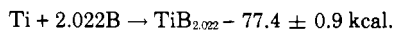
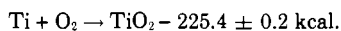
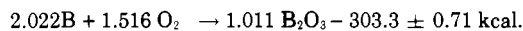
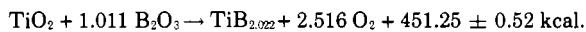


ant value, -451.25 ± 0.52 kcal. per mole, was combined with the values for the heat of formation of amorphous B_2O_3 , -300.0 ± 0.7 kcal. per mole (3), and with the heat of formation of TiO_2 (rutile) (5, 9) -225.4 ± 0.2 to give -77.4 ± 0.9 kcal. per mole for the heat of formation of $TiB_{2.022} \pm 0.006$, as shown in the following equations:



This value is somewhat more negative than those reported earlier. If it is assumed that most of the oxygen was present as B_2O_3 instead of TiO_2 , both the original formula of the material and the heat of formation lie well within the stated uncertainties.

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LITERATURE CITED

- (1) Brewer, L., Haraldsen, H., *J. Electrochem. Soc.* **102**, 399 (1955).
- (2) Epel'baum, V.A., Starostina, M.I., *Bor. Tr. Konf. po Khim. Bora i Ego Soedin.* **1955**, 97 (1958).
- (3) Huber, E.J., Jr., Head, E.L., Holley, C.E., Jr., *J. Phys. Chem.* **68**, 3040 (1964).
- (4) Huber, E.J., Jr., Matthews, C.O., Holley, C.E., Jr., *J. Am. Chem. Soc.* **77**, 6493 (1955).
- (5) Humphrey, G.L., *Ibid.*, **73**, 1587 (1951).
- (6) *Ibid.*, p. 2261.
- (7) Lowell, C.E., Williams, W.S., *Rev. Sci. Instr.* **32**, 1120 (1961).
- (8) Neumann, B., Kroger, C., Haebler, H., *Z. anorg. Chem.* **196**, 65 (1931).
- (9) Neumann, B., Kroger, C., Kunz, H., *Z. anorg u. allgem. Chem.* **218**, 379 (1934).

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Solubility of Cyclopropane in Some Lower Alcohols

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The solubility of cyclopropane was determined at 1-atm. partial pressure and 0° to 40° C. in methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol.

THE solubility of cyclopropane has been determined at 1-atm. partial pressure and temperatures ranging from 0° to 40° C. in five lower alcohols: methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol. A literature survey has shown that the solubilities of many of the common nonpolar gases have not been measured in several of the lower alcohols.

EXPERIMENTAL

Materials. The cyclopropane was obtained from the Matheson Co. and had a reported minimum purity of

99.5%, which was confirmed by mass spectrometry. No further purification was performed. The alcohols were dried with Linde Type 4A molecular sieves using a Soxhlet extraction unit (6). They were then distilled in a laboratory fractionation column of about 30 theoretical plates packed with ¼-inch i.d., single-turn helices. Central cuts were collected and used. The sources and physical properties of the alcohols are summarized in Table I. In each case, the alcohols had a purity of greater than 99.7% and a water content of 0.1% or less as indicated by chromatographic analysis.

Apparatus and Procedures. The apparatus and method have been described (7).

¹ Present address: Celanese Chemical Co., Corpus Christi, Tex.

Table I. Sources and Physical Properties of the Alcohols

Alcohol	Vendor's Specifications			Refractive Index, 25° C.	
	Source	Grade	B.P., ° C.	Exptl.	Lit.
Methanol	J. T. Baker Chemical Co.	Baker analyzed reagent	64.6	1.3266	1.32663(6) 1.32657(1)
Ethanol	U. S. Industrial Chemicals Co.	U.S.P. reagent quality	...	1.35946	1.35941(1, 6)
2-Propanol	J. T. Baker Chemical Co.	Baker analyzed reagent	82.3	1.37508	1.3747 (6) 1.37527(1)
1-Propanol			97.2	1.38323	1.38314(6) 1.38355(1)
1-Butanol			117.5	1.39726	1.3970 (5) 1.3974 (5) 1.3973 (1)

Table II. Solubility of Cyclopropane in Alcohols

(Partial pressure of cyclopropane = 1 atm.)

