Phosphine Solubilities

COMPONENTS:	EVALUATOR:
l. Phosphine; PH ₃ ; [7803-51-2] 2. Organic liquids.	P. G. T. Fogg, School of Chemistry, Polytechnic of North London, Holloway, London N7 8DB United Kingdom. August 1983

CRITICAL EVALUATION:

Data obtained by Palmer $et \ al$ (1) and by Devyatykh $et \ al$ (2) have been discussed in detail by Gerrard (3). Mole fraction solubilities calculated from measurements by Palmer $et \ al$. fall into a consistent pattern with a lower solubility in hydrogen bonded solvents compared with other solvents. There is also an increase in mole fraction solubility with increase in chain length in the case of straight chain alkanes. Solubilities are in the order:

in benzene < in cyclohexene < in cyclohexane

and

in benzene < in toluene < in xylene.

The variation of solubility in nitrobenzene, with change in temperature, was measured by both Palmer *et al.* and by Devyatykh *et al.* The ratio $vol_{PH_3}/vol_{solvent}$ for a temperature of 295.2 K has been estimated by

the compiler from data given by Devyatykh *et al*. to be 8.4. This may be compared with the value of 3.06 given by Palmer *et al*. for a pressure of 1 atm. There is a similar discrepancy between the solubility in liquid paraffin calculated from the data of Devyatykh *et al* and that measured by Palmer.

There is also a marked difference between the solubility of phosphine in didecyl phthalate calculated from data given by Devyatykh and that in dibutyl phthalate measured by Palmer. Expressed as $vol._{PH_3}/vol._{solvent}$

at 295.7 K the former gives 22.2 and the latter 3.23. If it could be assumed that Devyatykh's data could be extrapolated to a partial pressure of phosphine of 1 atm, the corresponding mole fraction solubility at 295.7 K for didecyl phthalate would be about 0.3 compared with the value of 0.0342 given by Palmer for dibutyl phthalate at this temperature.

Solubilities measured with conventional apparatus by Palmer *et al.* are likely to be reliable. Solubilities for a partial pressure of 1 atm calculated from distribution constants determined by gas chromatography by Devyatykh *et al.* are likely to be unreliable. They may, perhaps, be used to estimate relative solubilities in the solvents which were studied but such estimates may not be precise.

The solubility in cyclohexanol at 299.2 K was measured by Cauquil (4) using very simple apparatus. The mole fraction solubility at a partial pressure of 1 atm, calculated from the Ostwald coefficient reported by this author, is close to values for other polar solvents reported by Palmer *et al*. The value for cyclohexanol may therefore be accepted as a tentative value in the absence of other data for this solvent.

The solubility in trifluoroacetic acid was measured by Fujioka and Cady (5) who also used very simple apparatus. They calculated the Ostwald coefficient to be 15.9 from measurements at 653 mmHg and 299.2 K. This corresponds to a mole fraction solubility of 0.040 at this pressure and about 0.046 at 760 mmHg. These measurements are in sharp contrast to those of Palmer *et al.* who reported an Ostwald coefficient of 2.46 at 760 mmHg and 293.2 K for 95.3% trifluoroacetic acid and a value of 2.64 at 760 mmHg and 294.7 K for a 96.8% sample. Unfortunately the purity of the acid used by Fujioka and Cady was not stated and direct comparison of the two sets of work may not be justified.

(cont.)

