or Raoult's law value of 0.464 and the value for tetrachloromethane, under the same conditions, of 0.52 which the evaluator has estimated by extrapolation of mole fraction solubilities calculated from data given by Wolff and Würtz. A similar difference in solubilities of <i>N</i>-methylmethanamine in the two solvents has been reported and therefore these values for <i>N,N</i>-dimethylmethanamine fit into a general pattern of behaviour.</p> <p>Halban also measured the solubility in trichloromethane at 298 K but at partial pressures from 5 mmHg to 9 mmHg. Direct comparison with Gerrard's value is not possible but solubilities measured by the two workers are not inconsistent with the marked curvature of plots of mole fraction solubilities against partial pressure of amine which has been observed for other solvents such as benzenemethanol. Gerrard measured solubilities in chlorobenzene, iodobenzene and 1-bromo-3-methylbenzene at 283 K and pressures from 100 mmHg to 760 mmHg. In all cases values were close to those given by the equation:</p> $x_1 = p_1 / p_1^{\circ}$ <p>Gerrard also measured solubilities in 1-chloronaphthalene and in 1-bromonaphthalene at 298 K and pressures from 100 mmHg to 760 mmHg. Mole fraction solubilities were less than reference values based upon the above equation and there was little difference between values for the two solvents. Halban also measured solubilities in 1-bromonaphthalene at 298 K at pressures from 48 mmHg to 84 mmHg. Mole fraction solubilities calculated by the compiler from Halban's data, (H), are not consistent with mole fraction solubilities found by extrapolation of Gerrard's values to lower pressures, (G). i.e.</p> <p>Mole fraction solubility in 1-bromonaphthalene at 298 K</p> <table border="0" data-bbox="389 1471 873 1582"> <tr> <td>48 mmHg</td> <td>0.017 (H); 0.024 (G)</td> </tr> <tr> <td>60 mmHg</td> <td>0.020 (H); 0.030 (G)</td> </tr> <tr> <td>84 mmHg</td> <td>0.027 (H); 0.042 (G)</td> </tr> </table> <p style="text-align: right;">cont.</p>		48 mmHg	0.017 (H); 0.024 (G)	60 mmHg	0.020 (H); 0.030 (G)	84 mmHg	0.027 (H); 0.042 (G)
48 mmHg	0.017 (H); 0.024 (G)						
60 mmHg	0.020 (H); 0.030 (G)						
84 mmHg	0.027 (H); 0.042 (G)						

General pattern of the solubilities of ammonia, methanamine, *N*-methylmethanamine and *N,N*-dimethylmethanamine

Mole fraction solubilities may be fitted to equations of the form:

$$-RT \ln x_1 = a + bT$$

with a wide variation of values of a and b .

Approximate values of activity coefficients may be calculated from the relationship:

$$f_1 = p_1 / (p_1^0 x_1)$$

where p_1^0 is the vapor pressure of pure solute at temperature T and x_1 is the mole fraction solubility at a partial pressure p_1 and temperature T .

Systems fall into two groups:

- i) those in which values of f_1 decrease with increase in temperature;
- ii) those in which values of f_1 increase with increase in temperature.

For the first group the value of x_1 , as a percentage of the corresponding value of p_1/p_1^0 , increases with increase in temperature. The reverse is true for the second group.

Increase in temperature will disrupt short range order associated with solvent-solvent interaction and this will favor dissolution of gas. Increase in temperature will also disrupt short range order associated with solvent-solute interaction and this will have the opposite effect on the solubility. The variation of activity coefficient with temperature is a measure of the variation of mole fraction solubility relative to the corresponding value of p_1/p_1^0 and gives an indication of the comparative significance of the above two factors which lead to an increase in disorder in the liquid phase.

Heats of vaporization of ammonia, methanamine, *N*-methylmethanamine and *N,N*-dimethylmethanamine at 298 K may be estimated from the Clausius-Clapeyron equation, i.e.,

$$d \ln p^0 / dT = \Delta H^0 / RT^2.$$

Values of ΔH^0 estimated by the evaluator from vapor pressure data are as follows:

ammonia	22420 J mol ⁻¹
methanamine	26070 J mol ⁻¹
<i>N</i> -methylmethanamine	27400 J mol ⁻¹
<i>N,N</i> -dimethylmethanamine	23970 J mol ⁻¹ .

