Vapor-Liquid Equilibria Data for Helium–Carbon Monoxide and Helium–Nitrous Oxide Systems

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Liquid-vapor data are reported for the helium–carbon monoxide system at 80, 85, 90, 100, and 120K and for the helium–nitrous oxide system at 195, 215, 235, 245, 255, 265, and 285K at pressures up to 138 bars. The data are analyzed for internal consistency using pseudo-Henry's law constants and enhancement factors.

Cryogenic systems containing helium have been of practical interest for applications ranging from separation processes to pressurized systems. However, few data exist in the literature for helium systems containing carbon monoxide or nitrous oxide. Sinor and Kurata (*7*) determined liquid-phase compositions of helium–carbon monoxide mixtures at four temperatures between 77 and 128K and at pressures up to 138 bars. Kling (*5*) made an extensive experimental study of nitrous oxide systems including the helium–nitrous oxide system; however, his data are presented in graphical form only, and the internal consistency of the data could not be assessed. The work reported here was performed to provide a more complete set of phase equilibrium data for these two binary systems.

Experimental Method

The phase equilibrium apparatus used here is basically the vapor-recirculation system described by Duncan and Hiza (*2*); therefore, only pertinent details are given here.

Equilibrium pressures were measured by using either a double revolution 0–20 bar Bourdon gauge or a 0–2000 psia Bourdon gauge. The 0–20 bar gauge, calibrated against an air piston gauge, exhibited a maximum negative deviation of 0.02 bars below 3 bars and a constant negative deviation of 0.008 bars above 8 bars. The 2000 psia gauge, calibrated against an oil dead weight gauge, has an estimated overall uncertainty of 1.0 psi.

The fluid temperatures were measured with a platinum resistance thermometer. Comparisons were made between readings of this thermometer and temperatures obtained from vapor-pressure measurements with pure nitrogen and the vapor-pressure data of Wagner (*8*). These comparisons, together with the specifications of the measuring instruments, indicate that the overall uncertainty of the temperature measurements is no greater than ±0.013K.

Liquid-phase samples were withdrawn from the bottom of the equilibrium cell through a stainless-steel capillary; vapor samples were isolated in the room temperature recirculation loop. To obtain reproducible analyses in the nitrous oxide system, liquid samples were slowly bled into a warm, evacuated 75 cm^3 chamber and allowed to reach thermal equilibrium ($\sim$20 min) prior to gas analysis. The same procedure was used for vapor sampling except that it was not necessary to wait before analyzing the sample. In each case, the sample chamber was filled to about 2 bars gauge to allow for adequate purging of the gas analysis equipment and to provide at least two analyses.

A gas chromatograph containing a thermal conductivity detector was used to determine mixture compositions. It was not possible to obtain both liquid and vapor analyses during the same run because a different carrier gas and column were required for each phase. For liquid-phase analyses argon was used as the carrier gas with a 6-m long molecular sieve column. The chromatograph was calibrated against a 5.27 mol % helium in argon mixture. Helium carrier gas and a 0.5-m long silica gel column were used for vapor-phase analyses. In this case, the chromatograph was calibrated against pure carbon monoxide or nitrous oxide, and the response in the peak area was assumed to be linear over the composition range of interest. A previous calibration for nitrogen verified the linearity assumption for this detector. In each case, only the peak area of one component and total sample pressure were measured. We used a 0–75 psia quartz spiral Bourdon gauge to determine sample pressure. The gauge was calibrated to better than 0.1% of the reading using an air dead weight gauge. We estimate that the compositions are accu-

Table I. He–CO Liquid-Phase Composition

Temperature		Pressure		Mol %
K	°R	Bars	Psia	He
79.50	143.1	0.787[a]	11.41[a]	0.0
		41.2	597	0.47
		41.5	602	0.48
		69.1	1002	0.77
		69.4	1007	0.79
		102.7	1489	1.15
		103.4	1500	1.16
		134.9	1956	1.43
		136.1	1974	1.46
84.71	152.5	1.41[a]	20.40[a]	0.0
		69.0	1000	1.05
		69.4	1007	1.07
		102.9	1493	1.52
		103.9	1507	1.52
		135.3	1962	1.85
		136.2	1976	1.86
90.0	162.0	2.37[a]	34.35[a]	0.0
		35.6	516	0.72
		69.4	1006	1.41
		103.6	1503	2.03
		135.6	1967	2.53
		136.9	1985	2.54
100.0	180.0	5.41[a]	78.5[a]	0.0
		37.1	538	1.16
		70.1	1017	2.27
		104.3	1513	3.33
		136.9	1985	4.19
120.0	216.0	18.74[a]	271.8[a]	0.0
		36.5	530	1.74
		69.9	1014	4.78
		105.1	1524	7.67
		138.0	2002	10.03