COMPON	IENTS:	EVALUATOR:
1.	Phosphine; PH ₃ ; [7803-51-2]	P. G. T. Fogg, School of Chemistry, Polytechnic of North London,
2.	Organic liquids.	Holloway, London N7 8DB United Kingdom.
		August 1983
CRITIC	AL EVALUATION:	
Ref	erences:	
1.	Palmer, M. G.; Lessels, R.W.M.;	; Childs, A. F.; McCoubrey, J. C.
	Albright & Wilson (Mfg.) Ltd., T	Fechnical Note No. 60, <u>1963</u> .
	(Quoted by Gerrard, w. Gas Sound Borgsmon Bress, Oxford, 1980.)	bilities – Widespread Applications,
	Pergamon riess, oxiora, <u>1900</u> ,	
2.	Devyatykh, G. G.; Ezheleva, A.	E.; Zorin, A. D.; Zueva, M. V.
	Zh. Neorgan. Khim. <u>1963</u> , 8, 1307	7.
	(Russ. J. Inorg. Chem. <u>2003</u> , 0,	678.)
3.	Gerrard, W.	
	Solubility of Gases in Liquids, Plenum Press, New York, <u>1976</u> .	
4.	Cauquil, G.	
	J. Chim. Phys. Phys. chim. Divi.	. <u>1927</u> , 24, 53.
5.	Fujioka, G.S.; Cady, G.H.	
	J. Amer. Chem. Soc. <u>1957</u> , 79, 2451.	
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COMPONENTS: 1. Phosphine; PH ₃ ; 2. Alkanes	[7803-51-2]	ORIGINAL MEASUREMENT Palmer, M. G.; Childs, A. F.; Albright & Wilso Technical Note N Quoted by Gerrar bilities - Wides 1980, Pergamon P	S: Lessels, R. W. M.; McCoubrey, J. C. n (Mfg.) Ltd., 'o. 60, <u>1963</u> . cd, W., "Gas Solu- pread Applications", rress, Oxford.
VARIABLES:		PREPARED BY: P. G	. T. Fogg
EXPERIMENTAL VALUES:			
Solvent	т/к	Mole fraction $x_{\rm PH_3}$ (1 atm)	Ostwald Coefficient, L
Pentane; C_5H_{12} ; [109-66-0]	294.65	0.0200	4.33
Hexane; C_6H_{14} ; [110-54-3]	294.65	0.0354	6.79
Heptane; C ₇ H ₁₆ ; [142-82-5]	294.65	0.0413	7.12
2,2,4-Trimethylpenta C ₈ H ₁₈ ; [540-84-1	ne; 294.4]	0.0400	6.19
Decane; $C_{10}H_{22}$; [124-18-5]	294.05	0.0432	5.73
Dodecane; C ₁₂ H ₂₆ ; [112-40-3]	293.15	0.0469	5.35
Measurements were pressure (unspec a partial pressu Henry's law.	e made at a tota ified) and solub re of phosphine (l pressure equal t ility values were of 101.325 kPa (l	o barometric adjusted to atm) using
	AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE	:	SOURCE AND PURITY OF	MATERIALS:
Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re-		 Prepared from phosphorus an acid; contai as impurity; H₃PO₄ and wit C₅H₁₂; C₆H₁₄ pure material Petroleum Ltd technical gra by distillati 	<pre>a zinc amalgam; ad dilute phosphoric .ned 2.5% hydrogen dried with conc. ch P₂O₅. ; C₇H₁₆; C₈H₁₈: .s supplied by Esso l; C₁₀H₂₂; C₁₂H₂₆: ade samples purified .on.</pre>
peated several times value of the solubil: The apparatus was shi draughts and measured room temperature.	and the mean ity was taken. ielded from ments made at	ESTIMATED ERROR:	
In calculating the set the gas, account was a partial vapor pressure solvent and the part of hydrogen present a in the phosphine.	olubility of taken of the re of the ial pressure as an impurity	REFERENCES :	

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COMPONENTS: 1. Phosphine; PH ₃ ; [7803-51-2] 2. 2,6-Dimethyl-2-heptane; C ₉ H ₁₈ ; [5557-98-2] VARIABLES:	ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, 1963. Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", 1980, Pergamon Press, Oxford. PREPARED BY:	
	P. G. T. Fogg	
EXPERIMENTAL VALUES:		
T/K Ostwald Coefficient, L		
293.65 5.87		
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (l atm) using Henry's law.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re-	 Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H₃PO₄ and with P₂O₅. G.P.R. grade, distilled under reduced pressure (ca. 17 mmHg), to remove dissolved gases. 	
peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts and measurements made at room temperature.	ESTIMATED ERROR:	
In calculating the solubility of the gas, account was taken of the partial vapor pressure of the solvent and the partial pressure of hydrogen present as an impurity in the phosphine.	REFERENCES:	

