COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

The solubilities of hydrogen sulfide in a wide range of organic solvents have been measured at pressures above and below barometric pressure. These measurements are of varying reliability. Error limits are likely to vary from about ± 2% to about ± 10% but it is not always possible to quantify these error limits. This must be borne in mind when attempts are made to deduce a general pattern of solubilities of hydrogen sulfide from the experimental data which have been reported.

Non-aromatic hydrocarbons

Propane; C_3H_8; [74-98-6]
Butane; C_4H_{10}; [106-97-8]
2-Methylpropane; C_4H_{10}; [75-28-5]
Pentane; C_5H_{12}; [109-66-0]
Hexane; C_3H_{14}; [110-54-3]
Heptane; C_7H_{16}; [142-82-5]
Octane; C_8H_{18}; [111-65-9]
Nonane; C_9H_{20}; [111-84-2]
Decane; $C_{10}H_{22}$; [124-18-5]
Undecane; $C_{11}H_{24}$; [1120-21-4]
Dodecane; $C_{12}H_{26}$; [112-40-3]
Tridecane; $C_{13}H_{28}$; [629-50-5]
Tetradecane; $C_{14}H_{30}$; [629-59-4]
Pentadecane; $C_{15}H_{32}$; [629-62-9]
Hexadecane; $C_{16}H_{34}$; [544-76-3]
Cyclohexane; C_6H_{12}; [110-82-7]
Methylcyclohexane; C_7H_{14}; [108-87-2]
Ethylcyclohexane; C_8H_{16}; [1678-91-7]
Propylcyclohexane; C_9H_{18}; [1678-92-8]
(1-Methylethyl)-cyclohexane; C_9H_{18}; [696-29-7]
Decahydronaphthalene; $C_{10}H_{18}$; [91-17-8]
1,1'-Bicyclohexyl; $C_{12}H_{22}$; [92-51-3]
Liquid paraffin

The solubilities of hydrogen sulfide at a partial pressure of 1.013 bar and temperatures in the range 288 - 343 K in hexane, octane, decane, dodecane, tetradecane, hexadecane have been reported by King & Al-Najjar (1). Makranczy *et al.* (2) reported solubilities in the straight chain alkanes from pentane to hexadecane also at a partial pressure of 1.013 bar at temperatures of 298.15 K and 313.15 K. Mole fraction solubilities reported by Makranczy *et al.* for 298.15 K are all within 4% of values reported by King & Al-Najjar. The mole fraction solubility at 313.15 K in hexadecane reported by Makranczy differs from the interpolated value from King & Al-Najjar by 7%. Measurements of solubilities in other alkanes at 313.15 by Makranczy are within 5% of interpolated values from King & Al-Najjar. Measurements by the two groups indicate that mole fraction solubilities at a partial pressure of hydrogen sulfide of 1.013 bar increase with the length of the carbon chain, in the temperature range 288 - 303 K. This pattern was found by Bell (3) at 293 K for hexane, octane, dodecane and hexadecane. Bell, however, used rather simpler apparatus and individual values are likely to be less reliable than those of King & Al-Najjar or of Makranczy. This pattern of solubilities is not substantiated by measurements of the solubility in hexane by Hayduk & Pahlevanzadeh (4), nor that in heptane measured by Ng *et al.* (5), nor that in decane measured by Gerrard (6) and by Reamer *et al.* (7), nor that in hexadecane measured by Tremper & Prausnitz (8). Mole fraction solubilities at 298.15 K from measurements by the different authors are shown in fig. 2. The biggest discrepancy is between the value of the mole fraction solubility in hexadecane of 0.040 by extrapolation of measurements by Tremper & Prausnitz and the value of 0.0573 given by Makranczy *et al.* and also by King & Al-Najjar. There are similar discrepancies between mole fraction solubilities of sulfur dioxide in alkanes from measurements by different authors. These differences have been discussed by Young (9).

Phase equilibria between propane and hydrogen sulfide from 341 K to 367 K and total pressures from 27.6 bar to 41.4 bar were investigated by Gilliland and Scheeline (10). Data may be extrapolated to give approximate values of mole fraction solubilities for partial pressures of hydrogen sulfide of 1.013 bar in this temperature range. These are consistent with the pattern shown by the higher alkanes mentioned above.

The butane-hydrogen sulfide system was investigated by Robinson *et al.* (11) in the temperature range 311 K to 394 K and pressure range 4.2 to 78.5 bar. An approximate value of the mole fraction solubility at 298.15 K and a partial pressure of 1.013 bar may be estimated by extrapolation of these measurements. The value of 0.041 is consistent with the pattern of mole fraction solubilities for higher straight chain alkanes given by Makranczy (2).

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

The 2-methylpropane-hydrogen sulfide system has been studied by Besserer & Robinson (12) over the temperature range 278 K to 378 K and pressure range 1.8 to 61.7 bar. Approximate values for mole fraction solubilities for a partial pressure of 1.013 bar may be estimated. The value for 298.15 K is 0.038, apparently slightly less than the value for the straight chain isomer.

Phase equilibria between pentane and hydrogen sulfide at high pressures have also been investigated. Reamer, Sage and Lacey (13) made measurements on this system between 278 K and 444 K and total pressures from 1.4 bar to 89.6 bar. These measurements are consistent with the data presented by Makranczy *et al.* (2). Extrapolation of mole fraction compositions of the liquid phase at 298.15 K to a partial pressure of hydrogen sulfide of 1.013 bar gives a value differing from the Makranczy value by less than 1%. The extrapolated value for 313.15 K differs from the corresponding Makranczy value by 5%.

The mole fraction solubility in hexane of 0.0372 at a partial pressure of 1.013 bar and 298.15 reported by Hayduk & Pahlevanzadeh (4) is significantly lower than the Makranczy value of 0.0429. These recent measurements by Hayduk were carried out using apparatus of high precision but the relative reliability of the two values cannot be judged. The solubility in hexane was also measured by Bell (3). Bell's value at 293.15 is lower than the value by extrapolation of Makranczy's measurements. Bell used very simple apparatus and more recent measurements are likely to be of greater reliability.

The heptane-hydrogen sulfide system has been investigated by Ng, Kalra, Robinson & Kubota (5) from 311 - 478 K and 1.6 to 8.4 bar. In this case extrapolated values of mole fraction solubilities for partial pressures of hydrogen sulfide of 1.013 bar are considerably lower than found by Makranczy (2). At 298.15 the value from Ng *et al.* is 0.037 whereas the Makranczy value is 0.0439. The corresponding values for 313.15 K are 0.028 and 0.0325 respectively. Measurements reported by Ng *et al.* were made over a pressure range and are internally self-consistent. They cast further doubt on the pattern indicated by Makranczy *et al.* (2) and by King & Al-Najjar (1).

The nonane-hydrogen sulfide system was investigated by Eakin & DeVaney (14) at temperatures from 311 K to 478 K and pressures from 1.37 bar to 27.6 bar. Measurements are self-consistent. The data may be used to estimate mole fraction solubilities at a partial pressure of 1.013 bar. Extrapolation of these estimated values to 298.15 K gives a mole fraction solubility at this temperature of 0.037 which is appreciably below the Makranczy (2) value of 0.0465.

The decane-hydrogen sulfide system was studied by Reamer *et al.* (7) in the temperature range 278 K to 444 K and pressure range 1.4 bar to 124 bar. Measurements are self-consistent. Extrapolation of mole fraction solubilities to a partial pressure of hydrogen sulfide of 1.013 bar and a temperature of 298.15 K gives a value of 0.040, close to the value of 0.039 by extrapolation of measurements by Gerrard (6) but appreciably lower than the figures of 0.0481 and 0.0465 from measurements by Makranczy (2) and by King (1) respectively.

The solubilities in hexadecane reported by Tremper & Prausnitz (8) were given as Henry's constants based on measurements made at an unspecified pressure or pressures below 1.33 bar. Mole fraction solubilities may be estimated on the assumption that there is a linear variation of mole fraction solubility with pressure to 1.013 bar. The interpolated value of the mole fraction solubility at 298.15 is 0.040 compared with the value of 0.0573 from measurements by Makranczy (2) and also by King (1). The higher value is also supported by the estimation of a value of 0.0535 from gas chromatographic measurements by Lenoir *et al.* (15) and by the value of 0.058 at 293.15 K published by Bell (3).

As may be seen in fig 2, data for the solubility of hydrogen sulfide in alkanes fall into two groups. Some data indicate that the mole fraction solubility does not change appreciably with the length of the hydrocarbon chain. Other data indicate a marked increase with increase in chain length. Further experimental measurements are needed to clarify the situation. When solubility data for these systems are used the discrepancies between different measurements should be borne in mind.