[a] Vapor pressure.

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rate to within ±0.2 mol % or ±2%, whichever is greater; reproducibility, especially for the carbon monoxide system, was much better.

The carbon monoxide was ultrapure (>99.8%), and the nitrous oxide was of USP quality (>98%), with the major impurities of both being nitrogen and oxygen. No attempt was made to further purify the carbon monoxide; however, after condensing nitrous oxide into the equilibrium cell, the vapor space had to be vented three or four times before the vapor pressure remained constant after venting. This venting also provided additional purification of the nitrous oxide.

Carbon monoxide poses a safety problem because it is toxic and not readily detected since it is odorless, colorless, and tasteless. To prevent exposure of personnel to the gas, all vent lines were vented directly outdoors. Before any carbon monoxide was used, the complete system was leak-checked to 138 bars with pure helium. As a further precaution, CO detector badges were worn; these badges are reportedly sensitive to carbon monoxide down to the ppm range.

Nitrous oxide is not considered toxic, but it is an anesthetic. This fluid can explosively autodecompose at high temperature

Table II. He–CO Vapor-Phase Compositions

Temperature		Pressure		Mol %
K	°R	Bars	Psia	CO
80.0	144.0	0.830^a	12.04^a	100.0
		11.9	172	7.96
		13.7	198	6.97
		28.8	417	3.64
		42.3	614	2.68
		56.3	817	2.13
		69.8	1012	1.79
		136.4	1978	1.15
84.71	152.5	1.41^a	20.4^a	100.0
		6.9	100	12.91
		7.0	101	12.87
		15.2	220	10.54
		28.8	418	6.05
		42.8	621	4.37
		56.4	818	3.51
		70.9	1028	2.97
		104.0	1508	2.28
90.0	162.0	2.37^a	34.35^a	100.0
		14.6	211	18.73
		26.7	387	10.82
		40.1	582	7.61
		55.6	806	5.87
		71.2	1032	4.85
		104.0	1509	3.72
		137.6	1996	3.11
100.0	180.0	5.41^a	78.5^a	100.0
		13.4	195	45.29
		27.4	398	24.06
		27.9	405	24.04
		29.3	425	22.88
		39.0	565	18.05
		41.4	601	17.21
		57.0	826	13.32
		69.8	1012	11.37
		70.2	1018	11.35
		103.9	1507	8.46
		131.0	1900	7.26
		131.8	1912	7.25
		132.7	1925	7.19
		132.9	1928	7.18
120.0	216	18.74^a	271.8^a	100.0
		29.3	425	75.99
		42.5	616	59.47
		56.7	822	49.18
		70.5	1023	41.94
		103.8	1505	32.65
		137.1	1988	27.44

^{a} Vapor pressure.