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COMPONENTS: 1. Phosphine; PH ₃ ; [7803-51-2] 2. Alicyclic compounds	ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, 1963. Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", 1980, Pergamon Press, Oxford.
VARIABLES:	PREPARED BY:
	P. G. T. Fogg
EXPERIMENTAL VALUES:	
Solvent	T/K Mole Ostwald T/K fraction Coefficient, x^{PH_3} (1 atm) L
Cyclohexene; $C_{6}H_{10}$; [110-83-8]	294.15 0.0280 6.85
Cyclobevane: CcHup: [110-82-7]	291.65 0.0326 7.47
Undegaflyoro(triflyoromethyl) =	
cyclohexane; $C_7F_{1,k}$; [355-02-2]	2)4.90 T.9T
1,2,3,4-Tetrahydronaphthalene; $C_{10}H_{12}$; [119-64-2]	295.25 0.0291 5.34
2,6,6-Trimethylbicyclo[3.1.1]- hept-2-ene,(α-pinene); C ₁₀ H ₁₆ ; [80-56-8]	292.65 19.5
Decahydronaphthalene; C ₁₀ H ₁₈ ; [91-17-8]	295.35 0.0316 5.05
a partial pressure of phosphine Henry's law.	of 101.325 kPa (1 atm) using
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re- peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts and measurements made at room temperature. In calculating the solubility of	 Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H₃PO₄ and with P₂O₅. Cyclohexene Technical grade, purified by dis- tillation. Other solvents "Analar" or G.P.R. grade, dis- tilled under reduced pressure (ca. 17 mmHg) to remove dis- solved gases. ESTIMATED ERROR:
the gas, account was takin of the partial vapor pressure of the solvent and the partial pressure of hydrogen present as an impurity in the phosphine.	

COMPONENTS: 1. Phosphine; PH ₃ ; [7803-51-2] 2. Aromatic compounds	ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, 1963. Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", <u>1980</u> , Pergamon Press, Oxford.	
VARIABLES:	PREPARED BY: P. G. T. Fogg	
EXPERIMENTAL VALUES:		
Solvent	Mole fraction Ostwald T/K x_{PH_3} (1 atm) Coefficient, L	
<pre>Benzene; C₆H₆; [71-43-2] Benzenamine; C₆H₇N; [62-53-3] Dimethylbenzene; C₈H₁₀; [1330-20-7] (1-Methylethyl)benzene; C₉H₁₂; [98-82-8] 1,2-Benzenedicarboxylic acid, dibutyl ester; C₁₆H₂₂O₄;</pre>	295.15 0.0260 7.26 295.15 0.0105 2.80 294.65 0.0320 6.52 294.65 0.0316 5.68 295.65 0.0342 3.23	
<pre>[119-64-2] Hexafluorobenzene 98.5%; C6F6; [392-56-3]</pre>	295.4 4.36	
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (1 atm) using Henry's law.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE: Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re- peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts and measurements made at room temperature. In calculating the solubility of the gas, account was taken of the partial vapor pressure of the solvent and the partial pressure of hydrogen present as an impurity in the phosphine.	<pre>SOURCE AND PURITY OF MATERIALS: 1. Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H₃PO₄ and with P₂O₅. 2. C₆H₆; C₆H₇N; C₈H₁₀: "Analar" or G.P.R. grade; distilled under re- duced pressure (ca. 17 mmHg) to remove dissolved gases; C₃H₁₂; C₁₆H₂₂O₄: technical grade, puri- fied by distillation. ESTIMATED ERROR: REFERENCES:</pre>	

