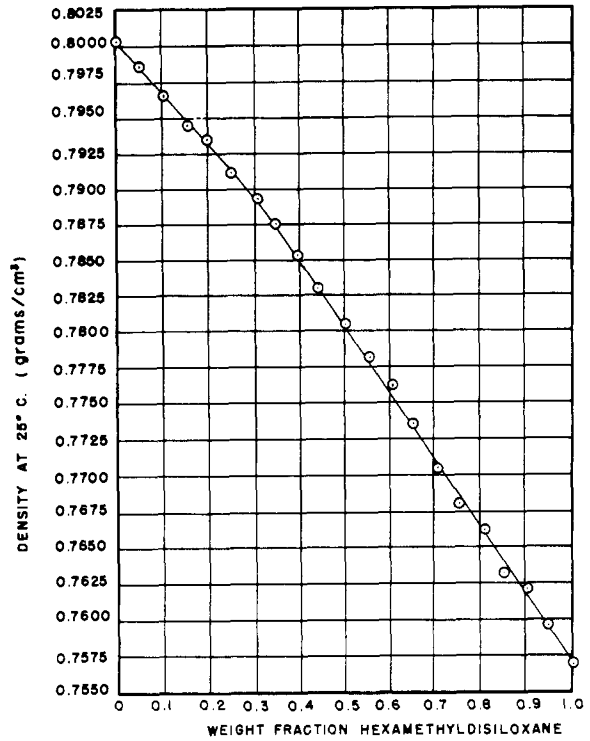

Figure 3. Density at 25° C. vs. weight fraction hexamethyldisiloxane for the system hexamethyldisiloxane–*n*-propyl alcohol

NOMENCLATURE

P_i = vapor pressure of pure component i at equilibrium temperature, mm. of Hg
x_i = mole fraction of component i in the liquid phase
y_i = mole fraction of component i in the vapor phase
γ_i = activity coefficient of component i
π = total pressure, mm. of Hg

Subscripts

1 = hexamethyldisiloxane
2 = *n*-propyl alcohol

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LITERATURE CITED

(1) "Dow-Corning Silicone Notebook," Reference No. **2003**, June 1952.
(2) Griffiths, Ezer, "Methods of Measuring Temperature," Charles Griffin & Co., Ltd., London, 1947.
(3) Orr, Virgil, Ph.D. dissertation, Louisiana State University, Baton Rouge, La., 1950.
(4) Othmer, D.F., *Anal. Chem.* **20**, 763 (1948).
(5) Othmer, D.F., *Ind. Eng. Chem.* **35**, 614 (1943).
(6) Perry, J.H., "Chemical Engineers' Handbook," McGraw-Hill, New York, 1941.
(7) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).

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Solubility of Helium in Liquid Argon, Oxygen, and Carbon Monoxide

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Data were obtained for the solubility of helium at pressures up to 2000 p.s.i.a. in liquid argon at temperatures of −125°, −140°, −160°, and −180° C.; in liquid oxygen at −130°, −145°, −160°, −180°, and −195.8° C.; and in liquid carbon monoxide at −145°, −160°, −180°, and −195.8° C. A static sampling technique was used and samples were analyzed by gas chromatography. The data are presented in temperature-composition and pressure-composition diagrams. A comparison is made between the data of this study and previously published data for the helium-argon and helium-oxygen systems.

THE SOLUBILITY of helium in certain liquefied gases is of interest because of the limited availability of helium and the method of producing it. Helium is obtained by extraction from either liquefied natural gases or liquefied air. The efficiency of the recovery process depends upon the solubility of helium in the liquid.

A number of investigators (*3-7, 9, 12*) have directed their attention to the solubility of helium in liquid nitrogen. Several studies of the solubility of helium in liquid methane also have been made (*8, 10, 14, 15*) and data have recently been reported for the helium-argon system (*11*) and the helium-oxygen system (*1, 2*). The object of this investigation was to determine the solubility of helium in the liquefied gases argon, oxygen, and carbon monoxide.

EXPERIMENTAL

Materials. The helium used was a special analyzed stock furnished by the United States Bureau of Mines and had a maximum impurity of 12.0 p.p.m. The argon and oxygen were commercial grades, purchased from the Linde Co. with specified purities of 99.996 and 99.7%, respectively. Carbon monoxide was obtained from Olin-Matheson with a purity of 99.5%. All gases were used without further purification.