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

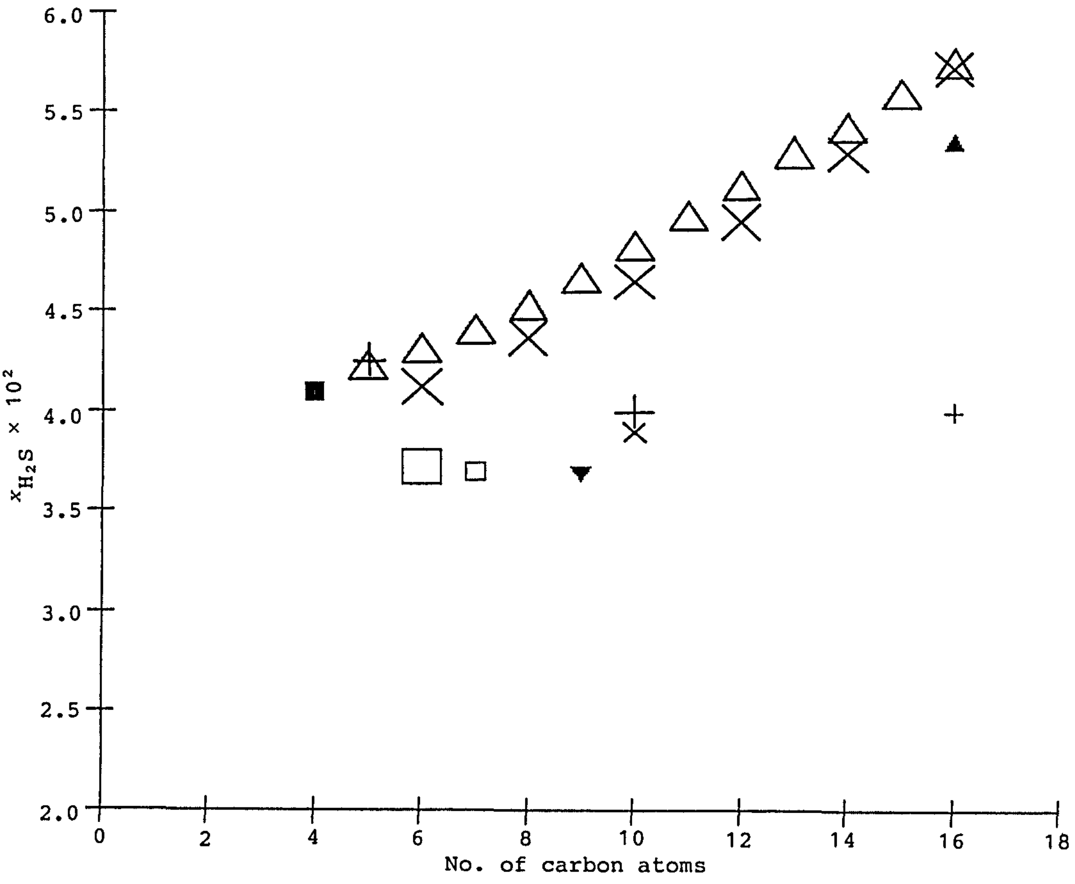

Fig. 2. Values of the mole fraction solubility of hydrogen sulfide in straight chain alkanes at 298.15 K and a partial pressure of 1.013 bar from measurements reported by different authors

╳	King & Al-Najjar (1)	┼	Reamer *et al.* (7, 13)
△	Makranczy *et al.* (2)	+	Tremper & Prausnitz (8)
□	Hayduk & Pahlevanzadeh (4)	■	Robinson *et al.* (11)
◻	Ng *et al.* (5)	▼	Eakin & DeVaney (14)
×	Gerrard (6)	▲	Lenoir *et al.* (15)

COMPONENTS:

1. Hydrogen sulfide; H_2S; [7783-06-4]

2. Non-aqueous solvents

EVALUATOR:

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July 1987

CRITICAL EVALUATION:

The solubility of hydrogen sulfide in octane in the presence of methane at various pressures to 103 bar in the temperature range 233 K to 293 K has been studied by Asano *et al.* (16) using a chromatographic method. K-values or ratios of the mole fraction of hydrogen sulfide in the vapor phase to that in the liquid phase are reported. These correspond to very low partial pressures of hydrogen sulfide and may be taken to be equivalent to values for infinite dilution of hydrogen sulfide. These ratios may be used to estimate limiting values of Henry's law constants which are subject to the uncertainties associated with Henry's law constants determined by chromatographic methods. These Henry's law constants can then be used to estimate approximate mole fraction solubilities for a partial pressure of hydrogen sulfide of 1.013 bar. Values indicate that the solubility of hydrogen sulfide decreases with increasing concentration of methane in the liquid phase which is in accord with the apparent decrease of solubility of hydrogen sulfide with decrease in chain length of alkane as discussed above. These apparent Henry's law constants may be extrapolated to zero concentration of methane and the extrapolated value used to estimate solubility of pure hydrogen sulfide in octane to enable direct comparison with data discussed above. At a temperature of 293.15 K the extrapolated value, calculated from the experimental values of K rather than the smoothed values, indicates a mole fraction solubility of about 0.06 for a partial pressure of 1.013 bar. This may be compared with the value of 0.0474 given by King & Al-Najjar (1) at this temperature. In the opinion of the compiler the measurements presented by Asano *et al.* (16) are likely to correspond to the general pattern of behaviour of the hydrogen sulfide-methane-octane system. It must be borne is mind that errors can arise from surface effects when the gas-chromatographic method is used to determine solubilities of gases in liquids.

Solubilities in cyclohexane were measured at pressures from 0.133 to 1.067 bar and temperatures from 283.2 to 313.2 K by Tsiklis & Svetlova (17). These are a self-consistent set of measurements. Bell (3) reported the mole fraction solubility at 293.2 K and a partial pressure of 1.013 bar to be 0.0338. This is appreciably different from the interpolated value of 0.0422 from measurements by Tsiklis & Svetlova. The measurements by Tsiklis & Svetlova are probably the more reliable because they were carried out over a temperature and pressure range although they do not fit into the pattern shown by alkyl substituted cyclohexanes.

Solubilities in methyl, ethyl and propylcyclohexane were measured by Robinson and co-workers (18,19) and in (1-methylethyl)-cyclohexane by Eakin & DeVaney (14) at pressures above 1.013 bar and temperatures in the range 311 K to 478 K. These measurements are consistent with one another and may be accepted on a tentative basis. Mole fraction solubilities for a partial pressure of 1.013 bar may be found by extrapolation. There is an increase in these mole fraction solubilities as the number of carbon atoms in the side chain is increased with the values for (1-methylethyl)-cyclohexane close to those for propylcyclohexane. Values for cyclohexane itself, from measurements by Tsiklis (17), do not fall into the pattern.

Smoothed and extrapolated values of solubilities of cyclohexanes estimated by the evaluator are shown below:

Solvent	mole fraction solubility, x_{H_2S} (1.013 bar)		
	300 K	350 K	400 K
Cyclohexane	0.038		
Methylcyclohexane	0.034	0.015	0.009
Ethylcyclohexane	0.036	0.018	0.011
Propylcyclohexane	0.043	0.023	0.014
(1-Methylethyl)-cyclohexane	0.041	0.023	0.015

Solubilities in 1,1'-bicyclohexyl, published by Tremper & Prausnitz (8), and those in decalin, found by Lenoir *et al.* (15) from chromatographic measurements, are consistent with solubilities reported for cyclohexanes.

Solubilities in liquid paraffin, reported by Devyatykh *et al.* (20), are subject to the uncertainties associated with measurements by chromatography.

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

Hannaert *et al.* (21) have reported the solubilities, in a form equivalent to Henry's constants, in kerosene A-1 (distillation range 423 - 553 K; average relative molecular mass 170). Values are similar to those for pure dodecane which also has a relative molecular mass of 170.

Aromatic hydrocarbons

Benzene; C_6H_6; [71-43-2]   Methylbenzene; C_7H_8; [108-88-3]
1,2-Dimethylbenzene; C_8H_{10}; [95-47-6]   1,3-Dimethylbenzene; C_8H_{10}; [108-38-3]
Ethylbenzene; C_8H_{10}; [100-41-4]   1,3,5-Trimethylbenzene; C_9H_{12}; [108-67-8]
Propylbenzene; C_9H_{12}; [103-65-1]   (1-Methylethyl)-benzene; C_9H_{12}: [98-82-8]
1-Methylnaphthalene; $C_{11}H_{10}$; [1321-94-4]   1,1'-Methylenebisbenzene; $C_{13}H_{12}$;
9-Methylanthracene; $C_{15}H_{12}$; [779-02-2]   [101-81-5]

Solubilities in methylbenzene have been measured by Gerrard (6) and by Bell (3) at barometric pressure from 265 K to 298 K. Ng, Kalra, Robinson and Kubota (5) investigated phase equilibria at total pressures from 2 bar to 116 bar in the temperature range 311 K to 478 K. Mole fraction solubilities at partial pressures of 1.013 bar may be found by extrapolating mole fraction solubilities at higher pressures calculated from data given by Ng *et al.* These extrapolated values are consistent with mole fraction solubilities at lower temperatures calculated from data presented by Gerrard and by Bell. All mole fraction solubilities at a partial pressure of 1.013 bar lie above the reference line defined by the Raoult's law relationship and may be fitted to the equation :

$$\log_{10} x_{H_2S} = -3.811 + 768 / (T/K)$$

The standard deviation in values of x_{H_2S} is ± 0.005. The equation in based upon data for the range 265 K - 478 K.

Phase equilibria between hydrogen sulfide and 1,3,5-trimethylbenzene have been investigated by Eakin & DeVaney (14) at total pressures from 1.3 bar to 32.6 bar at 311, 366 and 478 K. The solubility at a partial pressure of 1.013 bar and 298 K has been reported by Patyi *et al.* (22). This value is consistent with mole fraction solubilities estimated by extrapolation of data provided by Eakin and DeVaney to a partial pressure of 1.013 bar. The four values of mole fraction solubilities at a partial pressure of 1.013 bar lie above the reference line corresponding to the Raoult's law equation but below values for methylbenzene . They fit the equation :

$$\log_{10} x_{H_2S} = -3.495 + 648 / (T/K)$$

The standard deviation in values of x_{H_2S} is ± 0.001. The equation is based upon data for the range 298 K to 478 K.