COMPONENTS: 1. Phosphine; PH ₃ ; [7803-51-2] 2. Methylbenzene; C ₇ H ₈ ; [108-88-3] VARIABLES:	ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, 1963. Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", 1980, Pergamon Press, Oxford. PREPARED BY: P. G. T. Fogg		
T/K Mole fraction $x_{\rm PH_3}$ (1 atm)	Ostwald Coefficient, L		
293.85 0.0290 295.15 0.0304 313.4 0.0194 334.95 0.0129	- 7.15 -		
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (1 atm) using Henry's law.			
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE: Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re- peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts for measurements at room temperature (293.85 K). Tempera- tures were thermostatically control- led for other measurements. In calculating the solubility of the gas, account was taken of the partial vapor pressure of the solvent and the partial pressure of hydrogen present as an impurity in the phosphine.	SOURCE AND PURITY OF MATERIALS: 1. Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H ₃ PO ₄ and with P ₂ O ₅ . ESTIMATED ERROR: REFERENCES:		

COMPONENTS:	ORIGINAL MEASUREMENTS:	
1. Phosphine; PH3; [7803-51-2]	Cauquil, G.	
2. Cyclohexanol; C ₆ H ₁₂ O; [108-93-0]	J. Chim. Phys. Phys. Chim. Biol. <u>1927</u> , 24, 53 - 55.	
VARIABLES:	PREPARED BY: P. G. T. Fogg	
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·	
T/K P _{PH3} /mmHg Co	Ostwald Mole fraction* Defficient, x_{PH_3} (1 atm.)	
299.2 766	2.856 0.01226	
760 mmHg = 1 atm = 1.013×10^5 Pa. * Value of $x_{\rm PH_3}$ (1 atm) has been calculated by the compiler using densities of cyclohexanol at 293.2 K and 303.2 K given in refs. (1) and (2), respectively, and values of van der Waals constants for phosphine given in ref. (1).		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
A measured volume of cyclohexanol was put into contact with a measured volume of phosphine in a graduated tube over mercury. The final volume of gas and the temperature and pressure were measured when equilibrium had been reached. The author considered	2. All dissolved air was removed by boiling; b.p. 334.1 K (766 mmHg).	
that no allowance for the vapor	ESTIMATED ERROR:	
pressure of cyclohexanol at the		
temperature of measurement was		
necessary.	 REFERENCES: 1. Handbook of Chemistry and Physics, (61st edition), C.R.C. Press, Cleveland, Ohio, <u>1980</u>. 2. Timmermans, J. Physico-Chemical Constants of Pure Organic Com- pounds, Vol. II, Elsevier, London, <u>1965</u>. 	

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COMPONENTS: 1. Phosphine; PH ₃ ; [7803-51-2] 2. Petroleum ethers and liquid paraffin	ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, 1963. Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", 1980, Pergamon Press, Oxford.	
VARIABLES:	PREPARED BY:	
	P. G. T. Fogg	
EXPERIMENTAL VALUES:		
Solvent T/K	Ostwald Coefficient, L	
Liquid paraffin 292.35 40/60 Petroleum ether 292.15 60/80 " " 292.15 80/100 " " 296.15 100/120 " " 295.65 120/160 " " 293.9	4.86 4.36 8.02 6.42 6.15 6.14	
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (1 atm) using Henry's law.		
AUXILIARY	INFORMATION	
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS.	
Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re- peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts and measurements made at room temperature.	 Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H₃PO₄ and with P₂O₅. Solvents were "Analar" or G.P.R. grade; distilled under reduced pressure (ca. 17 mmHg) to remove dissolved gases. ESTIMATED ERROR: 	
In calculating the solubility of the gas, account was taken of the partial vapor pressure of the sol- vent and the partial pressure of hydrogen present as an impurity in the phosphine.	REFERENCES :	