APPARATUS AND PROCEDURE

The experimental apparatus and operating procedures have been described in detail (*13,14*). A static sampling cell of approximately 100-cc. volume was placed in a controlled low temperature bath. The contents of the cell

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were agitated by means of a solenoid-operated plunger. After obtaining two-phase equilibrium conditions within the cell, liquid samples were withdrawn through capillary tubing and analyzed by gas chromatography.

Temperatures within the low temperature bath were maintained constant to within ± 0.01° C. A platinum resistance thermometer was used for temperature measurements and is believed to be accurate to ±0.02° C., as related to the International Temperature Scale.

Pressures were measured with bourdon tube gages, which had been calibrated against a dead-weight tester. All reported pressures are accurate to within ±1.5 p.s.i.

The component peaks in the gas chromatograph were separated using a column packed with Linde Type 4-A molecular sieve for the argon and oxygen mixtures and with silica gel for the carbon monoxide mixtures.

The carrier gas was nitrogen and the column temperature was approximately 100° C. Sample pressures were kept constant to within ± 0.1% by means of an aneroid-type absolute pressure gage. The accuracy of the analytical procedure is estimated to be ± 1% of the helium concentration, or ± 0.03 mole % helium, whichever is greater.

EXPERIMENTAL RESULTS

Five different isotherms of the helium-oxygen system were investigated and four each in the systems helium-argon and helium–carbon monoxide. In each case the isotherms were spaced to cover as completely as possible the temperature range between the melting point and critical point of the heavy component. For each temperature, liquid compositions were determined at intervals of 250 p.s.i. from some pressure greater than the vapor pressure of the heavy component to 2000 p.s.i.a. At least two samples were taken at each temperature and two chromatographic analyses made of each sample. The results in Tables I, II, and III, therefore, represent an average of at least four chromatograph runs for each data point. The data were taken at the same pressures along each isotherm, making it possible to present the experimental results directly, without interpolation, on both *P-X* (pressure-composition) and *T-X* (temperature-composition) diagrams.

Figure 1 is the *P-X* plot obtained for the helium-argon system. It shows regular increases in the solubility of helium with pressure at every temperature. The data exhibit very little scatter about the smooth lines; the deviations are not much larger than the estimated accuracy of the analytical procedure. The data for each isotherm extrapolate smoothly through the vapor pressure of pure argon at 0% helium concentration. The lowest of the temperatures studied is about 9° above the melting point of argon and the highest is approximately 3° below the critical temperature. Liquid compositions as functions of temperature are presented in Figure 2. The data of Mullins and Ziegler (*11*) are included for comparison. Their results indicate a somewhat lower solubility for helium than was found in this study. Figure 2 shows that at higher pressures, as with the helium-nitrogen and helium-methane systems, the solubility of helium in liquid argon increases with temperature. At lower pressures the solubility passes through a maximum value, and for pressures less than the critical pressure of argon, intersects the 0% helium axis at the temperature corresponding to the vapor pressure of pure argon. In general, the behavior of the helium-argon system is like that of the helium-nitrogen (*3-7, 9, 11*) and helium-methane (*8. 10, 14, 15*) systems.

Table I. Helium-Argon

Pressure, P.S.I.A.	Liquid Composition, Mole % Helium −125° C.	−140° C.	−160° C.	−180° C.
250			0.25	0.15
500		0.68	0.75	0.35
750	1.21	1.71	1.19	0.52
1000	3.93	2.76	1.64	0.71
1250	6.50	3.70	2.10	0.87
1500	8.95	4.61	2.49	1.02
1750	11.38	5.49	2.87	1.14
2000	13.80	6.32	3.25	1.29

Table II. Helium-Oxygen

Pressure, P.S.I.A.	Liquid Composition, Mole % Helium −130° C.	−145° C.	−160° C.	−180° C.	−195.8° C.
250			0.27	0.14	0.04
500		0.86	0.74	0.33	0.14
750	1.80	1.59	1.13	0.53	0.20
1000	3.30	2.37	1.54	0.68	0.25
1250	4.61	3.14	1.95	0.83	0.32
1500	5.98	3.84	2.32	0.99	0.36
1750	7.25	4.46	2.67	1.14	0.43
2000	8.60	5.08	3.02	1.27	0.48

