# Liquid-Vapor Equilibria of the Helium–Carbon Dioxide System

R. F. MACKENDRICK,[1] C. K. HECK,[2] and P. L. BARRICK
Department of Chemical Engineering, University of Colorado, Boulder Colo.

**The liquid-vapor equilibria of the helium–carbon dioxide system were studied in a vapor-recirculation apparatus. Six isotherms were studied, from 219.9° to 289.9° K., with pressures up to 200 atm. The accuracy is believed to be within about ±5% of the reported values.**

THE LIQUID-VAPOR EQUILIBRIA of the helium-carbon dioxide system were studied because of the lack of data in the literature. The data presented here are thought to be the first such equilibria available for this system. The data were obtained isothermally at 219.9°, 229.9°, 244.9°, 259.9°, 274.9°, and 289.9° K. Most of the isotherms were studied up to about 200-atm. pressure. In all, 97 data points were collected and are presented in both graphical and tabular form.

## EXPERIMENTAL

The apparatus and procedure were those of Herring and Barrick (*2*), modified by Spano, Heck, and Barrick (*3*). The apparatus and procedure have also been discussed elsewhere (*1*). The experiment basically consisted of a vapor-recirculation apparatus with direct sampling of the liquid and vapor phases. The samples were analyzed by gas chromatography. The vapor phase was continuously recirculated through the system by a magnetic reciprocating pump, and was intimately brought in contact with the liquid until equilibrium was reached. The liquid phase was kept in the equilibrium cell at the desired temperature, which was controlled and measured to within 0.1° K. of the values reported, using a platinum resistance thermometer in conjunction with a temperature controller. The pressures were measured within ±0.1% of full scale using 0 to 100-atm. and 0 to 300-atm. Heise gages. The samples were analyzed using a gas chromatograph with a digital-integrating-voltmeter for measurement of the peak areas. The carbon dioxide used had maximum impurities of 100 p.p.m. The helium had maximum impurities of 50 p.p.m.

## RESULTS

The data are presented in Table I. The liquid and vapor phases were always analyzed for their minor component composition. The vapor phase data are reported as mole per cent carbon dioxide, and shown as a function of total pressure in Figure 1. The liquid phase data are reported as mole per cent helium, and shown as a function of total pressure in Figure 2. The compositions are believed to be accurate within ±5% of the minor component composition.

The experimental data were fitted by simple, algebraic equations to facilitate the use of the data, and to obtain a measure of the deviations of the data from smooth curves.

The equations used to fit the data were those of a previous investigation (*3*). Each vapor phase isotherm was fitted, by the method of least squares, to an equation of the form

$$\ln \phi = a_1(P - p^\circ) + a_2(P - p^\circ)^2 + a_3(P - p^\circ)^3 \qquad (1)$$

where $\phi$ is the enhancement factor, defined as the ratio of the partial pressure of carbon dioxide in the vapor to the vapor pressure of carbon dioxide at the same temperature. The values of $a_1$, $a_2$, and $a_3$ for each isotherm are given in Table II along with the standard per cent error (SPE), defined as the square root of the sum of the square of the individual per cent errors, and the maximum absolute per cent error (MAPE). The vapor phase data are represented by the equations with standard errors of less than 2% in all cases.

The liquid phase data were fitted in terms of the Henry's law constant, defined as the ratio of the total pressure minus the vapor pressure of carbon dioxide to the mole fraction of helium in the liquid phase, by an equation similar to Equation 1. The equation used was

$$\ln H = a_1 + a_2(P - p^\circ) + a_3(P - p^\circ)^2 \qquad (2)$$

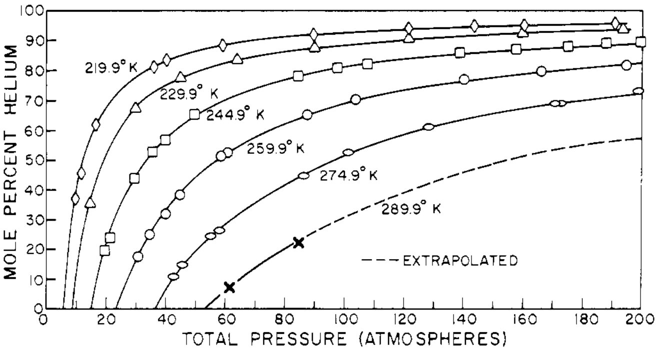

Figure 1. Composition of vapor phase helium vs. total pressure

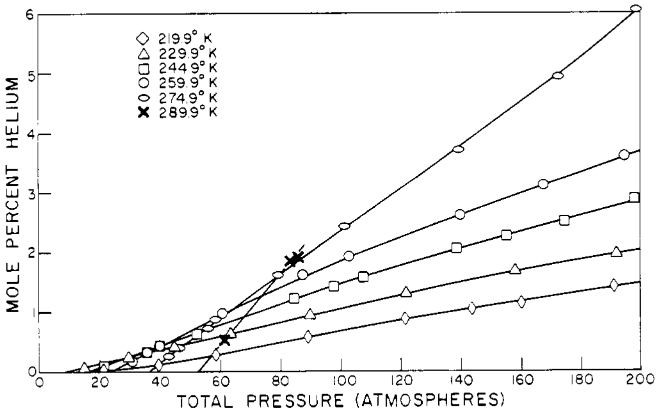

Figure 2. Composition of liquid phase helium vs. total pressure

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[1] Present address: Shell Chemical Co., Martinez, Calif.
[2] Present address: Shell Development Co., Emeryville, Calif.

