Stibine Solubilities

COMPONENTS:	EVALUATOR:
l. Stibine; SbH3; [7803-52-3] 2. Organic liquids	P. G. T. Fogg, School of Chemistry, Polytechnic of North London, Holloway, London, N7 8DB, UNITED KINGDOM.
	August 1983

CRITICAL EVALUATION:

Distribution constants for systems consisting of the gas and eight different liquids have been measured by Devyatykh *et al.* (1) using a chromatographic technique. (See comments under arsine evaluation and on compiled tables.) It is, however, unwise to equate these constants with Ostwald coefficients in order to calculate solubilities for a particular partial pressure of gas. Analogy with measurements on phosphine reported by these authors makes it likely that such estimates could be several hundred per cent too large. The data may perhaps be used to estimate relative solubilities of stibine in different solvents but such estimates are unlikely to be very precise.

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).

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COMPONENTS:	ORIGINAL MEASUREMENTS:			
 Stibine; SbH₃; [7803-52-3] Various liquids 	Devyatykh, G.G.; Ezheleva, A.E.; Zorin, A.D.; Zueva, M.V.			
	Russ. J. Inorg. Chem. <u>1963</u> ,8, 678-682			
VARIABLES:	PREPARED BY:			
Temperature	P.G.T. Fogg			
EXPERIMENTAL VALUES:				
Solvent Dist vo	ribution constant Heat of solution SbH ₃ solvent /kcal mol ⁻¹			
2-Furancarboxaldehyde; C ₅ H ₄ O ₂ ; [98-01-1]	25.2 -4.1			
Triethoxysilane; C ₆ H ₁₆ O ₃ Si; [998-30-1]	39.8 -6.0			
Silicic acid, tetraethyl ester; C ₈ H ₂₀ O ₄ Si; [78-10-4]	28.5 - 5.4			
Silicone VKZh-94B	58.8 - 6.2			
Temperature = 293.2 K.				
Distribution constants were measured between 278.2 K and 323.2 K. The partial pressures of stibine at which these measurements were made were not stated. The total pressure of stibine 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 temperature, were given.				
If it is assumed that distribution constants vary with temperature accord- ing to equations of the form :				
AUXILIARY	INFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS;			
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 ₁ , 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 _g , was equated with the retention volume for hydroge	 Prepared from SbCl₃ and aqueous sodium tetrahydroborate; purified by vacuum distillation; chromatographic analysis indicated about 5% H₂. H₂ & N₂: passed through activated carbon and through molecular sieve. 			
en gas. The distribution constant, K, was calculated from the James and Martin equation:	ESTIMATED ERROR:			
$V_{\rm R} = V_{\rm cr} + KV_{\rm L}$	DEFEDENCYC.			
where V_R is the retention volume for stibine.	REFERENCES:			

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COMPONENTS: ORIGINAL MEASUREMENTS: 1. Stibine; SbH₃; [7803-52-3] Devyatykh, G.G.; Ezheleva, A.E.; Zorin, A.D.; Zueva, M.V. 2. Various liquids. Russ. J. Inorg. Chem. 1963,8, 678-682. EXPERIMENTAL VALUES: $\ln K = (-\Delta H/RT) + A$ where K is the distribution constant for a temperature T, ΔH is the heat of solution 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 correspond-ing 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 Α B/K 2-Furancarboxaldehyde -3.8142064 Triethoxysilane -6.620 3021 Silicic acid, tetraethyl ester -5.924 2719 Silicone VKZh-94B -6.573 3122 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 stibine at the stationary phasecarrier gas interface may have lowered the accuracy of the results.

COMPONENTS:	ORIGINAL M	EASUREMENTS:		
1. Stibine; SbH ₃ ; [7803-52-3]	Devyaty	kh, G. G.; Ezhe	leva, A. E.;	
2. Various liquids	Zorin,	Zorin, A. D.; Zueva, M. V.		
-	Russ. J	Russ. J. Inorg. Chem.		
	<u>1963</u> , 8	, 678-682.		
VARIABLES:	PREPARED B	Y:		
Temperature		P. G. T. Fogg		
EXPERIMENTAL VALUES:		Distribution	Nost of	
Solvent	P _{SbH} ,/mmHg	constant volge	solution_	
		/vol	/kcal mol '	
		solvent		
2-Ethoxyethanol; C ₄ H ₁₀ O ₂ ; [110-80-5]	0.3	40.7	-1.2	
l,l'-oxybis[2-chloroethane]; C ₄ H ₈ Cl ₂ O; [lll-44-4]	0.2	28.9	-3.5	
Nitrobenzene; C ₆ H ₅ NO ₂ ; [98-95-3]	0.2	22.9	-1.82	
Liquid paraffin	0.3	39.7	-	
Temperature = 293.2 K. 760 mm	Hg = 1 atm =		<u></u>	
Distribution constants were measur	ed between 2	78.2 K and 323.2	K with a	
total pressure of stibine and carr	ier gas of a	bout 760 mmHg.	Distribu-	
said to have been calculated from with temperature, were given. If constants vary with temperature ac	the variatio it is assum cording to e	e only but heats n of distributio ed that distributions of the	of solution, on constants ition form:	
$\ln K = (-\Delta H/R)$	T) + A			
where K is the distribution consta	nt for a tem	perature T, AH i	s the heat	

(cont.)

AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
A chromatographic method was used. Temperatures were controlled to ±0.5 K. The support phase consisted of Nichrome spirals. The carrier	1. Prepared from SbCl ₃ and aqueous sodium tetrahydroborate; puri- fied by vacuum distillation; chromatographic analysis indi- cated about 5% H ₂ .			
gas was either nitrogen or hydrogen. The volume, V_{ℓ} , of the liquid phase was calculated from the weight of the column before and after filling	H ₂ and N ₂ : passed through activated carbon and through mole- cular sieve.			
with liquid and allowing to drain.	ESTIMATED ERROR:			
The free volume, V _g , was equated with the retention volume for hydrogen				
gas. The distribution constant, K,	DEDEDRIVOUS			
was calculated from the James and	REFERENCES:			
Martin equation:				
$v_{R} = v_{g} + \kappa v_{k}$				
where V_{R} is the retention volume for				
stibine.				

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<pre>l. Stibine; SbH₃;</pre>	[7803-52-3]	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.

EXPERIMENTAL VALUES:

of solution of stibine 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	А	В/К
2-Ethoxyethanol	1.645	604
1,1'-oxybis[2-chloroethane]	-2.647	1762
Nitrobenzene	0.006	916

In the opinion of the compiler these distribution constants can not 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 stibine at the stationary phasecarrier gas interface may have lowered the accuracy of the results.