<pre>COMPONENTS: 1. Phosphine; PH₃; [7803-51-2] 2. Aliphatic compounds containing</pre>	ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, <u>1963</u> . Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", <u>1980</u> , Pergamon Press, Oxford. PREPARED BY: P. G. T. Fogg	
Solvent	Mole fraction Ostwald T/K x_{PH_3} (1 atm) Coefficient, L	
Trifluoroacetic acid 95.3%; C ₂ HF ₃ O; [76-05-1]	293.15 2.46	
Trifluoroacetic acid 96.8%; C ₂ HF ₃ O; [76-05-1]	294.65 2.64	
Acetic acid; C ₂ H ₄ O ₂ ; [64-19-7]	294.15 0.0075 3.19	
1,2-Ethanediol; C ₂ H ₆ O ₂ ; [107-21-1]	292.35 0.0033 1.45	
2-Propanone; C ₃ H ₆ O; [67-64-1]	295.55 0.0132 4.45	
1,2-Epoxypropene [*] ; C ₃ H ₆ O; [75-56-9]	295.95 0.0088 3.06	
Nitropropane [*] ; C ₃ H ₇ NO ₂ ; [25322-01-4]	294.4 0.0157 4.26	
3-oxo-butanoic acid, ethyl ester [‡] ; C ₆ H ₁₀ O ₃ ; [141-97-9]	294.95 0.0114 2.23	
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (1 atm) using Henry's law.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re- peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts and measurements made at room temperature. In calculating the solubility of the gas, account was taken of the partial vapor pressure of the solvent and the partial pressure of budregen present	 Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H₃PO₄ and with P₂O₅. Compounds marked with * were technical grade and purified by distillation. Other solvents were "Analar" or G.P.R. grade distilled under reduced pressure (ca. 17 mmHg) to remove dissolved ESTIMATED ERROR: gases. 	
in the phosphine.		

<pre>COMPONENTS: 1. Phosphine; PH₃; [7803-51-2] 2. Tetrahydrofuran; C₄H₈O; [109-99-9]</pre>	<pre>ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, <u>1963</u>. Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", <u>1980</u>, Pergamon Press, Oxford.</pre>	
VARIABLES:	PREPARED BY:	
	P. G. T. Fogg	
EXPERIMENTAL VALUES:		
T/K Mole fraction ^x PH ₃ (1 atm)	Ostwald Coefficient, L	
295.15 0.0245	7.49	
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (1 atm) using Henry's law.		
AUXILIARY		
METHOD/APPARATUS/PROCEDURE: Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re- peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts and measurements made at room temperature. In calculating the solubility of the gas, account was taken of the partial vapor pressure of the solvent and the partial pressure of hydrogen present as an impurity in the phosphine.	<pre>SOURCE AND PURITY OF MATERIALS: 1. Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H₃PO₄ and with P₂O₅. 2. "Analar" or G.P.R. grade, distilled under reduced pressure (ca. 17 mmHg) to remove dis- solved gases. ESTIMATED ERROR: REFERENCES: REFERENCES:</pre>	

COMPONENTS: 1. Phosphine; PH ₃ ; [7803-51-2] 2. Nitrobenzene: CoHaNOa:	ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, 1963.	
[98-95-3]	Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", 1980, Pergamon Press, Oxford.	
VARIABLES:	PREPARED BY: P. G. T. Fogg	
EXPERIMENTAL VALUES:		
T/K Mole fraction $x_{\rm PH_3}$ (1 atm)	Ostwald Coefficient, L	
293.65 0.0139 295.65 0.0127 313.25 0.0100	- 3.06 -	
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (1 atm) using Henry's law.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE: Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re-	SOURCE AND PURITY OF MATERIALS: 1. Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H ₃ PO ₄ and with P ₂ O ₅ .	
peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts for measurements at room temperature (293.65 K). Tempera- tures were thermostatically con- trolled for other measurements.	ESTIMATED ERROR: REFERENCES:	
In calculating the solubility of the gas, account was taken of the partial vapor pressure of the solvent and the partial pressure of hydrogen present as an impurity in the phosphine.		

