**Arsine Solubilities** 

COMPONENTS: l. Arsine; AsH3; [7784-42-1] 2. Organic liquids	EVALUATOR: P. G. T. Fogg, School of Chemistry, Polytechnic of North London, Holloway, London, N7 8DB, UNITED KINGDOM.
	August 1983

CRITICAL EVALUATION:

The data published by Devyatykh *et al*. (1) and those published by Corriez and Berton (2) have been discussed in detail by Gerrard (3). The data of Devyatykh *et al*. (1) were determined using a gas chromatographic technique. The solubility refers to that at a very low pressure of arsine and it is unlikely that extrapolation to one atmosphere pressure is valid. In addition, possible adsorption at the stationary phase-carrier gas interface could have occurred and the results should be viewed with caution. It is unwise to use the data given by Devyatykh to predict gas solubilities at 1 atmosphere pressure. The data may, perhaps, be used to estimate relative solubilities in the solvents which were studied but such estimates may not be very percise.

Solubilities measured by Corriez and Berton are consistent with the properties of the solvents which were studied and may be accepted as provisional values.

## References

- Devyatykh, G. G.; Ezheleva, A. E.; Zorin, A. D.; Zueva, M. V. Zh. Neorgan. Khim. <u>1963</u>, 8, 1307 (Russ. J. Inorg. Chem. <u>1963</u>, 8, 678).
- Corriez, P.; Berton, A. Bull. Soc. Chim. France <u>1950</u>, 43.
- Gerrard, W.
   Gas Solubilities Widespread Applications, Pergamon Press, Oxford, <u>1980</u>.

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COMPONENTS:	ORIGINAL MEASUREMENTS:		
l. Arsine; AsH <sub>3</sub> ; [7784-42-1]	Corriez, P.; Berton, A.		
2. Hydrogen cvanide and aliphatic	Bull. Soc. Chim. France		
nitriles.	<u>1950</u> ,	43-45.	
VARIABLES:	PREPARED	BY:	
		P. G. T. Fo	ogg
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EXPERIMENTAL VALUES:			
Solvent	т/к	Bunsen coefficient ∝	Mole fraction* $x_{ASH_3}$ (1 atm)
Hydrocyanic acid; HCN; [74-90-8]	287.2	0.7	0.0012
Acetonitrile; C <sub>2</sub> H <sub>3</sub> N; [75-05-8]	287.2	5.3	0.0122
Propanenitrile (propionitrile).	297 2	7 0	0.0240
$C_{3}H_{5}N;$ [107-12-0]	207.2	7.5	0.0242
Butanenitrile (butyronitrile); C.H-N; [109-74-0]	287.2	8.0	0.0302
* Calculated by compiler using the density of arsine given in ref. (1) and the densities of solvents given in refs. (2) and (3).			
AUXILIARY	INFORMATIO	ריי אכ אר	
METHOD/APPARATUS/PROCEDURE:	SOURCE AN	D PURITY OF MATERI	ALS;
The initial volume of gas was measured		<b>5</b>	
over mercury in a gas burette at the	NO 11.	cormation given	•
barometric pressure. This volume was			
adjusted to 0 °C and 1 atm by the			
relation PV = RT. Gas was passed			
into an absorption pipette containing			
a known volume of rac was measured at			
the barometric pressure. D			
The final pressure of arsine, P	REFERENC	CES:	
was taken to be p, minus vapor	. No.1.1		
pressure of pure solvent. The final	Treat	tise on Inorgan	enensive ic &
volume of gas was adjusted from $p_{A_{GH_{adj}}}$	Theor Long	retical Chemist: Nans, London	ry, Vol. IX,
to 1 atm and 0 °C. The Bunsen ab-	2. Timme	ermans, J., Phys	sico-Chemical
sorption coefficient, $\alpha$ , was the	Vol.	cants of Pure Or 1, Elsevier . M	<i>rganic Compounds</i> Amsterdam. 1950
difference between the initial and	3. Timme	ermans, J., Phys	sico-Chemical
final adjusted volumes divided by	Vol.	2, <u>1965</u> .	gunic compounds

the volume of solvent.