The mole fraction solubility in benzene at a partial pressure of 1.013 bar was reported by Bell (3) to be 0.0563 at 293.15 K. Gerrard (6) made measurements of solubility at barometric pressure in the range 265.15 K to 293.15 K. The mole fraction solubility at 293.15 K from Gerrard's measurements, corrected to a partial pressure of 1.013 bar is 0.062. Measurements by Bell and by Gerrard are incompatible with the value of 0.0358 at 298.15 K calculated from a solubility measurement by Patyi *et al.* (22). Gerrard's measurements at three temperatures are consistent with each other and may be more reliable than the single measurements reported by Patyi.

Gerrard measured solubilities in 1,2-dimethylbenzene at barometric pressure in the temperature range 265 K to 293 K. Huang & Robinson (23) measured solubilities in 1,3-dimethylbenzene at various total pressures from 1.5 to 131 bar in the temperature range 311 K to 478 K. These data for the xylenes may be accepted on a tentative basis.

The mole fraction solubilities at a partial pressure of 1.013 bar and 298 K of ethylbenzene, propylbenzene and (1-methylethyl)-benzene may also be calculated from solubility data given by Patyi *et al.* (22). The values for propylbenzene and (1-methylethyl)-benzene are close to values for methylbenzene and 1,3,5-trimethylbenzene. The value for ethylbenzene is about 20% lower and

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

closer to the value for benzene, discussed above, from measurements by these authors. The merit of these measurements cannot be judged.

Tremper & Prausnitz (8) reported Henry's constant for solubilities in 1-methylnapthalene and in 1,1'-methylenebisbenzene for the temperature range 300 K to 475 K. No other measurements on these systems are available for comparison but there is no reason to doubt the reliability of these measurements. Mole fraction solubilities for a partial pressure oa 1.013 bar may be calculated on the assumption that mole fraction solubility varies linearly with pressure at pressures to 1.013 bar.

Kragas & Kobayashi (24) measured limiting values of Henry's constants for dissolution of hydrogen sulfide in 9-methylanthracene. A chromatographic method was used with hydrogen at pressures of 13 bar to 58 bar as the carrier gas. Temperatures were in the range 373 K to 423 K. Values of Henry's constant in the absence of hydrogen were found by extrapolation. These Henry's constants should be used with caution in the estimation of solubilities for finite pressures of hydrogen sulfide because of the uncertainties associated with the chromatographic method of measuring solubilities.

Apparent values of mole fraction solubilities in aromatic hydrocarbons at a partial pressure of 1.013 bar and 298.15 K based on the measurements discussed above, are given below.

Hydrocarbon	x_{H_2S} at p_{H_2S} = 1.013 bar and T = 298.15 K	Source
Benzene	0.056	Gerrard (6) (extrapolated)
	0.036	Patyi *et al.* (22)
Methylbenzene	0.058	Eqn. given above
1,2-dimethylbenzene	0.060	Gerrard (6) (extrapolated)
1,3-dimethylbenzene	0.037	Huang & Robinson (23) (extrap.)
1,3,5-trimethylbenzene	0.048	Eqn. given above
Ethylbenzene	0.042	Patyi *et al.* (22)
Propylbenzene	0.052	Patyi *et al.* (22)
(1-methylethyl)-benzene	0.053	Patyi *et al.* (22)
1-methylnapthalene	0.033	Tremper & Prausnitz (8)
1,1'-methylenebisbenzene	0.031	Tremper & Prausnitz (8)
Value from Raoult's law equation	0.049	

Solubilities in alcohols

Methanol; CH_4O; [67-56-1]
Ethanol; C_2H_6O; [64-17-5]
1-Butanol; $C_4H_{10}O$; [71-36-3]
1-Octanol; $C_8H_{18}O$; [111-87-5]
Benzenemethanol; C_7H_8O; [100-51-6]
2-Ethoxyethanol; $C_4H_{10}O_2$; [110-80-5]
1,2-Ethanediol (*ethylene glycol*); $C_2H_6O_2$; [107-21-1]

Solubilities in methanol, ethanol, butanol and octanol have been reported. Available data indicate that mole fraction solubilities for a partial pressure of 1.013 bar increase from ethanol to octanol. Below 273 K the mole fraction solubility in methanol is less than that in ethanol but extrapolation of the values for methanol indicates that the solubility in methanol would be higher than that of ethanol at higher temperatures. Methanol shows an apparently similar anomaly when the mole fraction solubilities of amines in alkanols are compared (25).

Solubilities in methanol in the range of total pressures from 2.0 to 5.9 bar and from 248 - 273 K have been measured by Yorizane, Sadamoto, Masuoka and Eto (26). Short, Sahgal and Hayduk (27) reported mole fraction solubilities at 263 K and 333 K and a partial pressure of hydrogen sulfide of 1.013 bar. The mole fraction solubilities at high pressures reported by Yorizane *et al.* are self-consistent. In addition mole fraction solubilities at a partial pressure

COMPONENTS:

1. Hydrogen sulfide; H_2S; [7783-06-4]

2. Non-aqueous solvents

EVALUATOR:

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July 1987

CRITICAL EVALUATION:

of 1.013 bar estimated by extrapolation of these data are consistent with the mole fraction solubilities reported by Short *et al.*

Bezdel & Teodorovich (28) measured solubilities in methanol at partial pressures to 0.080 bar at temperatures 223.2 K, 243.2 K and 303.2 K. Mole fraction solubilities may be calculated from these data. Extrapolation to a partial pressure of 1.013 bar, assuming linear variation of mole fraction solubility with pressure at pressures to 1.013 bar, gives values of 0.35 at 223.2 K, 0.16 at 243.2 K and 0.021 at 303.2 K. The mole fraction solubility, estimated from data given by Short *et al.* and by Yorizane *et al.* is 0.12 at 243.2 K and 0.028 at 303.2 K. The evaluator considers that measurements by Short *et al.* and by Yorizane *et al.* are more reliable than those published by Bezdel & Teodorovitch.

Solubilities in ethanol and octanol were measured by Gerrard (6). Values for ethanol at 283 K and 293 K are within 5% and the value for 273 K is within 10% of values reported many years ago by Fauser (29). Gerrard's data for these two alcohols may be accepted as tentative values.

The solubilities in butanol at a partial pressure of 1,013 bar reported by Short, Sahgal and Hayduk (27) are likely to be reliable and can be accepted as tentative values.

Lenoir, Renault and Renon (15) used a gas-liquid chromatographic technique to measure the Henry's constant for dissolution of hydrogen sulfide in benzenemethanol 298.2 K and very low partial pressures. This measurement may be unreliable because of surface adsorption of gas. The estimated mole fraction solubility at 298 K and 1.013 bar, assuming a linear relationship between mole fraction solubility and pressure to 1.013 bar, is close to the value for 1-octanol mentioned above and about 85% of the Raoult's law value.

Solubility data for 2-ethoxyethanol, obtained using a chromatographic method by Devyatykh *et al.* (20) should also be considered to be of semi-quantitative significance until they can be independently confirmed.

Measurements of solubilities in 1,2-ethanediol made by Short *et al.* (27) agree closely with earlier measurements by Gerrard (6). This may be seen in the following table:

T/K	Mole fraction solubility for P_{H_2S} = 1.013 bar	
	Gerrard	Short *et al.* (interpolated)
265.15	0.0352	0.0309
267.15	0.032	0.0288
273.15	0.023	0.0235
283.15	0.017	0.0175
293.15	0.013	0.0136

Lenoir *et al.* (15) measured the Henry's constant at 298.15 by a chromatographic method. The corresponding mole fraction for a partial pressure of gas of 1.013 bar is 0.0189 compared with a value of 0.0122 given by Short *et al.* (27) Since solubilities measured by chromatographic methods are prone to errors due to surface effects this high value may be disregarded. Measurements of solubility at 297.1 K have been reported by Byeseda *et al.* (30) The Ostwald coefficient given by these workers corresponds to a mole fraction solubility at a partial pressure of 1.013 bar of 0.016 compared with the value of 0.0125. The apparatus used by Short *et al.* is likely to have yielded the more reliable solubility data and the higher value should be disregarded. Data published by Short *et al.* are recommended by the evaluator.

Triethylene glycol and polyethylene glycols are discussed below.

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

<u>Compounds containing carbon-oxygen-carbon links</u>

1,1'-Oxybisethane; (*diethyl ether*); $C_4H_{10}O$; [60-29-7]
1,1'-Oxybisoctane; (*dioctyl ether*); $C_{16}H_{34}O$; [629-82-3]
Ethoxybenzene; $C_8H_{10}O$; [103-73-1]
Tetrahydrofuran; C_4H_8O; [109-99-9]   1,4-Dioxane; $C_4H_8O_2$; [123-91-1]
Oxybispropanol (*dipropylene glycol*); $C_6H_{14}O_3$; [25265-71-8]
2,2'[1,2-Ethanediylbis(oxy)]bisethanol (*triethylene glycol*); $C_6H_{14}O_4$; [112-27-6]
α-hydro-ω-hydroxy-poly(oxy-1,2-ethanediyl) (*polyethylene glycol*); $(C_2H_4O)_nH_2O$; [25322-68-3]
2-(2-Methoxyethoxy)ethanol (*diethylene glycol monomethyl ether*); $C_5H_{12}O_3$; [111-77-3]
3,6,9,12-Tetraoxahexadecan-1-ol (*tetraethylene glycol monobutyl ether*); $C_{12}H_{26}O_5$; [1559-34-8]
1,1'-Oxybis(2-methoxyethane) (*diethylene glycol dimethyl ether*); $C_6H_{14}O_3$; [111-96-6]
2,5,8,11-Tetraoxadodecane (*triethylene glycol dimethyl ether*); $C_8H_{18}O_4$; [112-49-2]
2,5,8,11,14-Pentaoxapentadecane (*tetraethylene glycol dimethyl ether*); $C_{10}H_{22}O_5$; [143-24-8]
2-Methyl-3,6,9,12,15,18-hexaoxanonadecane (*pentaethylene glycol methyl isopropyl ether*); $C_{14}H_{30}O_6$;
®Sepasolv MPE (A mixture of oligo methyl isopropyl ethers developed by BASF)
1,4,7,10-Tetraoxacyclododecane (12-crown-4); $C_8H_{16}O_4$; [294-93-9]
1,4,7,10,13-Pentaoxacyclopentadecane (15-crown-5); $C_{10}H_{20}O_5$; [33100-27-5]
4-Methyl-1,3-dioxolan-2-one (*propylene carbonate*); $C_4H_6O_3$; [108-32-7]

The solubility in diethyl ether at 299.15 K and a total pressure of 0.986 bar was measured by Parsons (31). The average concentration of hydrogen sulfide in the liquid corresponds to a mole fraction of 0.026. The vapor pressure of pure diethyl ether is about 0.074 bar at this temperature so the partial pressure of solvent was much greater than the partial pressure of hydrogen sulfide in these experiments. The data indicate that the mole fraction solubility for a partial pressure of gas of 1.013 bar is about 0.10, more than double the Raoult's law value of 0.047. There are, however, no other measurements of the solubility in diethyl ether with which to make comparison so the measurements must be classified as tentative.