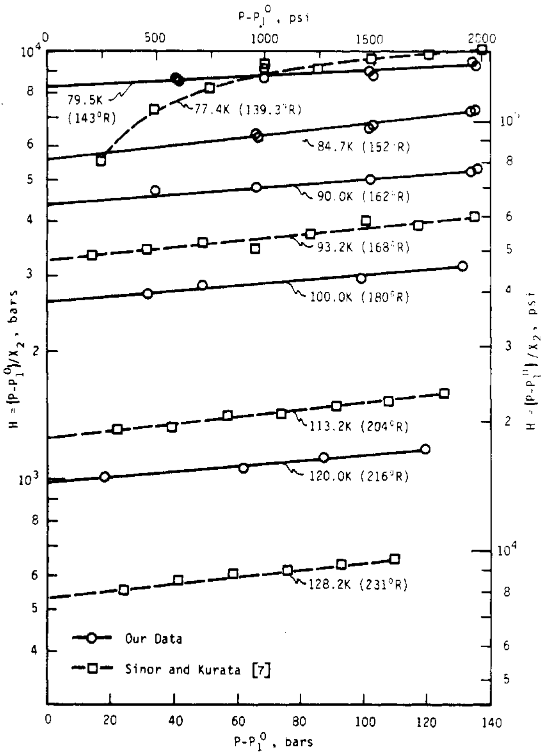

Figure 1. Pseudo-Henry's law constant for He–CO system as function of pressure

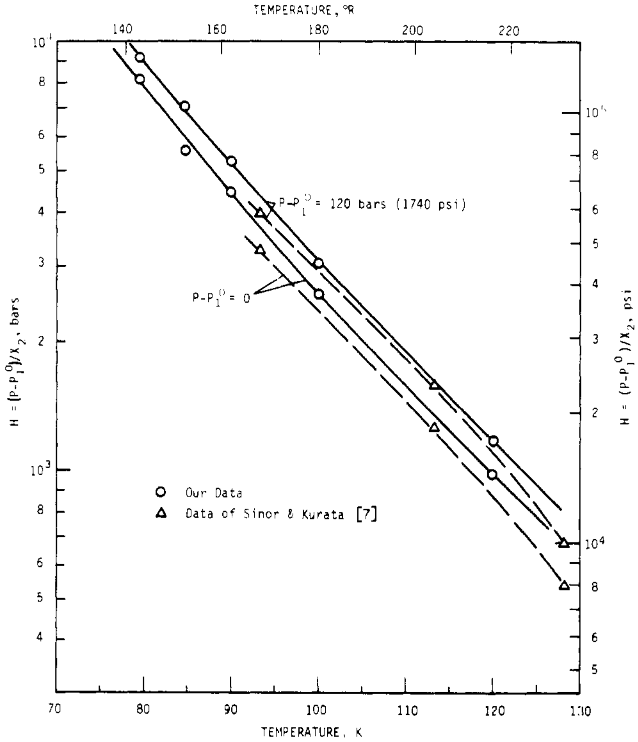

Figure 2. Pseudo-Henry's law constant for He–CO system as function of temperature