For systems in which $(a + \Delta H^0)$ is positive the value of the activity coefficient, f_1 , decreases with increase in temperature (i.e., x_1 increases relative to p_1/p_1^0). For systems in which $(a + \Delta H^0)$ is negative the reverse is true.

Values of a , b , and $(a + \Delta H^0)$ for a partial pressure of gas, p_1 , of 1 atm are given in Table 2. The corresponding smoothing equations are valid only for the ranges of temperature of the experimental measurements. In some cases values of a and b are based upon data for only two temperatures. These are included so as to indicate the general pattern of values.

The solubilities of ammonia in hexadecane, bicyclohexyl and 1-methylnaphthalene were measured by Tremper and Prausnitz (17) over a wide temperature range. Mole fraction solubilities for 1 atm partial pressure, based upon these data, fall on smooth curves when plotted against temperature. However, the smoothing equation with two constants, a and b , is not fully adequate for the whole temperature range. The values of a and b for these systems, given in the table and corresponding to the best fit of data with the smoothing equation used, are for qualitative comparison with values for other systems. They should not be used for precise calculation of values of solubilities.

Systems in which a monohydric or polyhydric alcohol is the solvent have positive values for $(a + \Delta H^\circ)$ with the exception of *N,N*-dimethylmethanamine in 1,2-ethanediol which has a small negative value. For most of these systems the ratio of mole fraction solubility to the value of (p_1/p_1^0) increases with increase of temperature. Compared with other solvents, alcohols show smaller variation of $(a + \Delta H^\circ)$ with increase in number of methyl groups in the gas. These observations are in accord with the hypothesis that the breaking of hydrogen bonds between alcohol molecules with increase in temperature is a factor favoring the solubility of these gases.

The values of $(a + \Delta H^\circ)$ for methanamine and methylmethanamine from measurements by Gerrard (1), fall into the pattern for these gases in hexane and nonane from the more detailed measurements by Wolff *et al.* (3,4). In general, the values of $(a + \Delta H^\circ)$ which are available for solubilities in the straight chain alkanes, butane, hexane, nonane and decane are negative, in contrast with values for alcohols. Solubilities of all four gases have been measured in hexane and there is very marked variation of values of $(a + \Delta H^\circ)$ with change of gas, again in contrast with alcohol systems. The ammonia-hexadecane system appears to be anomalous when compared with systems in lower alkanes because $(a + \Delta H^\circ)$ is positive. However the ammonia-bicyclohexyl system also has a positive value of $(a + \Delta H^\circ)$.

The variation of the mole fraction solubilities of the three amines with variation of temperature has been measured in *N,N*-dimethylformamide and in tetrachloromethane. In the first case values of $(a + \Delta H^\circ)$ become increasingly negative with number of methyl groups in the amine suggesting a corresponding increase in the tendency for hydrogen bonding between amine and solvent. In the case of the second solvent the value of $(a + \Delta H^\circ)$ is negative for methanamine but is increasingly positive from *N*-methylmethanamine to *N,N*-dimethylmethanamine, suggesting a corresponding decrease in the interaction between solute and solvent.

There are insufficient measurements of the solubilities of the gases in other solvents to justify generalisations about the effect of temperature or to pick out apparently anomalous behaviour.

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COMPONENTS:
 1. Methanamine (methylamine); CH_5N ;
 [74-89-5]
N-Methylmethanamine (dimethylamine);
 $\text{C}_2\text{H}_7\text{N}$; [124-40-3]
N,N-Dimethylmethanamine (trimethyl-
 amine); $\text{C}_3\text{H}_9\text{N}$; [75-50-3]
 2. Organic liquids

EVALUATOR:
 P. G. T. Fogg,
 School of Chemistry,
 Polytechnic of North London,
 Holloway,
 London, U.K.
 August 1983

CRITICAL EVALUATION:

Table 2. Values of the constants a and b in the smoothing equation for solubilities at a partial pressure of gas of 1 atm, together with values of $(a + \Delta H^\circ)$.