Gerrard (6) measured solubilities in 1,1'-oxybisoctane at a total pressure of 1.015 bar and temperatures of 265 K to 293 K. Extrapolation of these measurements to 298.15 K and correction to a partial pressure of 1.013 bar gives a mole fraction solubility of 0.088, comparable with the value estimated for diethyl ether. In the absence of other data for comparison, Gerrard's data for 1,1'-oxybisoctane should be accepted on a tentative basis.

Solubilities in ethoxybenzene and 1,4-dioxane reported by Gerrard (6) are consistent with the general pattern found for ethers and may be accepted on a tentative basis. Measurements of the solubility in tetrahydrofuran at 263.15 K and 298.15 K reported by Short *et al.* (27) are likely to be reliable but must also be accepted on a tentative basis in the absence of measurements on this system by other workers.

Byeseda *et al.* (30) reported the Ostwald coefficient for dissolution in 2,2'[1,2-ethanediylbis(oxy)]bisethanol (triethylene glycol) at 297.1 K. The mole fraction solubility for a partial pressure of 1.013 bar corresponding to this Ostwald coefficient is 0.0618. This is close to the value of 0.065 estimated from graphs of solubilities from 273.15 K to 373.15 K and partial pressures of gas from 1.013 to 11.355 bar published by Blake (32). The data at other temperatures and pressures given by Blake cannot be confirmed by comparison with other measurements. Blake gave no information on the method used and data can only be considered to be tentative.

Solubility data for four polyethylene glycols of different average relative masses have been published by Gestrich & Reinke (33). This work appears to be self consistent and the measurements fit into a general pattern discussed below.

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

Solubilities in diethylene glycol monomethyl ether and in tetraethylene glycol monobutyl ether have been measured by Sciamanna (34). These measurements appear to be of high accuracy but must be considered to be tentative until other measurements on these systems are reported.

Measurements of solubilities in polyglycol ethers have been made by Sciamanna (34), by Härtel (35) and by Sweeney (36). Each of these workers measured the solubility in tetraethylene glycol dimethyl ether. Solubilities were reported as Henry's constants, H. Sciamanna made measurements in the temperature range 288 K to 373 K and reported limiting values for zero partial pressure in the form of equations of the form:

$$\ln (H/\mathrm{kPa}) = A/T + B$$

Härtel based his values on measurements with the mole fraction of hydrogen sulfide in the liquid phase not greater than 0.16. In this range the variation of mole fraction solubility was found to be almost linear with a correlation coefficient greater than 0.99. The Henry's law constant published by Sweeney is based upon gas chromatographic measurements. Henry's law constants in tetraglyme from measurements by the different authors are as follows:

T/K	H/bar		
	Sciamanna	Härtel	Sweeney
293.15	3.71	3.390	
298.15	4.22	3.97*	3.91
313.15	6.07	6.179	
323.15	7.58	7.20*	7.46
333.15	9.35	8.310	
353.15	13.73	11.321	
373.15	19.34	16.901	

* interpolated values.
(Henry's law constant = partial pressure of gas / mole fraction solubility)

The evaluator recommends that, for the temperature range 298.15 to 323.15, the Henry's constant is taken to be the mean of values from measurements by Sciamanna and Härtel. Outside this temperature range the divergence of measurements is too great for values to be recommended.

Sciamanna (34) also measured solubilities in diethylene glycol dimethyl ether and triethylene glycol dimethyl ether.

The available experimental solubility data for glycols, polyglycols and ethers derived from these compounds can be correlated with the number of carbon-oxygen -carbon links in these molecules. The evaluator has estimated mole ratio solubilities (H_2S/solvent) at 298.15 K for a partial pressure of 1.013 bar. If the value for ethylene glycol, propylene glycol triethylene glycol and the polyethylene glycols are plotted against the number of carbon-oxygen-carbon links in the molecule then the points lie close to a straight line (see fig.3). In the case of the polyethylene glycols the number of links is taken as the average number calculated from the average relative molecular masses of the samples.

Mole ratio solubilities for five of the glycol diethers fall close to a similar straight line if a value for ®Sepasolv MBE based upon measurements by Wolfer *et al.* (37) is included. The mole ratio solubility of dioctyl ether also lies close to this line. The estimated value for pentaethylene glycol methyl isopropyl ether does not fit into the pattern. Härtel (35) published Henry's law constants for this compound and has shown that the mole fraction solubility is proportional to pressure to a mole fraction of 0.16, with a correlation coefficient of better than 0.99. The evaluator has estimated the mole ratio solubility at 298.15 K and 1.013 bar from an apparent mole fraction solubility of 0.323 calculated from an interpolated value of Henry's law constant. This may be an over-estimate because it is outside the range in which a linear relationship between mole fraction solubility and pressure has been experimentally demonstrated.

COMPONENTS:

1. Hydrogen sulfide; H_2S; [7783-06-4]

2. Non-aqueous solvents

EVALUATOR:

Peter G.T. Fogg,
Department of Applied Chemistry
and Life Sciences,
Polytechnic of North London,
Holloway, London N7 8DB, U.K.

July 1987

CRITICAL EVALUATION:

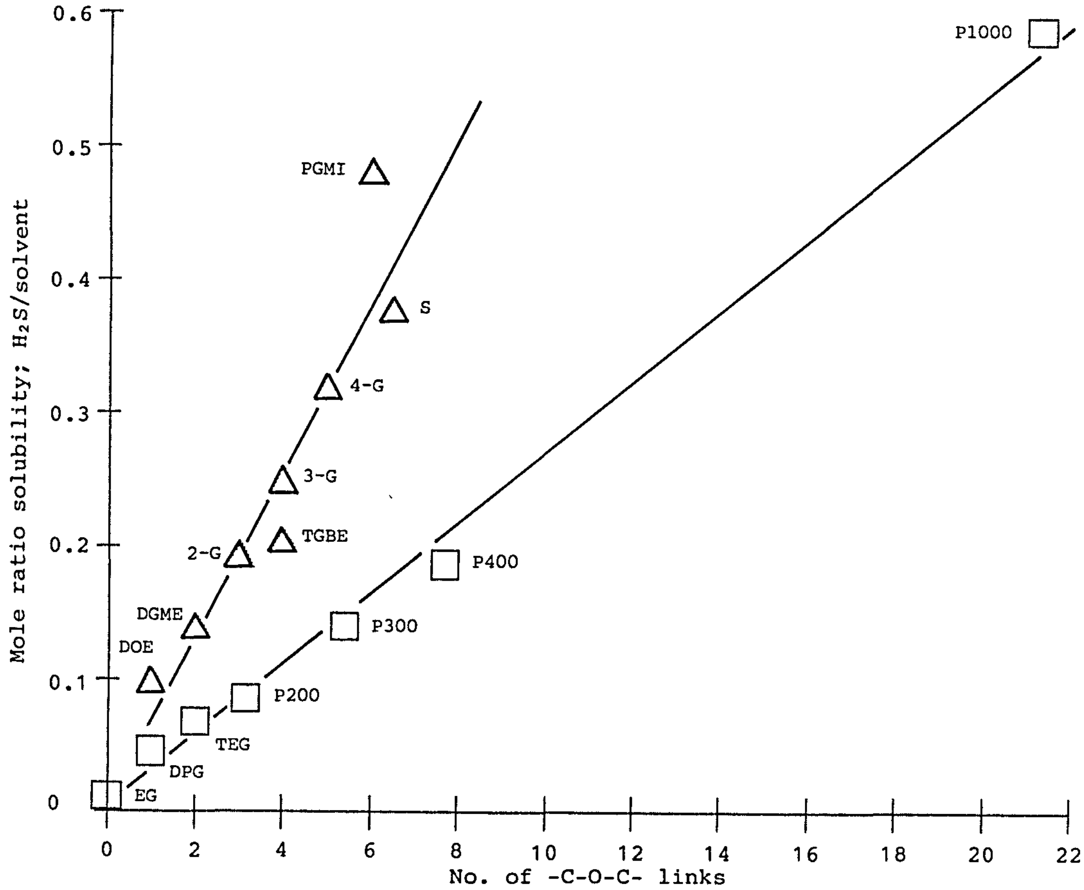

Fig. 3 Mole ratio solubilities at 298.15 K and a partial pressure of 1.013 bar in glycols, glycol ethers and dioctyl ether as a function of the number of -C-O-C- links in a molecule of solvent

glycols

EG *ethylene glycol* (6,27)

DPG *dipropylene glycol* (15)

TEG *triethylene glycol* (30,32)

P200; P300; P400; P1000 *polyethylene glycols* (33)

glycol ethers; dioctyl ether

DOE *dioctyl ether* (6)

DGME *diethylene glycol monomethyl ether* (34)

2-G *diethylene glycol dimethyl ether* (34)

3-G *triethylene glycol dimethyl ether* (34)

4-G *tetraethylene glycol dimethyl ether* (34,35)

TGME *tetraethylene glycol monobutyl ether* (34)

PGMI *pentaethylene glycol methyl isopropyl ether* (35)

S ®*Sepasolv MBE* (37)

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

The overall graphical pattern of measurements on the two series of compounds indicates that most of the solubilities in individual solvents are likely to be reliable.