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<pre>COMPONENTS: 1. Phosphine; PH₃; [7803-51-2] 2. Dinonylamine, (N-nonyl-1-nonan- amine); C₁₀H₃₉N; [2044-21-5] VARIABLES:</pre>	ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, 1963. Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications" <u>1980</u> , Pergamon Press, Oxford. PREPARED BY: P. G. T. Fogg		
EXPERIMENTAL VALUES:			
Mole fractio T/K ^x PH ₃ (l at	n Ostwald Coefficient, m) L		
294.4 0.0593	4.55		
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (1 atm) using Henry's law.			
AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE: Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re- peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts and measurements made at room temperature. In calculating the solubility of the gas, account was taken of the partial vapor pressure of the solvent and the partial pressure of hydrogen present as an impurity in the phosphine.	<pre>SOURCE AND PURITY OF MATERIALS: 1. Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H₃PO₄ and with P₂O₅. 2. Technical grade purified by distillation. ESTIMATED ERROR: REFERENCES: REFERENCES:</pre>		

294 Phosphine Solubilities			
<pre>COMPONENTS: 1. Phosphine; PH₃; [2. Tetrachloromethane; [56-23-5] or 1,2-Dichloroethane; [107-06-2] VARIABLES:</pre>	7803-51-2] CCl₄; C2H₄Cl2;	ORIGINAL MEASUREME Palmer, M. G.; Childs, A. F.; Albright & Wil Technical Note Quoted by Gerr bilities - Wid <u>1980</u> , Pergamon PREPARED BY:	NTS: Lessels, R. W. M.; McCoubrey, J. C. son (Mfg.) Ltd., No. 60, <u>1963</u> . ard, W., "Gas Solu- espread Applications" Press, Oxford. P. G. T. Fogg
EXPERIMENTAL VALUES:			
Solvent	т/к	Mole fraction $x_{\rm PH_3}$ (1 atm)	Ostwald Coefficient, L
Tetrachloromethane	293.65	0.0165	4.19
1,2-Dichloroethane	294.4	0.0176	5.48
pressure (unspeci a partial pressure Henry's law.	of phosphine o	of 101.325 kPa (e adjusted to L atm) using
	AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:		SOURCE AND PURITY	OF MATERIALS:
Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re- peated several times and the mean value of the solubility was taken. The apparatus was shielded from draughts and measurements made at room temperature. In calculating the solubility of		 Prepared fi phosphorus acid; cont as impurity H₃PO₄ and v Solvents we grade; dis pressure (c dissolved c ESTIMATED ERROR: 	com zinc amalgam, and dilute phosphoric cained 2.5% hydrogen 7; dried with conc. with P ₂ O ₅ . ere "Analar" or G.P.R. stilled under reduced ca. 17 mmHg) to remove gases.
solvent and the partial hydrogen present as an the phosphine.	e of the ll pressure of impurity in		

COMPONENTS: 1. Phosphine; PH ₃ ; [7803-51-2] 2. Carbon disulfide; CS ₂ ; [75-15-0]	ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, 1963. Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", 1980, Pergamon Press, Oxford.		
VARIABLES:	PREPARED BY: P. G. T. Fogg		
EXPERIMENTAL VALUES:	L		
T/K Mole fraction x_{PH_3} (l atm)	Ostwald Coefficient, L		
294.15 0.0250	10.25		
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (1 atm) using Henry's law.			
AUXILIARY	INFORMATION		
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:		
Gas saturated with solvent vapor was passed into a glass absorption vessel connected to a gas burette. A measured volume of liquid was introduced into the vessel and stirred with a magnetic stirrer. A measured volume of gas was added from a gas burette to restore the total pressure in the absorption vessel to its original value which was apparently equal to barometric pressure. The procedure was re- peated several times and the mean	 Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H₃PO₄ and with P₂O₅. No details given. 		
value of the solubility was taken. The apparatus was shielded from draughts and measurements made at room temperature.			
In calculating the solubility of the gas, account was taken of the partial vapor pressure of the solvent and the partial pressure of hydrogen present as an impurity in the phosphine.	REFERENCES :		