Table I. Liquid-Vapor Equilibria of He-$CO_2$ System

| Temp., °K. | Pressure, Atm. | Liquid, Mole % He | Vapor, Mole % $CO_2$ |
|---|---|---|---|
| 219.9 | 9.8 | . . . | 62.8 |
| | 11.6 | . . . | 54.0 |
| | 16.3 | . . . | 37.9 |
| | 35.7 | . . . | 18.3 |
| | 89.2 | 0.581 | 7.75 |
| | 121.4 | 0.868 | 5.81 |
| | 143.5 | 1.03 | 5.02 |
| | 160.1 | 1.14 | 4.57 |
| | 190.8 | 1.41 | 3.88 |
| 229.9 | 14.4 | . . . | 64.6 |
| | 14.6 | 0.064 | . . . |
| | 29.4 | 0.241 | 32.6 |
| | 44.8 | 0.409 | 22.1 |
| | 63.1 | 0.529 | 16.4 |
| | 89.8 | 0.944 | 12.0 |
| | 121.3 | 1.29 | 8.92 |
| | 158.0 | 1.67 | . . . |
| | 159.4 | . . . | 6.75 |
| | 191.8 | 1.95 | . . . |
| | 193.5 | . . . | 5.93 |
| 244.9 | 19.5 | . . . | 80.2 |
| | 29.4 | . . . | 55.9 |
| | 39.6 | 0.440 | 43.0 |
| | 49.3 | . . . | 34.7 |
| | 52.1 | 0.643 | . . . |
| | 84.2 | 1.21 | 21.6 |
| | 97.9 | 1.41 | . . . |
| | 98.3 | . . . | 19.0 |
| | 107.4 | 1.56 | 17.7 |
| | 138.4 | 2.04 | 13.8 |
| | 155.0 | 2.26 | . . . |
| 244.9 | 157.4 | . . . | 12.6 |
| | 174.4 | 2.49 | . . . |
| | 175.0 | . . . | 11.7 |
| | 188.0 | . . . | 10.7 |
| | 197.7 | 2.86 | . . . |
| | 199.6 | . . . | 10.2 |
| 259.9 | 39.7 | 0.428 | 67.8 |
| | 44.7 | . . . | 61.7 |
| | 58.3 | . . . | 48.5 |
| | 60.8 | 0.960 | 47.1 |
| | 87.1 | 1.60 | 34.7 |
| | 102.6 | 1.82 | . . . |
| | 103.4 | . . . | 29.2 |
| | 139.8 | 2.59 | 22.9 |
| | 166.2 | 3.12 | 19.9 |
| | 194.5 | 3.60 | 17.6 |
| 274.9 | 42.6 | 0.267 | 89.1 |
| | 45.7 | 0.384 | 85.1 |
| | 55.3 | 0.738 | 75.3 |
| | 58.0 | 0.857 | 73.8 |
| | 79.0 | 1.62 | . . . |
| | 86.1 | . . . | 53.9 |
| | 101.2 | 2.41 | 47.3 |
| | 128.4 | . . . | 38.2 |
| | 139.4 | 3.71 | . . . |
| | 170.5 | . . . | 30.5 |
| | 172.8 | 4.92 | 30.4 |
| | 198.6 | 6.04 | 26.4 |
| 289.9 | 61.2 | 0.537 | 92.40 |
| | 83.0 | 1.84 | . . . |
| | 84.6 | 1.92 | 77.3 |

Table II. Least Square Fit of Enhancement Factors

| Temp., °K. | $a_1$ X$10^3$ | $a_2$ X$10^5$ | $a_3$ X$10^7$ | SPE | MAPE |
|---|---|---|---|---|---|
| 219.9 | 4.82247 | −4.16916 | 1.21950 | 1.68 | 3.41 |
| 229.9 | 5.16485 | −4.51413 | 1.34767 | 1.32 | 2.93 |
| 244.9 | 5.70187 | −4.54354 | 1.30688 | 1.95 | 3.69 |
| 259.9 | 7.21590 | −6.54261 | 2.11017 | 1.63 | 2.85 |
| 274.9 | 8.05364 | −6.67420 | 1.96711 | 1.52 | 2.54 |

Table III. Least Square Fit of Henry's Law Constant

| Temp., °K. | $a_1$ | $a_2$ X$10^4$ | $a_3$ X$10^5$ | SPE | MAPE |
|---|---|---|---|---|---|
| 219.9 | 9.60965 | −7.21829 | 0 | 1.85 | 3.07 |
| 229.9 | 9.06607 | 2.53432 | 0 | 2.56 | 4.60 |
| 244.9 | 8.61155 | 8.51465 | 0 | 1.10 | 1.88 |
| 259.9 | 8.20377 | 16.1047 | 0 | 2.04 | 4.18 |
| 274.9 | 7.80830 | 22.5736 | −1.03440 | 0.90 | 1.99 |

The values of $a_1$, $a_2$, and $a_3$ for each isotherm are given in Table III along with the standard per cent error and the maximum absolute per cent error. The liquid phase data are represented by the equations with standard errors of less than 2.6%.

No comparison with other data is possible, since none were found in the literature. No attempt was made to correlate or predict the data, since this will be the subject of a later paper.

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## NOMENCLATURE

$a_1, a_2, a_3$ = parameters fitted to data
$H$ = Henry's law constant, atm.
$P$ = total pressure, atm.
$p°$ = vapor pressure of carbon dioxide, atm.
$Y$ = mole fraction of carbon dioxide in vapor phase
$\phi$ = enhancement factor $\equiv YP/p°$

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