Mole fraction solubilities in two of the crown ethers, 12-crown-4 and 15-crown-5, have been published by Linford & Thornhill (38). The values at 295.2 K for a partial pressure of 1.013 bar are 0.31 and 0.33 respectively and are greater than values for polyglycol ethers having the same number of carbon-oxygen-carbon bonds discussed above (0.20 and 0.24 at 298.15 K respectively). No other solubilities in crown ethers are available for comparison but these values may be accepted as being tentative.

Solubilities in propylene carbonate have been measured by several workers and there is fairly good agreement between different sets of measurement. Lenoir *et al.* (15) and Sweeney (36) reported Henry's constants measured by a chromatographic method. Mole fraction solubilities from these constants are higher than those from other measurements and may be less reliable. Shakhova *et al.* (39) measured solubilities over the temperature range 273.2 K to 313.2 K and pressure range 0.267 to 1.013 bar. The apparent values of mole fraction solubilities do not vary linearly with pressure over this pressure range. Isaacs, Otto & Mather (40) measured solubilities at 313.2 K and 373.2 K over a pressure range of 1.847 to 49.60 bar. The evaluator has estimated the corresponding mole fraction solubilities at 1.013 bar by use of the Krichevskii-Il'inskaya equation. The apparent mole fraction solubility at 313.2 K is 0.023 and at 373.2 K is 0.009. The mole fraction solubility at 313.2 K and 1.013 bar from Shakhova *et al.* is 0.0264. Data given by Isaacs *et al.* appear to be reliable with the exception of the solubility at 373.2 K and 1.847 bar. The solubility which has been reported is less than the experimental error in the measurements and seems to be out of line with other measurements.

Henry's constants at temperatures from 263.15 K to 373.15 K have been reported by Rivas & Prausnitz (41). These may be used to estimate mole fraction solubilities at a partial pressure of 1.013 bar but the apparent deviation from a linear variation of mole fraction solubility with variation of pressure indicated by Shakhova's measurements should be borne in mind. Mole fraction solubilities for a partial pressure of 1.013 bar from measurements by Shakhova *et al.*, by Isaacs *et al.*, and by Rivas & Prausnitz are shown in fig.4. These values are fitted by the equation:

$$\log_{10} x_{H_2S} = -3.889 + 740/(T/K)$$
$$\delta x_{H_2S} = \pm 0.003$$

Other compounds of carbon, hydrogen and oxygen

Acetic acid; $C_2H_4O_2$; [64-19-7] Hexanoic acid; $C_6H_{12}O_2$; [142-62-1]
Acetic anhydride; $C_4H_6O_3$; [108-24-7] 2-Propanone; C_3H_6O; [67-64-1]
2-Hydroxybenzoic acid, methyl ester (*methyl salicylate*); $C_8H_8O_3$; [119-36-8]
Phenol; C_6H_6O; [108-95-2] 2-Furancarboxaldehyde; $C_5H_4O_2$; [98-01-1]
Benzenedicarboxylic acid, didecyl ester; $C_{28}H_{46}O_4$; [84-77-5]
Dibenzofuran; $C_{12}H_8O$; [132-64-9]

Solubilities in acetic acid at 298 K and 303 K were reported by Short, Sahgal and Hayduk (27) and in hexanoic acid over the range 265 - 293 K by Gerrard (6). In each case the mole fraction solubilities for a partial pressure of 1.013 bar fall below values corresponding to the Raoult's law equation. Extrapolation of solubilities to common temperatures shows a higher mole fraction solubility for the longer chain acid. Solubilities in either solvent can be accepted as tentative values.

Solubilities in acetic anhydride were also measured by Gerrard (6). Mole fraction solubilities lie above a reference line corresponding to Raoult's law in this case and when extrapolated to 303 K are about double the values for acetic acid. This difference may be due to stronger solvent-solvent hydrogen bonding in the case of acetic acid. There is no reason to doubt the data for acetic anhydride.

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

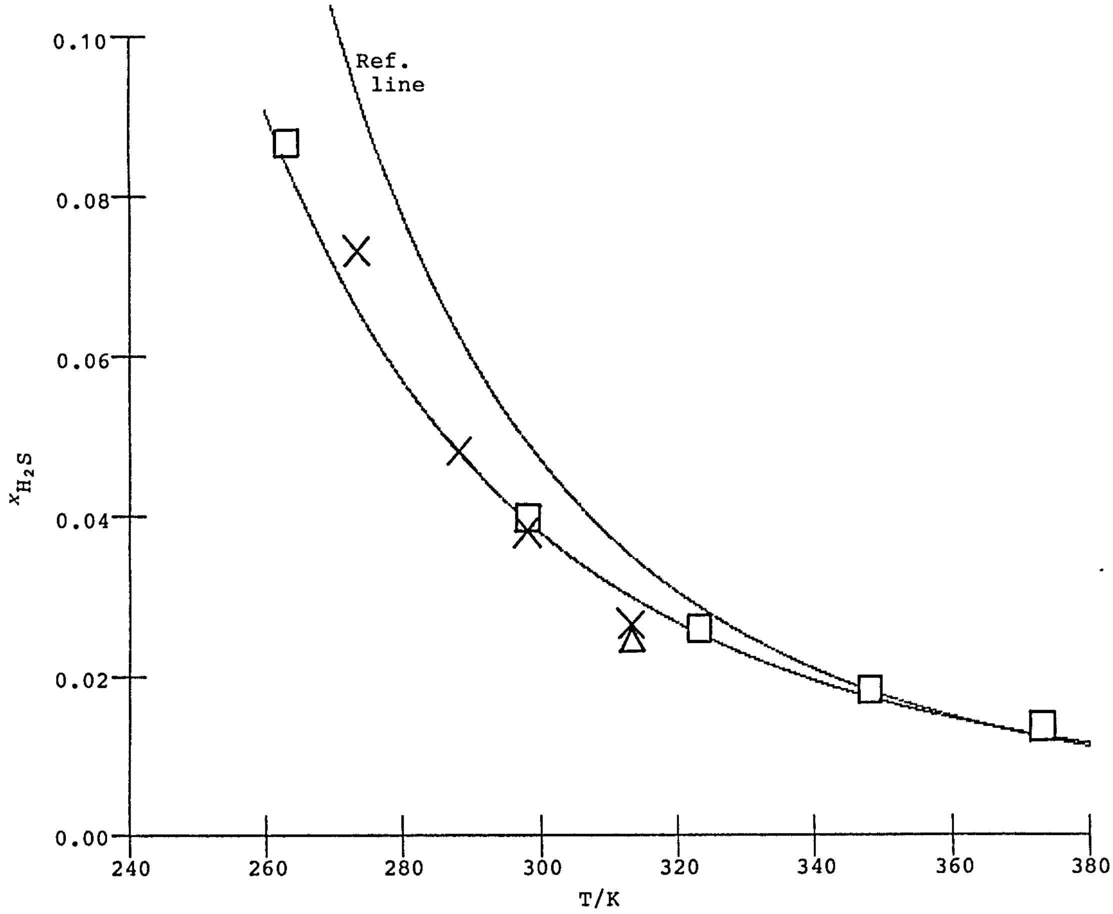

Fig. 4 <u>Variation with temperature of the mole fraction solubility of hydrogen sulfide in propylene carbonate at a partial pressure of 1.013 bar</u>

Points based upon experimental measurements have been superimposed upon a curve corresponding to the equation:

$$\log_{10} x_{H_2S} = -3.889 + 740/(T/K)$$

A reference line corresponding to values from the Raoult's law equation is also shown.

✕ Shakhova *et al.* (39) □ Rivas & Prausnitz (41)

△ Isaacs *et al.* (40)

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

Short *et al.* (27) reported solubilities at a partial pressure of 1.013 bar in 2-propanone at 263 K and 298 K. These measurements are likely to be reliable but must be accepted on a tentative basis in the absence of similar systems for comparison. Mole fraction solubilities, in this case, are greater than those in acetic anhydride under the same conditions.

Solubilities in methyl salicylate at a total pressure of 1.004 bar in the temperature range 265.15 K to 293.15 K have been measured by Gerrard (6). The values are self-consistent and may be accepted as tentative values until other measurements on this or similar systems are available for comparison.

Lenoir *et al.* (15) measured the Henry's law constant for phenol at 323.2 K by a chromatographic method. The reliability of this method cannot be judged because of uncertainties associated with the method used. No other measurements on this system are available for comparison. Devyatykh *et al.* (20) also used a similar chromatographic method to measure solubilities in 2-furancarboxaldehyde and in 2-benzenedicarboxylic acid, didecyl ester. Again there are no similar systems for comparison and no judgement of reliability can be made.