COMPONENTS :	ORIGINAL MEASUREMENTS:	
 Phosphine; PH₃; [7803-51-2] Various Liquids. 	Devyatykh, G.G.; Ezheleva, A.E.; Zorin, A.D.; Zueva, M.V. <i>Russ. J. Inorg. Chem.</i> <u>1963</u> ,8, 678-682.	
VARIABLES: Temperature	PREPARED BY: P.G.T. Fogg.	
EXPERIMENTAL VALUES:		
Solvent Distribution constant Heat of solution vol _{PH3} /vol _{solvent} /kcal mol ⁻¹		
2-Furancarboxaldehyde, C ₅ H ₄ O ₂ ; [98-01-1]	11.8 -3.4	
<pre>l,2-Benzenedicarboxylic acid, didecyl ester, C₂₈H₄₆O₄; [84-77-5]</pre>	23.5 -4.0	
Triethoxysilane, C ₆ H ₁₆ O ₃ Si; [998-30-1]	12.2 -5.4	
Silicic acid, tetraethyl ester, $C_{0}H_{20}O_{4}Si$; [78-10-4]	12.45 -5.0	
Silicone 702-DF	15.3 -3.6	
Silicone VKZh-94B	25.3 -6.0	
Temperature = 293.2 K.		
Distribution constants were measured between 278.2 K and 323.2 K. The partial pressures of phosphine at which these measurements were made were not stated. The total pressure of phosphine and carrier gas was about 760 mmHg. in each case. Distribution constants were reported at one		
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 hydrog-	 Prepared from phosphorus and aqueous alkali; purified by vacuum distillation; no impurities detected by chromatography. 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:	
$v_{R} = v_{g} + \kappa v_{l}$		
where V_R is the retention volume for phosphine.	REFERENCES:	

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Phosphine; PH ₃ ; [7803-51-2]	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:

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 :

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

where K is the distribution constant for a temperature T, ΔH is the heat of solution of phosphine 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	B/K
2-Furancarboxaldehyde	-3.371	1712
<pre>1,2-Benzenedicarboxylic acid, didecyl ester</pre>	-3.712	2014
Triethoxysilane	-6.772	2719
Silicic acid, tetraethyl ester	-6.065	2518
Silicone 702-DF	-3.455	1813
Silicone VKZh-94B	-7.073	3021

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 phosphine at the stationary phasecarrier gas interface may have lowered the accuracy of the results.

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COMPONENTS:		ORIGINAL MEASUREMENTS .	
1. Phosphine; PH ₃ ; [7803-51-2]		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, pressur	e	P.G.T. Fogg	J•
EXPERIMENTAL VALUES:			
Solvent	Pressure range /mmHg	Distribution constant vol _{PH3} /vol _{solvent}	Heat of solution /kcal mol ⁻¹
2-Ethoxyethanol, C ₄ H ₁₀ O ₂ ; [110-80-5]	0.3-25.0	9.4	-0.95
l,l'-oxybis [2-chloro- ethane]; C,HgCl20; [111-44-4]	0.05-19.0	20.0	-2.2
Nitrobenzene, C ₆ H ₅ NO ₂ ; [98-95-3]	0.02-18.0	8.59	-1.56
Liquid paraffin	0.1 -43.0	15.9	-3.0
Silicone PFMS-4F	0.03-23.0	16.5	-2.3
Temperature = 293.2K 760 mmHg = 1 atm = 1.013×10^5 Pa.			
Distribution constants were measured between 278.2 K and 323.2 K over a range of partial pressures of phosphine 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 :			
	AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:		SOURCE AND PURITY OF MATERIA	LS:
A chromatographic method wa Temperatures were controlle \pm 0.5 K. The support phase of Nichrome spirals. The c gas was either nitrogen or The volume, V ₁ , of the liqu was calculated from the wei column before and after fil liquid and allowing to drai free volume, V _g , was equate	s used. d to consisted arrier hydrogen. id phase ght of the ling with n. The d with the	 Prepared from phosy aqueous alkali; pur vacuum distillation impurities detected ography. H₂ and N₂: passed th ed carbon and throw sieve. 	phorus and rified by 1; no 1 by chromat- 1rough activat- 1gh molecular
retention volume for hydrog The distribution constant, calculated from the James a equation.	en gas. K, was nd Martin	ESTIMATED ERROR:	
$V_{R} = V_{g} + KV_{l}$			
where V_R is the retention v phosphine.	olume for	REFERENCES:	