Table III. Helium–Carbon Monoxide

Pressure, P.S.I.A.	Liquid Composition, Mole % Helium −145° C.	−160° C.	−180° C.	−195.8° C.
250			0.42	0.30
500		1.64	0.90	0.45
750	4.24	2.90	1.35	0.62
1000	6.93	3.96	1.89	0.73
1250	9.65	5.10	2.21	0.94
1500	12.14	6.05	2.49	1.06
1750	14.55	7.00	3.00	1.22
2000	16.73	7.81	3.28	1.34

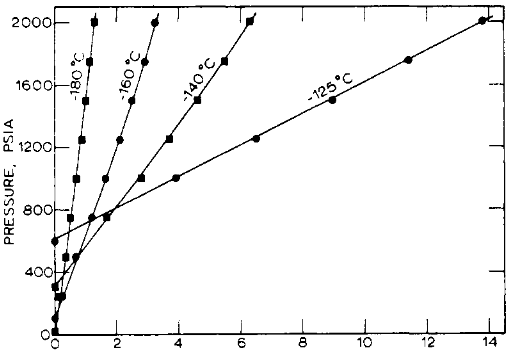

Figure 1. *P-X* diagram, helium-argon

Experimental results for the helium-oxygen system appear in Figures 3 and 4. Five isotherms were selected. The lowest and the highest were approximately 22° and 11° from the melting and critical points, respectively. The low-

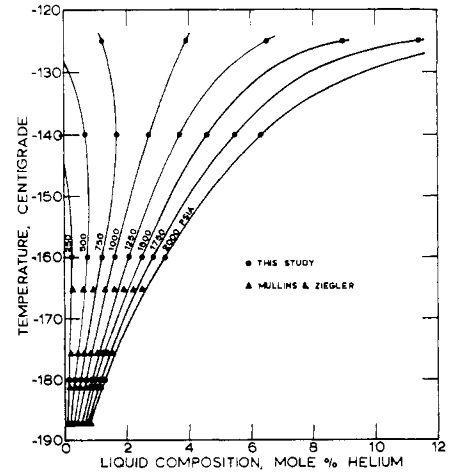

Figure 2. *T-X* diagram, helium-argon

est temperature for study was limited to that obtainable by the experimental apparatus—the boiling point of nitrogen. Figure 4 includes the data of Barrick and Herring (2) which fell within the range of this study. Their data in general were taken at higher pressures than were covered here. In view of the large disagreements often noted between the experimental work of different investigators in the field of low-temperature phase equilibria, the correspondence of the authors' data with those of Barrick and Herring is exceptionally good. The experimental data for the solubility of helium in liquid oxygen as a function of temperature and pressure follow very closely the behavior of the helium-argon data just discussed.

Four isotherms of the helium-carbon monoxide system were investigated, with the experimental results shown in Figures 5 and 6. In this case the lowest temperature is some 13° above the melting point of carbon monoxide and the highest is 6° below the critical temperature. The same type of behavior is evident as has been seen in the other helium-containing systems. The maximum solubility in carbon monoxide, however, is considerably higher than in argon or oxygen.