COMPONENTS:		ORIGINAL MEASUREMENTS:	
<pre>1. Arsine; AsH<sub>3</sub>; [7784-42-1]</pre>		Devyatykh, G.G.; Ezheleva, A.E.; Zorin, A.D.; Zueva, M.V.	
2. Various liquids		Russ. J. Inorg. Chem. <u>1963</u> ,8, 678-682.	
VARIABLES:	······	PREPARED BY:	
Temperature, press	ure	P.G.T. Fogg	
EXPERIMENTAL VALUES:		L	
Solvent	Pressure I range /mmHg	Distribution constant Vol <sub>AsH3</sub> /vol <sub>solvent</sub>	Heat of solution /kcal mol <sup>-1</sup>
2-Ethoxyethanol, C4H10O2; [110-80-5]	0.2 - 23.4	16.5	-0.98
1,1'-oxybis [2-chloro- ethane], C4H6Cl2O; [111-44-4]	0.05- 13.4	22.4	-2.5
Nitrobenzene, C <sub>6</sub> H <sub>3</sub> NO <sub>2</sub> ; [98-95-3]	0.01- 17.0	11.72	-1.80
Liquid paraffin	0.2 - 26.5	22.7	-3.5
Silicone PFMS-4F	0.02- 17.5	31.4	-3.2
Temperature = 293.2 K	760 mmHg = 1	$atm = 1.013 \times 10^5 Pa.$	
Distribution constants were measured between 278.2 K and 323.2 K over a range of partial pressures of arsine and a total pressure of about 760 mmHg. At a fixed temperature the distribution constants did not depart from the mean values by more than ±3%. These mean values were reported at one temperature only but heats of solution, said to have been calculated from the variation of distribution constants with temperature, were given. If it is assumed that distribution constants vary with temperature according to equations of the form :			23.2 K over of about ts did not values were d to have ts with on constants
	AUXILIARY	INFORMATION	
METHOD / APPARATUS / PROCEDURE :		SOURCE AND PURITY OF MATER	RIALS;
A chromatographic method was used. Temperatures were controlled to $\pm$ 0.5K. The support phase consisted of Nichrome spirals. The carrier gas was either nitrogen or hydrogen. The volume, V <sub>1</sub> , of the liquid phase was calculated from the weight of the column before and after filling with liquid and allowing to drain. The free volume, V <sub>g</sub> , was equated with the retention volume for hydrogen gas. The distribution constant, K.		1. Prepared by reaction between Zn <sub>3</sub> As <sub>2</sub> and aqueous acid; purified by vacuum distillation; no impurities detected by chromatography. H <sub>2</sub> & N <sub>2</sub> : passed through activated carbon and through molecular sieve.	
was calculated from the Martin equation:	James and	ESTIMATED ERROR:	
$V_{R} = V_{g} + KV_{l}$			
where V <sub>R</sub> is the retentio for arsine.	n volume	REFERENCES:	

COMPONENTS:

1. Arsine; AsH ; [7784-42-1]

2. Various liquids

ORIGINAL MEASUREMENTS:

Devyatykh, G.G.; Ezheleva, A.E.; Zorin, A.D.; Zueva, M.V.

Russ, J. Inorg. Chem. <u>1963</u>, 8, 678-682.

EXPERIMENTAL VALUES:

 $\ln K = (-\Delta H/RT) + A$ 

where K is the distribution constant for a temperature  $T, \Delta H$  is the heat of solution of arsine in the solvent and A is a constant for the solvent, then distribution constants at any temperature in the range 278.2 K to 323.2 K may be estimated from a value at 293.2 K and the corresponding value of the heat of solution. The equation for K may be written in the form.

 $K = \exp \left[A + (B/T)\right]$ 

The following values of A and B have been calculated by the compiler:

Solvent	A	В/К
2-Ethoxyethanol	1.120	493
1,1'-oxybis [2-chloroethane]	-1.184	1259
Nitrobenzene	-0.630	906
Liquid paraffin	-2.888	1762
Silicone PFMS-4F	-2.049	1611

In the opinion of the compiler these distribution constants cannot be equated with Ostwald coefficients unless the assumption is made that equilibrium was established between gas and liquid phases under the conditions of the experiment.

In addition, possible adsorption of arsine at the stationary phasecarrier gas interface may have lowered the accuracy of the results.