Kragas & Kobayashi (24) used a high pressure chromatographic method to measure limiting values of Henry's constants for dissolution of hydrogen sulfide in dibenzofuran in the presence of hydrogen. Hydrogen pressures ranged from 7 bar to 59 bar. Temperatures were 373.2 K and 398.2 K. At each temperature a plot of the reciprocal of the Henry's law constant against hydrogen pressure is close to a straight line enabling approximate values of Henry's constants at zero hydrogen pressure to be estimated. No other measurements on this system are available for comparison and the reliability of these Henry's constants, for estimation of solubilities at finite partial pressure, cannot be judged.

Halogenated compounds

Bromoethane; C_2H_5Br; [74-96-4]
1-Bromooctane; $C_8H_{17}Br$; [111-83-1]
Tribromomethane; $CHBr_3$; [75-25-2]
Trichloromethane; $CHCl_3$; [67-66-3]
Tetrachloromethane; CCl_4; [56-23-5]
Tetrachloroethene; C_2Cl_4; [127-18-4]
Pentachloroethane; C_2HCl_5; [76-01-7]
2,2-Dichloroacetic acid; $C_2H_2Cl_2O_2$; [79-43-6]
1,1'-Oxybis(2-chloroethane); $C_4H_8Cl_2O$; [111-44-4]
Chlorobenzene; C_6H_5Cl; [108-90-7]
Iodobenzene; C_6H_5I; [591-50-4]
1-Bromobutane; C_4H_9Br; [109-65-9]
1,2-Dibromoethane; $C_2H_4Br_2$; [106-93-4]
1,1,2,2-Tetrabromoethane; $C_2H_2Br_4$; [79-27-6]
1,1,2,2-Tetrachloroethane; $C_2H_2Cl_4$; [79-34-5]
2,2,2-Trichloroethanol; $C_2H_3Cl_3O$; [115-20-8]
Bromobenzene; C_6H_5Br; [108-86-1]

Solubilities in 1-bromooctane at a total pressure of 1.007 bar in the temperature range 265.15 K to 293.15 K were measured by Gerrard (6). Mole fraction solubilities for a partial pressure of 1.013 bar calculated from these measurements fall on a smooth curve lying above the reference line based on the Raoult's law equation when plotted against temperature. The mole fraction solubility in 1-bromobutane for 265.15 K and 1.013 bar partial pressure estimated from the solubility reported by Gerrard is 0.135 compared with 0.143 in 1-bromooctane under the same conditions. The mole fraction solubility in bromoethane given by Bell (3) for 1.013 bar partial pressure and 293.15 K is 0.126 compared with a value of 0.074 for 1-bromooctane at this temperature. The difference in this case could be due to bromoethane having the greater tendency to form hydrogen bonds with sulfur in hydrogen sulfide.

Gerrard's measurements (6) indicate that mole fraction solubilities in tribromomethane and 1,2-dibromoethane are within about 2% of each other at a partial pressure of 1.013 bar and 283.15 K and 293.15 K. Values at 293.2 K are close to values given by Bell (3). These mole fraction solubilities are about 20% lower than corresponding values for 1-bromooctane. Bell's value for mole fraction solubility in 1,1,2,2-tetrabromoethane at 293.15 K and 1.013 bar is about 60% of the value for 1-bromooctane under the same conditions. Steric factors may play an important role in determining the tendency for hydrogen bonding to occur and hence the solubility.

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

Solubilities in these brominated compounds measured by Bell and by Gerrard should be treated as tentative values.

Bell (3) also measured the mole fraction solubility in trichloromethane at a partial pressure of 1.013 bar and 293.15 K. The value at 265.15 K may be calculated from Gerrard's measurements and is consistent with Bell's value for 293.15 K. The value of 0.103 at 293.15 K may be compared with the value for tribromomethane mentioned above of 0.059 under these conditions. There would be less steric hindrance to hydrogen bond formation with hydrogen sulfide in the case of the chloro-compound and this may account for the apparent large difference in mole fraction solubilities. The corresponding reference value based upon Raoult's law is 0.055.

The mole fraction solubility in 1,1,2,2-tetrachloroethane at 293.15 K and 1.013 bar given by Bell (3) is 0.0702. This is close to the value of 0.0719 for 1,2-dichloroethane. The corresponding tetrabromo compound has a lower value 0.0446. Bell's values for mole fraction solubilities under these conditions in pentachloroethane and in trichloroethene are 0.0514 and 0.0482 respectively. Values for tetrachloromethane and tetrachloroethene, which contain no hydrogen, are even lower; 0.0419 and 0.0372 respectively.

The mole fraction solubility in 2,2,2-trichloroethanol, at 273.15 and 1.013 bar, calculated from Gerrard's data (6), is about 15% greater than the corresponding value for ethanol. The value for 2,2-dichloroacetic acid at 283.15 K from Gerrard's measurements is about 30% greater than the hypothetical value for acetic acid found by extrapolating solubilities measured at temperatures above the melting point. The mole fraction solubility in 1,1'-oxybis(2-chloroethane). at 293.2 K and 1.013 bar may be estimated from the chromatographic data given by Devyatykh *et al.* (20) to be 0.053. This may be compared with an approximate value for 1,1'-oxybisethane (diethyl ether) of 0.1 at 299.2 K and a more reliable value of 0.088 for 1,1'-oxybisoctane (dioctyl ether). However, values of solubilities from chromatographic data should be used with caution.

There is no reason, however, to doubt solubilities in chloro-compounds discussed above and reported by Bell and by Gerrard. Values should therefore be accepted as tentative.

Solubilities in chlorobenzene have been measured by Bell (3), by Gerrard (6), by Patyi *et al.* (20) and by Short *et al.* (27) in the temperature range 263.15 K to 333.15 K and at barometric pressures. Interpolated values of mole fraction solubilities for a partial pressure of 1.013 bar from data published by Short *et al.* are within 4% of values calculated from Gerrard's data for 273.15 K, 283.15 K and 293.15 K but are about 12% lower than Gerrard's values for 265.15 K and 267.15 K. The interpolated value for 293.15 is about 40% higher than Bell's value. The value for 298.15 is about 30% higher than the value given by Patyi *et al.* Despite these differences the evaluator is of the opinion that the measurements by Short *et al.* using modern techniques and apparatus are the most reliable and should be accepted on a tentative basis.

Solubilities in bromobenzene have been measured by Gerrard (6) at barometric pressure over the temperature range 266.15 K to 293.15 K. The mole fraction solubility for a partial pressure of gas of 1.013 bar calculated from Gerrard's data is about 49% greater than the figure given by Bell (3). The extrapolated value for 298.15 K is about 34% greater than the value given by Patyi *et al.* (20). Values from Gerrard's measurements are, however, close to interpolated values for chlorobenzene from the work by Short *et al.* (27) mentioned above. They are also close to values for iodobenzene and for benzene which may also be found from the data which he has reported.

Gerrard (6) measured the solubility of hydrogen sulfide at barometric pressure in iodobenzene over the range 265.15 K to 293.15 K. As indicated above, mole fraction solubilities fit into a general pattern but no other solubility data for this gas in this solvent have been found in the literature.

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

Compounds containing nitrogen

1-Methyl-2-pyrrolidinone; C_5H_9NO; [872-50-4]
Benzenamine (*aniline*); C_6H_7N; [62-53-3]
N,N-Dimethylbenzenamine (*dimethylaniline*); $C_8H_{11}N$; [121-69-7]
N-Methylbenzenamine (*methylaniline*); C_7H_9N; [100-61-8]
N-Ethylbenzenamine (*ethylaniline*); $C_8H_{11}N$; [103-69-5]
N,N-Diethylbenzenamine (*diethylaniline*); $C_{10}H_{15}N$; [91-66-7]
Pyridine; C_5H_5N; [110-86-1]
Quinoline; C_9H_7N; [91-22-5]
3-Methyl-1H-pyrazole; $C_4H_6N_2$; [1453-58-3]
1,3-Dimethyl-1H-pyrazole; $C_5H_8N_2$; [694-48-4]
Nitrobenzene; $C_6H_5NO_2$; [98-95-3]
Acetonitrile; C_2H_3N; [75-05-8]
Benzonitrile; C_7H_5N; [100-47-0]
N,N-Dimethylformamide; C_3H_7NO; [68-12-2]
N,N-Dimethylacetamide; C_4H_9NO; [127-19-5]
Hexahydro-1-methyl-2H-azepin-2-one (*N-methyl-ε-caprolactam*); $C_7H_{13}NO$; [2556-73-2]

Mole fraction solubilities of hydrogen sulfide in compounds containing basic nitrogen atoms are relatively high compared with solubilities in other compounds under the same conditions of temperature and pressure.

Various measurements of the solubilities in 1-methyl-2-pyrrolidinone under different conditions of temperature and pressure have been reported. (15, 36, 41-44). There are discrepancies between solubilities reported by different authors as may be seen below:

	Henry's constant/bar 298.15 K	 323.15 K
Lenoir *et al* (15)	5.56	
Sweeney (36)	5.81	12.3
Rivas & Prausnitz (41,43)	7.6	13.5
Yarym-Agaev *et al* (42)	6.41†	11.6†
Murrieta-Guevara & Rodriguez (44)	7.5	

† calculated by the evaluator from the solubility at 1.013 bar

The chromatographic method used by Lenoir *et al* and by Sweeney can give unreliable results. Murrieta-Guevara & Rodriguez have plotted their measurements at 298.2 K and partial pressures from 0.21 to 1.64 bar to show a linear variation of mole fraction solubility with pressure with a slope corresponding to a Henry's constant of 7.5, close to the value obtained by Rivas & Prausnitz. The line, however, does not pass through the origin. This may be an artefact of the apparatus or may reflect the limitations of Henry's law as applied to this system. The high pressure measurements by Yarym-Agaev *et al.* may be accepted on a tentative basis as reflecting the overall pattern of behaviour over the temperature and pressure range in which measurements were made. Mole fraction solubilities at a partial pressure of 1.013 bar may be estimated from Henry's constants reported by Rivas & Prausnitz but the evaluator cannot judge whether these estimated solubilities are more reliable than solubilities at this pressure reported by Yarym-Agaev *et al.*

Rivas & Prausnitz (43) also measured solubilities in methyl pyrrolidinone in the presence of about 12 mole % of 2-(2-aminoethoxy)-ethanol (diglycolamine). Muerieta-Guevara and Rodriguez (44) measured solubilities in the presence of 5.1 wt% and 14.3 wt% of 2-aminoethanol (monoethanolamine). These measurements may be accepted on a tentative basis.