Run No.	Alcohol	T, °C.	P_a from Equation 1			P_a from Raoult's Law					
			Solubility, Bunsen Coef.		Mole fraction	Total pressure	Solubility, Bunsen Coef.		Mole fraction	Total pressure	
			Individual	Av.			Individual	Av.			
M-1	MeOH	40	10.124	9.683	0.01796	1036.5	8.831	8.734	0.01623	1012.8	
M-2			9.548				8.625				
M-3			9.377				8.747				
M-4		30	13.20	13.14	0.02392	933.0	12.20	12.21	0.02226	914.6	
M-5			13.28				12.08				
M-6			12.93				12.34				
M-7		20	16.61	16.77	0.02998	865.7	16.45	16.54	0.02958	851.4	
M-8			16.87				16.58				
M-9			16.83				16.58				
M-10		10	22.97	23.08	0.04035	822.9	22.81	22.84	0.03994	811.9	
M-11			22.94				22.74				
M-12			23.34				22.98				
M-13		0	32.90	32.61	0.05546	796.6	32.60	32.50	0.05529	788.1	
M-14			31.92				32.12				
M-15			33.00				32.79				
E-1	EtOH	40	10.77	10.77	0.02839	905.3	10.55	10.45	0.02757	890.6	
E-2			10.96				10.33				
E-3			10.57				10.33				
E-4		30	14.44	14.30	0.03697	846.6	14.26	14.14	0.03658	835.7	
E-5			14.26				14.12				
E-6			14.19				14.04				
E-7		20	19.19	19.10	0.04831	810.3	19.00	18.97	0.04797	801.9	
E-8			19.07				18.97				
E-9			19.05				18.93				
E-10		10	26.49	26.48	0.06508	788.4	26.35	26.38	0.06484	782.0	
E-11			26.43				26.39				
E-12			26.52				26.39				
E-13		0	38.02	38.18	0.09034	775.7	37.89	38.06	0.09008	770.9	
E-14			38.26				38.12				
E-15			38.25				38.17				
iP-1	iPrOH	40	11.11	11.08	0.03793	873.0	10.92	10.92	0.03740	861.0	
iP-2			11.05				10.92				
iP-3			11.08				10.91				
iP-4		30	14.53	14.55	0.04874	825.7	14.42	14.46	0.04843	817.0	
iP-5			14.67				14.57				
iP-6			14.46				14.38				
iP-7		20	19.33	19.31	0.06305	797.0	19.21	19.23	0.06278	790.6	
iP-8			19.27				19.19				
iP-9			19.34				19.28				
iP-10		10	26.69	26.62	0.08407	780.1	26.59	26.56	0.08390	775.5	
iP-11			26.57				26.54				
iP-12			26.61				26.55				
iP-13		0	39.07	38.78	0.1169	770.7	38.11	38.53	0.1162	767.3	
iP-14			39.48				38.94				
iP-15			38.25				38.17				
nP-1	nPrOH	40	11.59	11.47	0.03829	817.5	11.32	11.29	0.03772	810.2	
nP-2			11.48				11.32				
nP-3			11.33				11.24				
nP-4		30	15.36	15.36	0.05012	791.9	15.21	15.24	0.04974	787.0	
nP-5			15.36				15.26				
nP-6			20.61				20.45				
nP-7		20	20.29	20.45	0.06504	776.8	20.30	20.27	0.06451	773.6	
nP-8			20.24				20.24				
nP-9			28.15				28.15				
nP-10		0	28.15	28.15	0.08661	768.4	28.10	28.11	0.08649	766.4	
nP-11			40.78				40.65				
nP-12			40.60				40.55				
B-1		nBuOH	40	11.88	11.80	0.04767	780.6	11.64	11.63	0.04701	777.4
B-2				11.72				11.62			
B-3			30	15.40	15.37	0.06069	770.8	15.30	15.27	0.06032	768.7
B-4	15.34			15.24							
B-5	20		20.43	20.43	0.07845	765.3	20.42	20.41	0.07838	764.1	
B-6			20.44				20.40				
B-7	10		28.33	28.28	0.1046	762.5	28.33	28.27	0.1046	761.7	
B-8			28.22				28.21				
B-9	0		40.78	40.78	0.1431	761.1	40.81	40.79	0.1431	760.7	
B-10			40.78				40.77				

RESULTS

The solubility data (Table II) were calculated in units of both mole fraction and Bunsen coefficient (volume of gas at 1 atm. and 0° per unit volume of solvent when the partial pressure of gas is 1 atm.). Because of low values of gas solubilities, many investigators use the ideal solution laws of Raoult and Henry in their calculations. However, as has been pointed out by Kretschmer and Wiebe (3), hydrocarbon-alcohol solutions exhibit large positive deviations from Raoult's law. In this investigation, only the total pressure is measured experimentally. In order to set the gas partial pressure at 1 atm., the partial pressure of the alcohol was calculated by

$$\log P_a = \log (P_a^0 x_a) + Ax_a^2 - \frac{(V_a - B_a)(P_a^0 - P_T)}{2.3RT} \quad (1)$$

where P_a is the partial pressure of the alcohol, P_a^0 its vapor pressure, V_a its liquid molal volume, and B_a its second virial coefficient. x_a and x_g are the mole fraction of alcohol and gas, respectively, in solution. P_T is the total pressure. A is a constant which is taken equal to 1.6 (3). Second virial coefficients were taken from Kretschmer and Wiebe (4) for

methanol, ethanol, and 2-propanol and the equation of Keyes *et al* (2) was used for 1-propanol and 1-butanol.

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LITERATURE CITED

- (1) American Petroleum Institute, "Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Institute of Technology, Pittsburgh.
- (2) Keyes, F.G., Smith, L.B., Gerry, H.T., *Proc. Am. Acad. Arts Sci.* **70**, 319 (1936).
- (3) Kretschmer, C.B., Wiebe, R., *J. Am. Chem. Soc.* **73**, 3778 (1951).
- (4) *Ibid.*, **76**, 2579 (1954).
- (5) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.
- (6) Weissberger, A., "Organic Solvents," Interscience, New York, 1955.
- (7) Yen, L.C., McKetta, J.J., *J. CHEM. ENG. DATA* **7**, 288 (1962).

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