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COMPONENTS:	ORIGINAL MEASUREMENTS:		
l. Arsine, AsH3; [7784-42-1] 2. Various liquids	Devyatykh, G.G.; Ezheleva, A.E.; Zorin, A.D.; Zueva, M.V.		
	678-682.	·· <u>1905</u> , 0,	
VARIABLES: Temperature	PREPARED BY: P.G.T. Fogg		
EXPERIMENTAL VALUES:			
Solvent	Distribution constant <sup>Vol</sup> AsH3 <sup>/Vol</sup> solvent	Heat of solution /kcal mol <sup>-1</sup>	
2-Furancarboxaldehyde; C5H4O2; [98-01-1]	15.68	-3.6	
l,2-Benzenedicarboxylic acid, didecyl ester; C28H46O4; [84-77-5]	31.8	-3.0	
Triethoxysilane, C <sub>6</sub> H <sub>16</sub> O <sub>3</sub> Si; [998-30-1]	19.7	-5.8	
Silicic acid, tetraethyl ester, $C_{\theta}H_{20}O_{4}Si; [78-10-4]$	17.0	-4.3	
Silicone 702-DF	38.0	-4.7	
Silicone VKZh-94B	26.2	-5.6	
Temperature = 293.2 K			
Distribution constants were measured between 278.2 K and 323.2 K. The partial pressures of arsine at which these measurements were made were not stated but would have been very small. The total pressure of arsine and carrier gas was about 760 mmHg in each case. Distribution constants were reported at one temperature only but heats of solution, said to have been calculated from the variation of distribution constants with			
AUXILIARY	INFORMATION		
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATER	HALS:	
A chromatographic method was used. Temperatures were controlled to $\pm$ 0.5 K. The support phase consisted of Nichrome spirals. The carrier gas was either nitrogen or hydrogen. The volume, V <sub>1</sub> , of the liquid phase was calculated from the weight of the column before and after filling with liquid and allowing to drain. The free volume, V <sub>g</sub> , was equated with the retention volume for hydrogen	<ol> <li>Prepared by react Zn<sub>3</sub>As<sub>2</sub> and aqueou purified by vacuu no impurities det chromatography.</li> <li>H<sub>2</sub> &amp; N<sub>2</sub> : passed activated carbon molecular sieve.</li> </ol>	tion between as acid; am distillation. tected by through and through	
gas. The distribution constant, $K$ , was calculated from the James and Martin equation : V = V + rV	ESTIMATED ERROR:		
$v_R - v_g + Av_l$ where $V_R$ is the retention volume for arsine.	REFERENCES:		

COMPONENTS:

1. Arsine, AsH<sub>3</sub>; [7784-42-1]

2. Various liquids

ORIGINAL MEASUREMENTS:

Devyatykh, G.G.; Ezheleva, A.E.; Zorin, A.D.; Zueva, M.V.

Russ. J. Inorg. Chem. <u>1963</u>,8, 678-682.

EXPERIMENTAL VALUES:

temperature, were given.

If it is assumed that distribution constants vary with temperature according to equations of the form :

 $\ln K = (-\Delta H/RT) + A$ 

where K is the distribution constant for a temperature T,  $\Delta H$  is the heat of solution of arsine in the solvent and A is a constant for the solvent, then distribution constants at any temperature in the range 278.2 K to 323.2 K may be estimated from a value at 293.2 K and the corresponding value of the heat of solution. The equation for K may be written in the form:

 $\mathcal{K} = \exp \left[A + (B/T)\right]$ 

The following values of A and B have been calculated by the compiler:

Solvent	А	B/K
2-Furancarboxaldehyde	-3.430	1813
<pre>1,2-Benzenedicarboxylic acid, didecyl ester</pre>	-1.693	1511
Triethoxysilane	-6.980	2920
Silicic acid, tetraethyl ester	-4.551	2165
Silicone 702-DF	-4.434	2367
Silicone VKZh-94B	-6.351	2820

In the opinion of the compiler these distribution constants cannot be equated with Ostwald coefficients unless the assumption is made that equilibrium was established between gas and liquid phases under the conditions of the experiment.