Solvent	NH_3			CH_3NH_2		
	$a/\text{J mol}^{-1}$	$b/\text{J mol}^{-1} \text{ K}^{-1}$	$(a + \Delta H^\circ)/\text{J mol}^{-1}$	$a/\text{J mol}^{-1}$	$b/\text{J mol}^{-1} \text{ K}^{-1}$	$(a + \Delta H^\circ)/\text{J mol}^{-1}$
Butane				-52320	197.5	-26250
Hexane	-61860	242.6	-39440	-40060	154.8	-13990
Nonane				-33530	131.4	-7460
Decane				-32320	125.6	-6250
Hexadecane	-6911	55.3	15509			
Bicyclohexyl	-6317	61.6	16103			
Cyclohexene	-17010	92.9	5410			
Benzene	-17360	86.4	5060			
1,3-Dimethylbenzene						
1-Methylnaphthalene	-10360	64.2	12060			
Methanol	-11570	48.7	10850			
Ethanol	-13720	57.7	8700			
2,2,2-Trichloroethanol				-8620	33.0	17450
1-Propanol	-15370	63.8	7050			
2-Propanol	-14710	62.3	7710			
1-Butanol				-12190	46.5	13880
1-Octanol				-12130	46.2	13940
Benzenemethanol				-9890	37.9	16180
1,2-Ethanediol						
1,2,3-Propanetriol						
1,1'-Oxybisoctane				-28470	108.4	-2400
2,2'-Oxybisethanol	-18850	70.9	3570			
Ethyl benzoate				-23970	90.6	2100
Hydrazine	-21690	94.1	730			
Methylhydrazine	-21820	92.3	600			
1,1-Dimethylhydrazine	-18210	80.3	4210			
1-Octanamine						
Benzenamine	-25180	101.1	-2760			
<i>N</i> -Methylbenzenamine				-17960	67.7	8110
<i>N</i> -Ethylbenzenamine				-17740	67.0	8330
<i>N,N</i> -Dimethylbenzenamine				-32730	123.1	-6660
<i>N,N</i> -Diethylbenzenamine				-38500	144.4	-12430
Benzenmethanamine						
Benzonitrile						
Nitrobenzene						
1-Methyl-2-nitrobenzene						
<i>N,N</i> -Dimethylformamide				-26250	98.5	-180
Tetrachloromethane				-34150	127.7	-8080

COMPONENTS:
 1. Methanamine (methanamine); CH_3N ;
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Table 2. Values of the constants a and b in the smoothing equation for solubilities at a partial pressure of gas of 1 atm, together with values of $(a + \Delta H^\circ)$.

Solvent	$(\text{CH}_3)_2\text{NH}$			$(\text{CH}_3)_3\text{N}$		
	$a/J \text{ mol}^{-1}$	$b/J \text{ mol}^{-1} \text{ K}^{-1}$	$(a + \Delta H^\circ)/J \text{ mol}^{-1}$	$a/J \text{ mol}^{-1}$	$b/J \text{ mol}^{-1} \text{ K}^{-1}$	$(a + \Delta H^\circ)/J \text{ mol}^{-1}$
Butane						
Hexane	-41420	147.5	-14020	-25230	91.2	- 1260
Nonane						
Decane	-36320	129.6	- 8920			
Hexadecane						
Bicyclohexyl						
Cyclohexane						
Benzene						
1,3-Dimethylbenzene	-29290	104.6	- 1890			
1-Methylnaphthalene						
Methanol	-13610	49.6	13790			
Ethanol	-15830	57.3	11570			
2,2,2-Trichloroethanol	-11470	41.4	15930	-12090	44.2	11880
1-Propanol	-15080	54.5	12320			
2-Propanol						
1-Butanol				-16420	60.7	7550
1-Octanol	-15040	54.0	12360	-16940	61.5	7030
Benzenemethanol	-14910	53.8	12490	-18670	67.9	5300
1,2-Ethanediol				-24750	90.7	780
1,2,3-Propanetriol				-22300	82.2	1670
1,1'-Oxybisoctane				-15320	56.1	8650
2,2'-Oxybisethanol						
Ethyl benzoate				-26050	94.5	- 2080
Hydrazine						
Methylhydrazine						
1,1-Dimethylhydrazine						
1-Octanamine	-24140	86.2	3260	-21020	76.2	2950
Benzenamine						
<i>N</i> -Methylbenzenamine						
<i>N</i> -Ethylbenzenamine						
<i>N,N</i> -Dimethylbenzenamine	-31410	112.3	- 4010			
<i>N,N</i> -Diethylbenzenamine						
Benzenmethanamine	-23480	84.6	3920			
Benzonitrile	-26700	95.7	700			
Nitrobenzene				-35370	127.9	-11400
1-Methyl-2-nitrobenzene				-35210	127.4	-11240
<i>N,N</i> -Dimethylformamide	-34560	123.3	- 7160	-51100	185.3	-27130
Tetrachloromethane	-26840	95.7	560	-19830	71.9	4140