Solubilities in benzenamine at pressures of about 1.013 bar have been measured by Gerrard (6) over the temperature range 265.15 K to 293.15 K and by Patyi *et al.* (22) at 298.15 K. Bancroft & Belden (45) made measurements over a pressure range from 0.14 to 1.55 bar at 295.15 K. Extrapolation of mole fraction solubilities for a partial pressure of 1.013 bar calculated from Gerrard's measurements give a value which is 24% above the value given by Patyi *et al.* and about 7% above a value from the work by Bancroft & Belden. The value calculated from the Henry's constant given by Lenoir *et al.* (15) is about 24% greater than the value from Gerrard.

COMPONENTS:

1. Hydrogen sulfide; H_2S; [7783-06-4]

2. Non-aqueous solvents

EVALUATOR:

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July 1987

CRITICAL EVALUATION:

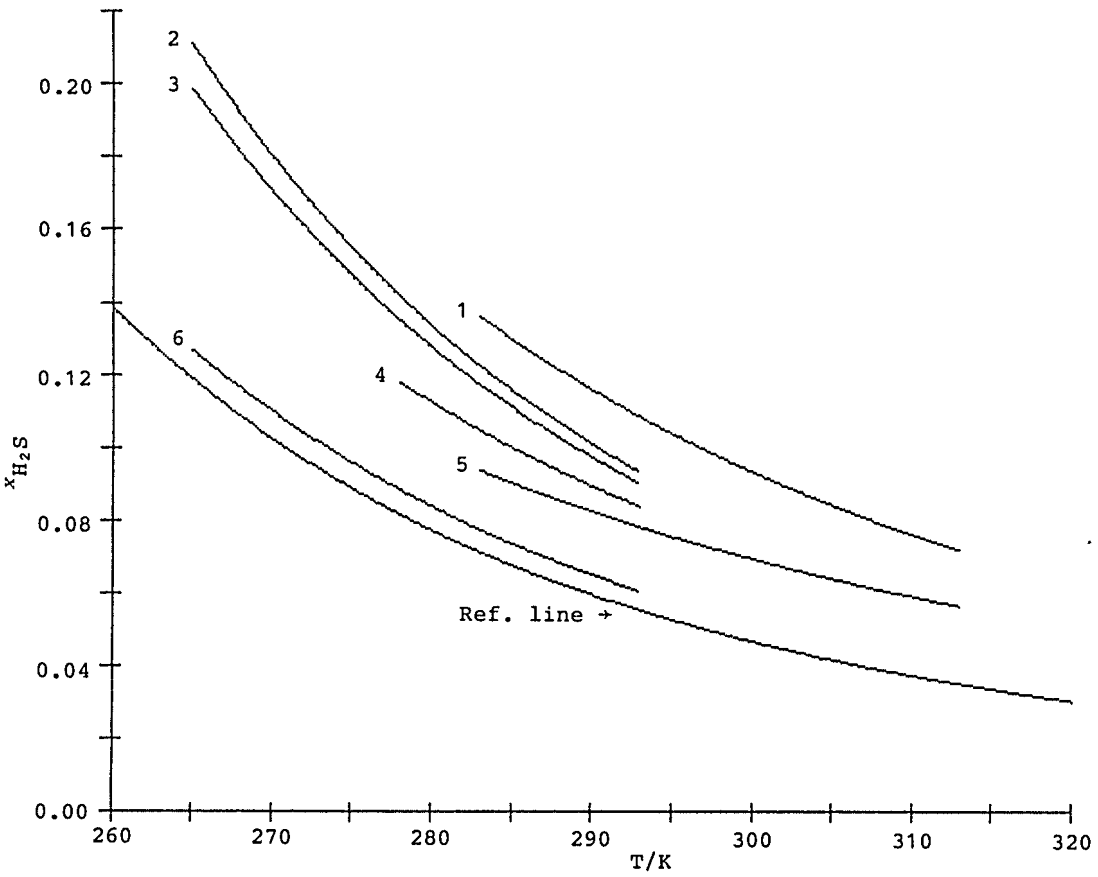

Fig. 5 The general pattern of mole fraction solubilities of hydrogen sulfide at a partial pressure of 1.013 bar in nitrogen bases

1. 1,3-dimethyl-1H-pyrazole; (ref.46)
2. pyridine; (ref.6)
3. quinoline; (ref.6)
4. N,N-dimethylbenzenamine (*dimethylaniline*); (ref.6)
5. 3-methyl-1H-pyrazole; (ref.46)
6. benzenamine (*aniline*); (ref.6)

The reference line corresponds to values from the Raoult's law equation.

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

The solubility measurement by Lenoir *et al.* can be rejected because of the uncertainties associated with the chromatographic technique which was used. In the case of other solvents solubilities reported by Patyi *et al.* tend to be lower than those reported by other workers and the solubility at a single temperature may be less reliable than those reported by Gerrard over a temperature range in this case. Gerrard's measurements should therefore be accepted on a tentative basis.

Solubilities in N,N-dimethylbenzenamine have been measured at barometric pressure by Gerrard (6) at 278.15 K, 283.15K & 293.15 K and by Patyi *et al.* (22) at 298.15 K. The extrapolated value of the mole fraction solubility at 298.15 K from Gerrard's measurements is again appreciably higher than the value from Patyi *et al.*; 0.076 compared with 0.056. The evaluator considers the Gerrard value to be the more reliable but the discrepancy should be borne in mind.

Solubilities in N-methylbenzenamine, N-ethylbenzenamine and N,N-diethylbenzenamine have been reported by Patyi *et al.* (22) but there are no other measurements on these compounds for comparison.

Solubilities in pyridine and in quinoline have been measured by Gerrard (6) at barometric pressure in the temperature range 265.15 K to 293.15 K. The mole fraction solubilities for a partial pressure of 1.013 bar are similar in the two compounds (see fig.5). The solubilities in these compounds can be accepted as tentative values.

Solubilities in 3-methyl-1H-pyrazole and in 1,3-dimethyl-1H-pyrazole were measured by Egorova *et al.* (46) at pressures below 1.013 bar in the temperature range 283.2 K to 313.2 K. Values of Henry's constants were reported. No other data on these compounds are available for comparison and these measurements should be accepted on a tentative basis.

The general pattern of solubilities in nitrogen bases at a partial pressure of gas of 1.013 bar, on the basis of measurements discussed above, is shown in fig.5.

Solubilities in nitrobenzene at barometric pressure were measured by Gerrard (6) at temperatures from 265.15 K to 293.15 K. Solubilities have also been measured by chromatographic techniques by Devyatykh *et al.* (20) and by Lenoir *et al.* (15) The mole fraction solubility at 293.15 K calculated from data given by Devyatkh *et al.* is 0.053. Although, by itself, this value is of uncertain status because it is based upon chromatographic measurements it does substantiate the data reported by Gerrard. However, mole fraction solubilities at other temperatures, estimated from the distribution coefficient at 293.15 K and the heat of solution given by Devyatykh *et al*, do not agree with values from Gerrard's measurements. The mole fraction solubility for a partial pressure of 1.013 bar from data given by Lenoir *et al.* is 0.0535 at 298.15 K compared with a value of 0.046 by extrapolation of values based upon Gerrard's work. The solubilities given by Gerrard may be accepted as tentative values, in preference to solubilities based upon chromatographic methods.

Solubility in acetonitrile has been measured by Hayduk & Pahlevanzadeh (4) at a total pressure close to 1.013 bar and temperatures in the range 268.15 K to 333.15 K. They found the corrected mole fraction solubility at 298.15 for a partial pressure of gas of 1.013 bar to be 0.0476. This value is in sharp contrast to the figure of 0.031 from measurements by Evans & Blount (47). In the opinion of the evaluator the data presented by Hayduk & Pahlevanzadeh are likely to be the more reliable and may be accepted on a tentative basis.

Gerrard (6) measured the solubility in benzonitrile at barometric pressure and temperatures from 265.15 K to 293.15 K. Mole fraction solubilities from this work lie close to a smooth curve above the reference line corresponding to the Raoult's law equation. There is no reason to doubt the reliability of these values which should be accepted on a tentative basis.

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

Solubilities in N,N-dimethylformamide measured at pressures of about 1 bar, have been reported by the following:

DuPont du Nemours and Co. (Inc.) (48)	(298.15 K)
Gerrard (6)	(265.15 K - 293.15 K)
Byeseda, Deetz & Manning (30)	(297.1 K)
Hayduk & Pahlevanzadeh (4)	(268.15 K - 333.15 K)

When measurements by Gerrard and by Hayduk are corrected to a partial pressure of 1.013 bar there is very good agreement between the two sets of results over the whole of the temperature range. The DuPont value is slightly lower and the Byeseda value appreciably lower than the Gerrard and the Hayduk values. The corrected mole fraction solubility at 298.15 K from Gerrard's measurements is 0.119 compared with a value of 0.116 given by Hayduk and 0.109 from the solubility given by DuPont. The value of 0.097 at 297.1 K from measurements by Byeseda must be disregarded. The following equation for mole fraction solubilities at a partial pressure of 1.013 bar is based upon measurements by Gerrard and by Hayduk & Pahlevanzadeh :

$$\log_{10} x_{H_2S} = -4.053 + 930/(T/K)$$

$$\delta x_{H_2S} = \pm 0.003 \text{ ; valid for } 265.15 \text{ K to } 333.15 \text{ K.}$$

Hayduk & Pahlevanzadeh (4) have also measured solubilities in N,N-dimethylacetamide over the temperature range 268.15 K to 333.15 K. These measurements are likely to be reliable but should be accepted on a tentative basis until other measurements on this system are available for comparison.