In addition, possible adsorption of the arsine at the stationary phasecarrier gas interface may have lowered the accuracy of the results. Arsine Solubilities

COMPONENTS .	OBTOTNAL	VEACUDENTINES -	
COM CREATS.	ORIGINAL MEASUREMENTS:		
1. Arsine; AsH <sub>3</sub> ; [7784-42-1]	Corriez, P.; Berton, A.		
2. Various liquids.	Bull. Soc. Chim. France,		
	<u>1950</u> , 43-45.		
VARIABLES :	PREPARED	BY:	
		P. G. T.	Fogg
	L		
EXPERIMENTAL VALUES:			
Solvent	T/K	Bunson coefficient ¤	Mole fraction* <sup>x</sup> AsH (1 atm) 3
Huile de vaseline (liquid paraffin)	290.2	8	-
2-Propanone (acetone); C <sub>3</sub> H <sub>6</sub> O; [67-64-1]	298.2	9.3	0.030
Tetrahydronaphthalene (tetralin). C <sub>10</sub> H <sub>22</sub> ; [119-64-2]	298.2	10	0.062
2-Aminoethanol (monoethanolamine); C <sub>2</sub> H <sub>7</sub> NO; [141-43-5]	285.2	1.75	0.0047
2,2',2"-Nitrilotris-ethanol (triethanolamine); C <sub>6</sub> H <sub>15</sub> NO <sub>3</sub> ; [102-71-6]	285.2	0.8	0.0047
$1 \text{ atm} = 1.015 \times 10^5 \text{ Pascal}$			
* Calculated by the compiler using th	o doncit	w of argino g	iven in ref (1)
and the densities of solvents given	in ref.	(2)	1000 IN 101. (1)
AUXILIARY	INFORMATI	ON	
METHOD /APPARATUS / PROCEDURE:	SOURCE AN	D PURITY OF MATE	RIALS:
The initial volume of gag was	2 700	tono was lour	ol grado
measured over mercury in a gas	Tet	ralin, monoet	hanolamine, and
burette at the barometric pressure.	tri	lethanolamine	were 'technical'
1  atm by the relation PV = RT. Gas	910	lues.	
was passed into an absorption pipette			
The final volume of gas was measured			
at the barometric pressure, p <sub>total</sub> .	1		
p <sub>AsH</sub> was taken to be p <sub>total</sub> minus			
the vapor pressure of the pure	ESTIMATEI	D ERROR:	
solvent. The final volume of gas was adjusted from part to latm and 0°C.			
The Bunsen absorption coefficient. «.			
was the difference between the	DEPENDING		
initial and final adjusted volumes divided by the volume of solvent.	REFERENCI	S:	-1
	I. Mell on I	or, J.W.Compr norganic & Th	enensive Treatise eoretical
	Chem	istry, Vol. I	X, Longmans,
	2. Timm	ermans, J., P	hysico-Chemical
	Cons	tants of Pure	Organic Compounds
	VOI.	2, LISEVIEL,	Amsteruam, 1903.

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COMPONENTS:	ORIGINAL MEASUREMENTS:		
l. Arsine; AsH <sub>3</sub> ; [7784-42-1]	Corriez, P.; Berton, A. Bull. Soc. Chim. France 1950, 43-45		
2. Chlorinated alkanes.	1		
VARIABLES:	PREPARED B	Y:	
		••	
		P. G. T. Fo	odâ
EXPERIMENTAL VALUES:			
		_	
	m /1/	Bunsen	Mole fraction*
Solvent	Т/К	COEILICTEUL	<sup>x</sup> AsH <sub>3</sub> (1 atm)
			5
Dichloromethane; CH <sub>2</sub> Cl <sub>2</sub> ; [75-09-2]	298.2	10.7	0.0300
Trichloromethane, (Chloroform);	298.2	10.9	0.0379
CHCl <sub>3</sub> ; [67-66-3]			i
Tetrachloromethane, (carbon	298.2	11.7	0.0485
tetrachloride); $CCl_{4}$ ; [56-23-5]	-		
1.2-Dichloroethane; C_H_Cl_;	298.2	8.8	0.0304
[107-06-2]			
1.1.2.2-Tetrachloroethane; C <sub>a</sub> H <sub>a</sub> Cl <sub>4</sub> ;	298.2	9.7	0.0440
[79-34-5]			
1.2-Dichloroethene; C.H.Cl.;	298.2	12.3	0.0404
[540-59-0]			
Trichloroethene: C_HCl.: [79-0]-6]	298.2	12.5	0.0482
1110110101010101010, 02 <sup>2101</sup> 3, (11 01 0)			0.0402
Tetrachloroethene; C <sub>2</sub> Cl <sub>4</sub> ; [127-18-4]	298.2	11.2	0.0490

\* Calculated by compiler using the density of arsine given in ref. (1) and the densities of solvents given in refs. (2), (3) and (4).