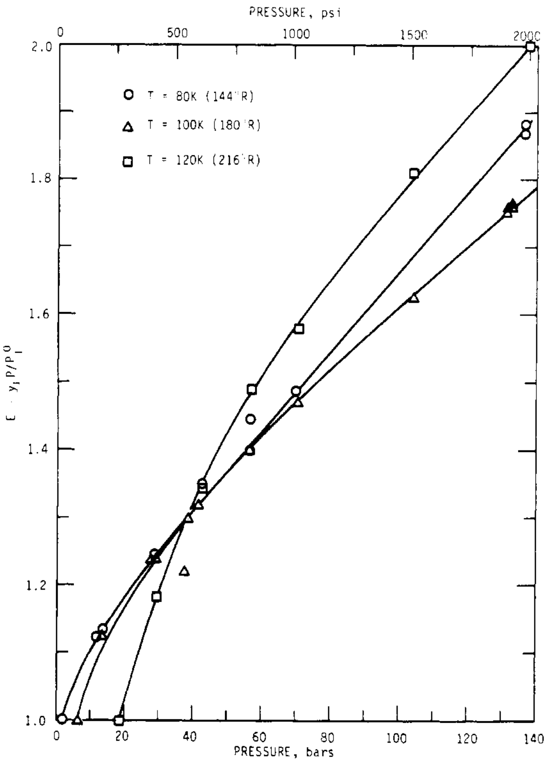

Figure 3. Enhancement factor for He–CO system as function of pressure

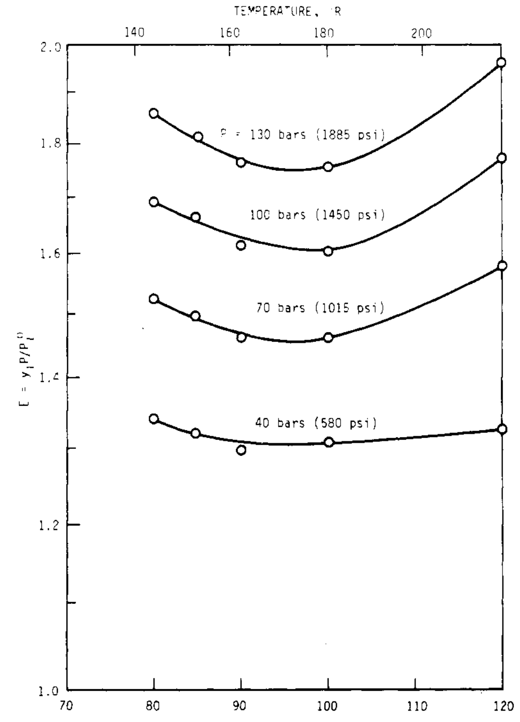

Figure 4. Enhancement factor for He–CO system as function of temperature

Table III. He–N_2O Liquid-Phase Compositions

Temperature		Pressure		Mol % He
K	°R	Bars	Psia	
195.0	351	1.82[a]	26.40[a]	0.0
		103.3	1498	0.52
		103.6	1502	0.52
		136.4	1978	0.70
		137.8	1998	0.68
215.0	387.0	4.70[a]	68.17[a]	0.0
		49.9	724	0.29
		51.8	751	0.27
		86.1	1248	0.54
235.0	423.0	10.13[a]	146.92[a]	0.0
		51.2	742	0.56
		51.6	749	0.55
		84.8	1230	0.96
		86.2	1250	1.04
		136.5	1980	1.70
245.0	441.0	14.14[a]	205.08[a]	0.0
		71.0	1030	0.98
		103.2	1497	1.57
		103.7	1504	1.55
		131.3	1904	2.04
		133.9	1942	2.05
		137.6	1996	2.09
		137.8	1998	2.09
255.0	459.0	19.22[a]	278.76[a]	0.0
		38.8	563	0.42
		38.9	564	0.41
		58.2	844	0.87
		58.3	846	0.90
		75.6	1096	1.27
		76.0	1102	1.30
		86.1	1248	1.45
		86.7	1258	1.47
		87.4	1267	1.54
		101.8	1476	1.86
		103.0	1494	1.82
		103.2	1497	1.80
		104.5	1515	1.84
		104.7	1518	1.85
		121.2	1758	2.09
		121.7	1765	2.14
		133.2	1932	2.41
		135.4	1964	2.46
		136.2	1975	2.42
265.0	477.0	25.38[a]	368[a]	0.0
		52.5	762	0.77
		52.8	766	0.75
		71.6	1038	1.27
		71.7	1040	1.28
		72.1	1045	1.22
		104.9	1522	2.15
		105.5	1530	2.22
		135.4	1964	2.91
		136.8	1984	2.99
285.0	513.0	42.18[a]	612[a]	0.0
		81.8	1186	1.73
		94.3	1367	2.38
		94.6	1372	2.33
		114.6	1662	1.77
		116.9	1695	3.34
		135.5	1965	4.14
		136.1	1974	4.16
		136.7	1983	4.18

[a] Vapor pressure.

Table IV. He–N_2O Vapor-Phase Compositions

Temperature		Pressure		Mol %
K	°R	Bars	Psia	N_2O
235.0	423.0	10.13[a]	146.92[a]	100.0
		19.7	285	54.37
		35.6	516	31.45
		52.0	754	22.25
		69.3	1005	17.31
		104.5	1515	11.81
		132.9	1928	9.45
245.0	441.0	14.14[a]	205.08[a]	100.0
		40.3	585	39.93
		51.7	750	32.20
		67.6	980	25.30
		98.2	1424	17.89
		125.9	1826	14.42
255.0	459.0	19.22[a]	278.76[a]	100.0
		50.0	739	43.89
		70.1	1017	33.72
		103.8	1506	23.70
		128.5	1863	19.58
265.0	477.0	25.6	372[a]	100.0
		41.6	603	68.72
		72.5	1052	43.26
		98.3	1426	33.72
		99.6	1444	33.30
		106.0	1538	31.72
		136.5	1980	25.97
285.0	513.0	Unable to obtain in vapor-phase data at this temperature because of rapid failure of circulating pump diaphragms. (Natural rubber and butyl swelled, and teflon, polypyromelitimide, and a fluoroelastomeric material failed to maintain suitable elastic properties.)		