Solubility in hexahydro-1-methyl-2H-azepin-2-one (N-methyl-ε-caprolactam) has been reported by Wehner *et al.* (49). The evaluator has estimated that the mole fraction solubility is about 0.18 at 293.2 K and a partial pressure of 1.013 bar. There are no data on comparable systems.

Compounds containing phosphorus

Phosphoric acid, trimethyl ester; $C_3H_9O_4P$; [512-56-1]
Phosphoric acid, triethyl ester; $C_6H_{15}O_4P$; [78-40-0]
Phosphoric acid, tripropyl ester; $C_9H_{21}O_4P$; [513-08-6]
Phosphoric acid, tributyl ester; $C_{12}H_{27}O_4P$; [126-73-8]
Phosphoric acid, tris(2-methylpropyl) ester; $C_{12}H_{27}O_4P$; [126-71-6]
Phosphoric triamide, hexamethyl; $C_6H_{18}NO_3P$; [680-31-9]

The solubility in tributyl phosphate has been measured by Härtel (35) over the temperature range 293 - 373 K. Measurements were reported as Henry's constants. based on measurements to a mole fraction concentration not greater than 0.16. The author found that mole fraction solubility varied approximately linearly with pressure. Henry's constants at infinite dilution were also reported by Vei *et al.* (50) for the temperature range 298 to 383 K and by Lenoir *et al.* (15) for 298.15 K and by Sweeney (36) for 298.15 & 323.15 K. Sergienko *et al.* (51) published small scale graphs showing variation of mole fraction solubility with pressure to 0.86 bar in the temperature range 223 to 313 K. These may be used to estimate limiting values of Henry's constant for comparison purposes. Values of Henry's constants from measurements by various workers are shown in fig.6.

Lenoir *et al.* (15) also published Henry's law constants, (partial pressure of gas/mole fraction solubility) for the trimethyl, triethyl, tripropyl and tris(2-methyl propyl) esters of phosphoric acid and also hexamethyl phosphoric triamide. These were also measured by gas chromatography at low partial pressures of hydrogen sulfide. , The evaluator has found no other measurements of solubilities of hydrogen sulfide in these compounds recorded in the literature. An estimation of the reliability of these measurements is not possible. The chromatographic technique can give unreliable solubility measurements. There are divergences between values of solubilities in other solvents published in this paper and values from other sources. The Henry's law constant reported for hexamethylphosphoric triamide is exceptionally low (1.63 bar or 1.61 atm). Even if this value is reliable it is incorrect to assume a

COMPONENTS: 1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	EVALUATOR: Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

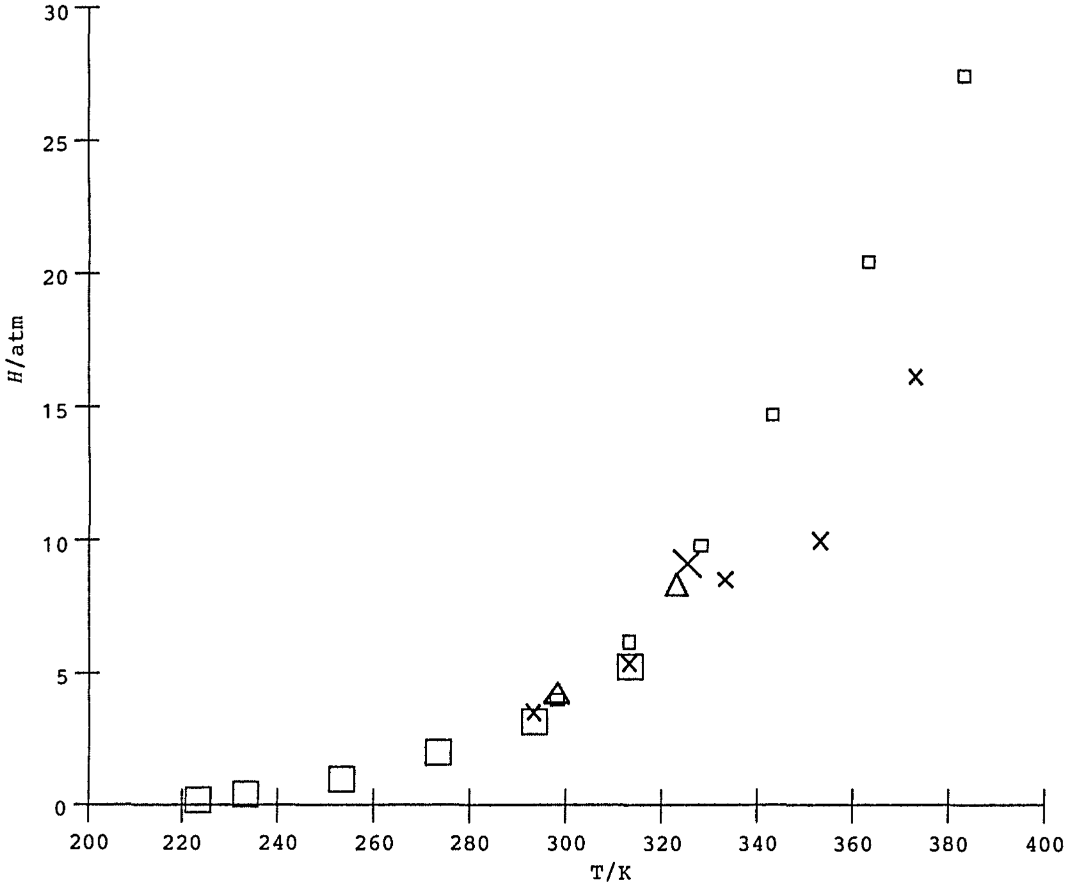

Fig. 6 The variation with temperature of Henry's constants at infinite dilution for dissolution of hydrogen sulfide in tributyl phosphate

╳ Lenoir *et al.* (15)

□ Vei *et al.* (50)

× Härtel (35)

△ Sweeney (36)

□ Sergienko *et al.* (51)

COMPONENTS:	EVALUATOR:
1. Hydrogen sulfide; H_2S; [7783-06-4] 2. Non-aqueous solvents	Peter G.T. Fogg, Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway, London N7 8DB, U.K. July 1987

CRITICAL EVALUATION:

linear variation of mole fraction solubility with partial pressure to 1.013 bar. Linear variation would give a mole fraction of 0.621 but appreciable deviation from proportionality will occur at a much lower concentration.

Compounds containing sulfur

Sulfinylbismethane (*dimethylsulfoxide*); C_2H_6OS; [67-68-5]
Tetrahydro-1,1-thiophene (®*Sulfolane*); $C_6H_8O_2S$; [126-33-0]
Carbon disulfide; CS_2; [75-15-0] Sulfur; S; [7704-34-9]

Lenoir *et al.* (15) measured Henry's constant in dimethylsulfoxide by a chromatographic method. The reliability of the measurement cannot be judged but it is subject to the same uncertainty as other chromatographic measurements of solubility.

Henry's constants for solubility in ®Sulfolane have been measured by Rivas & Prausnitz (41) at temperatures from 303.15 K to 373.15 and unspecified pressures below 1.013 bar. Mole fraction solubilities for a partial pressure of 1.013 bar may be calculated on the assumption that there is linear variation of mole fraction solubility with pressure. Extrapolation of these solubilities to 297.1 K gives a mole fraction solubility of 0.055. This value may be compared with the value of 0.0686 at this temperature which may be calculated from the data given by Byeseda *et al.* (30). The Rivas & Prausnitz data are, however, likely to be the more reliable and may be accepted on a tentative basis.

Vapor pressures of various mixtures of hydrogen sulfide and carbon disulfide have been measured by Gattow & Krebs (52) in the temperature range 153 - 213 K.. These measurements correspond to a self-consistent pattern of variation of mole fraction solubility with variation in partial pressure of hydrogen sulfide and can be accepted on a tentative basis. There are no other measurements on this system available for comparison.

The solubility of hydrogen sulfide in molten sulphur has been measured by Fanelli (53) at barometric pressure from 399.2 K to 623.2 K. The reversible absorption of hydrogen sulfide increases with increase in temperature until it reaches a maximum at about 644 K. It subsequently decreases as the boiling point of sulfur in approached. This behaviour is consistent with the reversible formation of unstable polyhydrogen sulfides by an endothermic process. The measurements reported by Fanelli form a consistent set but there are no other comparable measurements in the literature to judge them against. There is no reason to question their reliability and they can be accepted as tentative measurements.

Compounds containing silicon

Triethoxysilane; $C_6H_{16}O_3Si$; [998-30-1]
Silicic acid, tetraethyl ester; $C_8H_{28}O_4Si$; [78-10-4]
Silicone oils.

Devyatykh *et al.* (20) measured distribution constants for triethoxysilane, tetraethylsilicate, and three different silicones by a chromatographic method. It is uncertain whether these may be equated with Ostwald coefficients. Surface effects and non-equilibrium conditions can cause errors in the estimation of solubility by the chromatographic method.

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COMPONENTS:	EVALUATOR:
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