COM	IPONENTS:	ORIGINAL MEASUREMENTS:
1. 2.	Phosphine; PH₃; [7803-51-2] Various liquids.	Devyatykh, G.G.; Ezheleva, A.E. Zorin, A.D.; Zueva, M.V.
1		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, ΔH is the heat of solution of phosphine 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 293.2K and the corresponding value of the heat of solution. The equation for K may be written in the form:

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

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

Solvent	A	В/К
2-Ethoxyethanol	0.609	478
1,1'-oxybis [2-chloroethane]	-0.782	1108
Nitrobenzene	-0.528	785
Liquid paraffin	-2.386	1511
Silicone PFMS-4F	-1.147	1158

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 phosphine at the stationary phasecarrier gas interface may have lowered the accurary of the results.

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ORIGINAL MEASUREMENTS: Palmer, M. G.; Lessels, R. W. M.; Childs, A. F.; McCoubrey, J. C. Albright & Wilson (Mfg.) Ltd., Technical Note No. 60, 1963. Quoted by Gerrard, W., "Gas Solu- bilities - Widespread Applications", 1980, Pergamon Press, Oxford. PREPARED BY: P. G. T. Fogg			
of P ₄ Coefficient,			
11.31 6.25			
Measurements were made at a total pressure equal to barometric pressure (unspecified) and solubility values were adjusted to a partial pressure of phosphine of 101.325 kPa (l atm) using Henry's law.			
INFORMATION			
SOURCE AND PURITY OF MATERIALS: 1. Prepared from zinc amalgam, phosphorus and dilute phosphoric acid; contained 2.5% hydrogen as impurity; dried with conc. H ₃ PO ₄ and with P ₂ O ₅ . ESTIMATED ERROR: REFERENCES:			

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>1. Phosphine; PH₃; [7803-51-2] 2. Trifluoroacetic acid; C₂HF₃O₂;</pre>	Fujioka, G. S.; Cady, G. H. J. Amer. Chem. Soc.	
	<u>1957</u> , 79, 2451-2454.	
VARIABLES:	PREPARED BY: P. G. T. Fogg	
EXPERIMENTAL VALUES:	······································	
T/K ^p PH3 ^{/mmHg} Ostwald	Coefficient Mole fraction* L $x^{p_{H_3}}$	
299.2 653	15.9 0.040	
760 mmHg = 1 atm 1 atm = 1.013 x 10^5 Pa		
* Calculated by the compiler using the density of trifluoroacetic acid at 25°C given in ref. (1).		
AUXILIARY	INFORMATION	
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:	
This solubility measurement was carried out during investigations of inorganic reactions in anhydrous trifluoroacetic acid. Phosphine was confined over mercury in a gas measuring tube and a measured sample of trifluoroacetic acid was added above the mercury by a hypodermic syringe. The apparatus was shaken for several hours until the new volume of gas was constant. The	 No details given. Supplied by Minnesota Mining and Manufacturing Co. and used without further purification. 	
from the change in volume of the gas phase. In the calculation of the partial pressure of phosphine the total pressure was corrected to allow for the partial pressure of	ESTIMATED ERROR:	
trifluoroacetic acid but details of the correction were not given.	REFERENCES: 1. Encyclopedia of Chemical Technology, 3rd ed. Vol. 10, Wiley, New York, <u>1980</u> .	