[a] Vapor pressure.

and/or pressure (*6*). However, at the operating conditions of this study, the only problem with nitrous oxide was that it caused swelling in the recirculation pump diaphragm. Thus, periodic shutdowns for pump overhaul were required.

Results and Discussion

Tables I and II give liquid and vapor compositions as a function of pressure for the five isotherms of the helium carbon monoxide system. Measured vapor pressures are included because they differ from the correlation of Hust and Stewart (*4*). Figure 1 shows pseudo-Henry's law constants from our data and from Sinor and Kurata's (*7*) data. The Henry's law constant is defined here as

$$H = (P - P_1^\circ)/x_2 \tag{1}$$

Sinor and Kurata's data were reduced using vapor pressures from Hust and Stewart. Figure 2 shows a cross-plot of Henry's law constants as a function of temperature for helium pseudo partial pressures ($P - P_1^\circ$) of 0 and 120 bars. These figures show a fairly weak pressure dependence for the Henry's law constant.

A sensitive way to check the consistency of the vapor-phase data is to use the enhancement factor which is defined as

$$E = y_1 P/P_1^\circ \tag{2}$$

Figure 3 shows the enhancement factor as a function of pressure for three of the helium carbon monoxide isotherms. Figure 4 is a cross-plot showing the temperature dependence. The enhancement factor goes through a minimum between 90 and 100K. The vapor-phase data of Buzyna et al. (*1*) shows a similar minimum in the enhancement factor for the helium-nitrogen system in the same temperature range.

Liquid and vapor data for the helium-nitrous oxide system are given in Tables III and IV. Figure 5 shows Henry's law constants as a function of pressure; within the scatter of the data

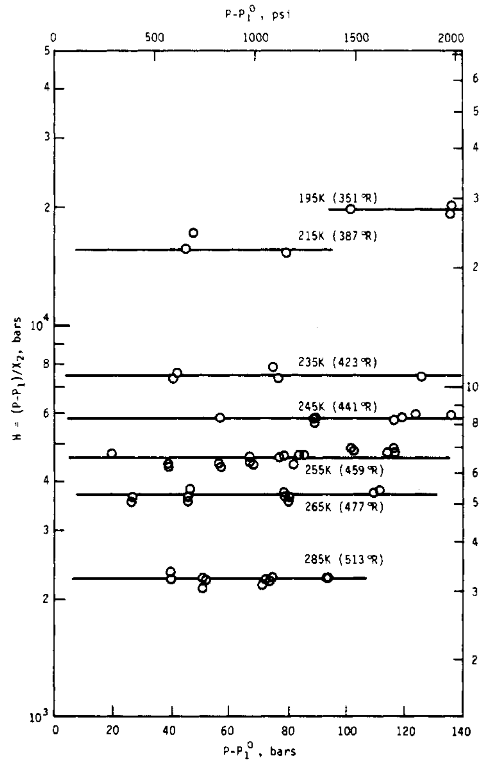

Figure 5. Pseudo-Henry's law constant for He-N_2O system as function of pressure

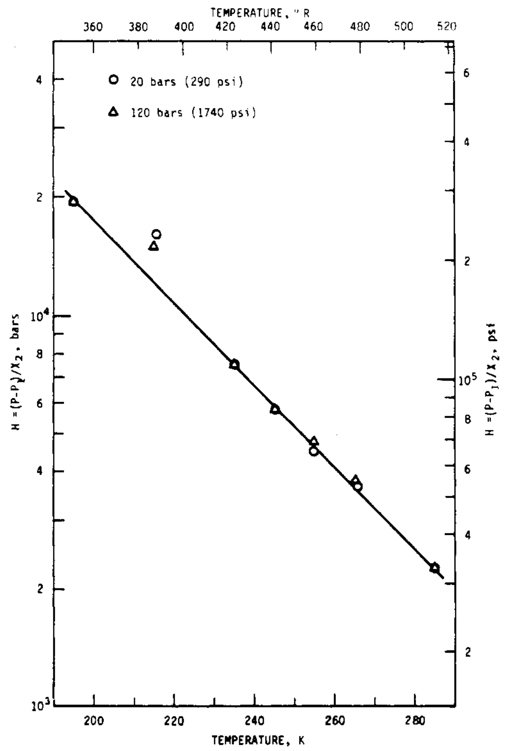

Figure 6. Pseudo-Henry's law constant for He-N_2O system as function of temperature