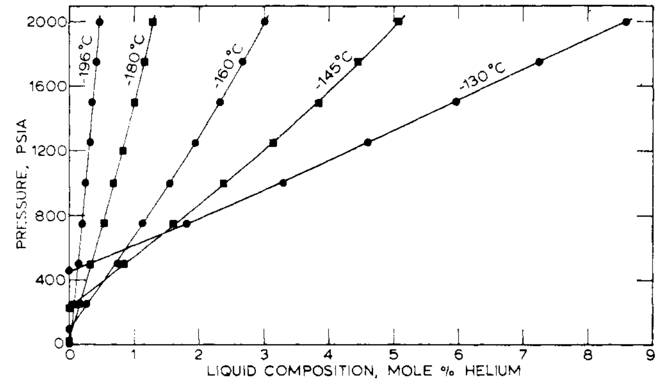

Figure 3. *P-X* diagram, helium-oxygen

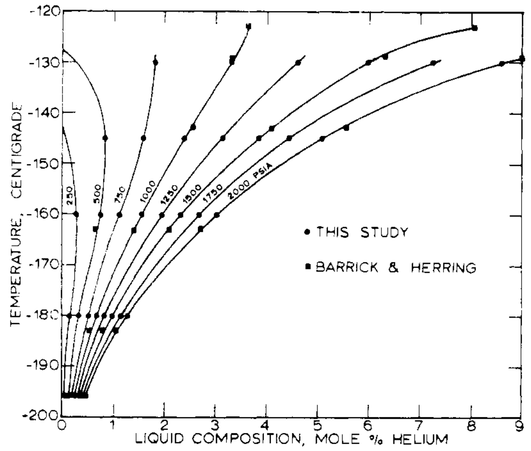

Figure 4. *T-X* diagram, helium-oxygen

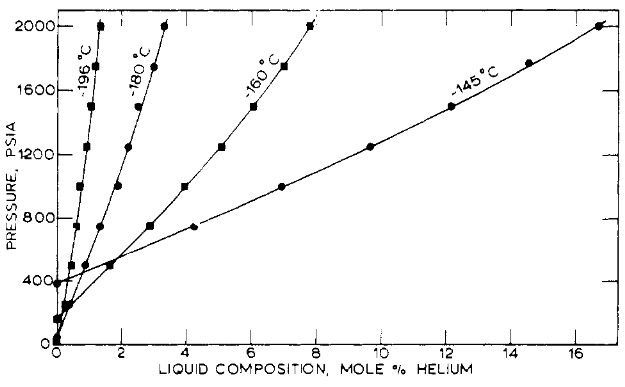

Figure 5. *P-X* diagram, helium-carbon monoxide

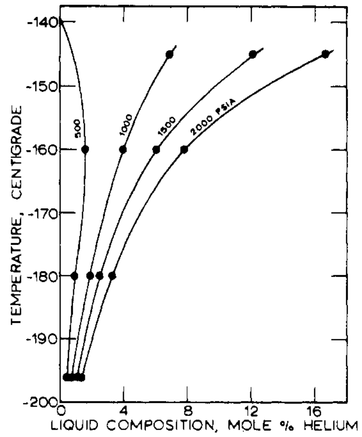

Figure 6. *T-X* diagram, helium-carbon monoxide

An interesting differentiation between the three heavy components studied in this investigation is the fact that the vapor pressure curve of oxygen crosses those of argon and carbon monoxide. Thus, oxygen has both a lower melting point and a higher critical temperature than either argon or carbon monoxide. The theory of perfect solutions suggests that the solubility of a gas in a liquid is a function, among other things, of the slope of the liquid vapor pressure curve. Since the oxygen vapor pressure curve has a lesser curvature than either of the other two, one might expect a somewhat lower solubility in oxygen. This generally is confirmed by the data, which show helium to be less soluble in oxygen than in the other components at the temperatures where the vapor pressures are equal.

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LITERATURE CITED

(1) Barrick, P.L., Herring, R.N., *Intern. Advan. Cryogenic Eng.* **10**, 151 (1965).
(2) Barrick, P.L., Herring, R.N., *U. S. Air Force Systems Command, Res. Technol. Div., Tech. Doc. Rept.* **ML-TDR-64-321**, 180 pp. (1964).
(3) Burch, R.J., J. CHEM. ENG. DATA **9**, 19 (1964).
(4) Buzyna, G., Macriss, R.A., Ellington, R.T., *Chem.Eng. Progr. Symp. Ser., No. 44* **59**, 101 (1963).
(5) DeVaney, W.E., Dalton, B.J., Meeks, J.C., J. CHEM. ENG. DATA **8**, 473 (1963).
(6) Fedoritenko, A., Ruehmann, M., *Tech. Phys. (USSR)* **4**, 36 (1937).
(7) Gonikberg, M.G., Fastovskii, W., *Acta Physicochimi. (USSR)* **12**, 67 (1940).
(8) Gonikberg, M.G., Fastovskiĭ, W., *Foreign Petroleum Technol.* **9**, No. 6, 214 (1941).
(9) Kharakhorin, F.F., *J. Tech. Phys. (USSR)* **10**, 1533 (1940).
(10) Kharakhorin, F.F., *Inzhenerno-Fizicheskii Zhur.* **2**, No. 5, 55 (1959).
(11) Mullins, J.C., Ziegler, W.T., *Intern. Advan. Cryogenic Eng.* **10**, 171 (1965).
(12) Rodewald, N.C., Davis, J.A., Kurata, F., *A.I.Ch.E. J.* **10**, 937 (1964).
(13) Sinor, J.E., Ph.D. thesis, University of Kansas, Lawrence, Kan., 1965.
(14) Sinor, J.E., Schindler, D.L., Kurata, F., *A.I.Ch.E. J.* **12**, 353 (1966).
(15) U. S. Bureau of Mines, "Open File of Information and Data Relating to the Extraction of Helium from Natural Gas by Low Temperature Processes," Amarillo, Tex., 1959.

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