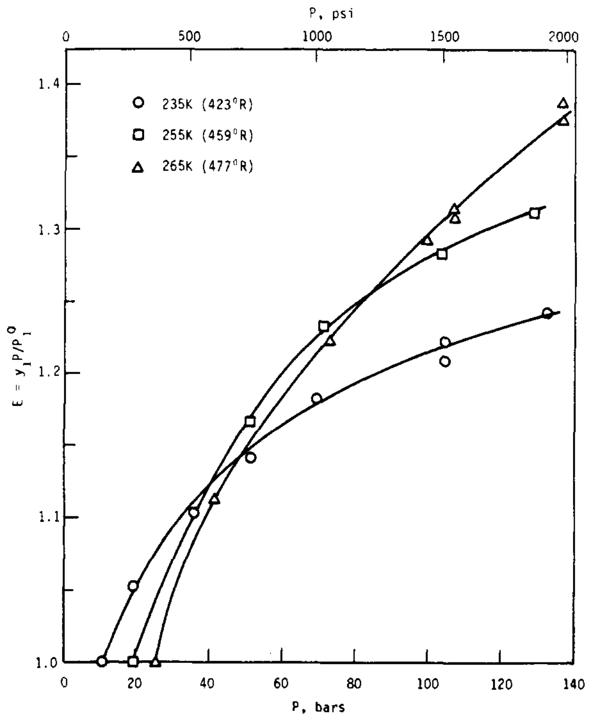

Figure 7. Enhancement factor for He–N_2O system as function of pressure

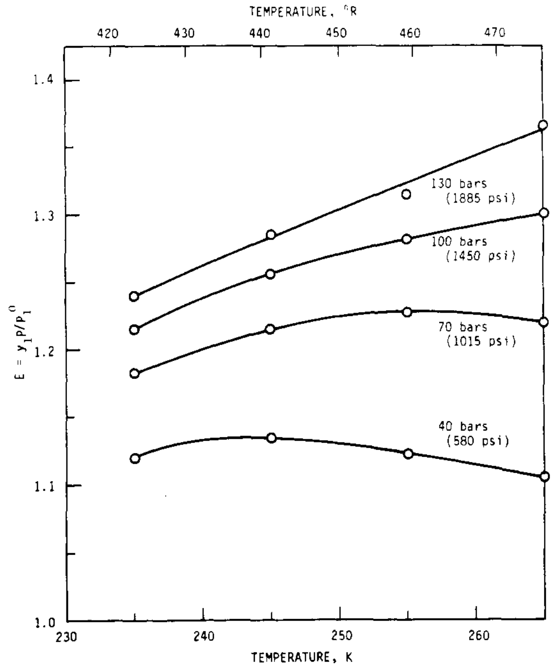

Figure 8. Enhancement factor for He–N_2O system as function of temperature

the Henry's law constants are independent of pressure. Figure 6 shows a cross-plot of the Henry's law constant as a function of temperature. Comparisons were not made with Kling's (*5*) data because the uncertainties involved in reading his graphs make the comparisons meaningless.

Figure 7 shows the enhancement factors for the helium–nitrous oxide system as a function of pressure for three of the isotherms, *and Figure 8 gives the temperature dependence.* This system shows no minimum in the enhancement factor because the temperatures are too high. This conclusion is based on a study of the enhancement factors for the helium–ethane system (ethane and nitrous oxide have similar normal boiling points and critical temperatures) which shows a minimum in the 160–190K range (3). However, Figure 8 shows a maximum in the enhancement factors at the lower pressures.

Nomenclature

E = enhancement factor, dimensionless
H = pseudo-Henry's law constant, bar
P = total pressure, bars
P_1^0 = vapor pressure, bars
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Subscripts

1 = less volatile component
2 = more volatile component

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