# Vapor-Liquid Equilibria and Dielectric Constants for the Helium-Carbon Dioxide System

**DIANA W. BURFIELD, H. P. RICHARDSON, and R. A. GUERECA**

**U.S. Department of the Interior, Bureau of Mines, Helium Research Center, Amarillo, Texas**

**Phase equilibria data are presented for the helium-carbon dioxide system at 253°, 273°, and 293°K. and pressures to 139 atm. Equilibrium is established under flow followed by nonflow conditions, and liquid and vapor samples are isolated without disturbing equilibrium. Liquid- and vapor-phase compositions are monitored with miniaturized capacitors, and compressibility factors are computed from resulting dielectric constants. The data are internally consistent and compare favorably with available literature values.**

Porter (*1*) did some early work on the phase equilibria of helium-carbon dioxide from 223° to 273°K. for design purposes for Bureau of Mines helium extraction plants, but the data are sparse. Barrick, Heck, and MacKendrick (*2*) recently published more extensive data in the temperature range from 220° to 290°K. and pressures to 200 atm.

A new type of apparatus, which eliminates equilibrium disturbances upon sampling, is described and tested from 250° to 293°K. and pressures to 139 atm. Capacitors are used to monitor liquid- and vapor-phase compositions (via the density-dependent dielectric constants) as an aid is determining sample homogeneity and equilibrium.

## EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus is shown in Figure 1. The main cell and the vapor and liquid traps are machined from 304 stainless steel. The nominal volume of the main cell is 350 cc.; the vapor and liquid traps are about 75 cc. each. Two fixed, parallel plate capacitors are located in the main cell and one in each trap. These stainless steel capacitors (I, II, III, and IV) are of reference standard type of design (*3*) but miniaturized to occupy less than 15 cc. bulk space and displace only 5 cc. volume. Six tension rods provide precise, parallel spacing (2 mm.) of the circular (15 mm. diameter) plates. Capacitances are measured with a transformer-ratio-arm capacitance bridge. A copper constantan thermocouple is located in the main cell; a pressure transducer is installed in a constant temperature enclosure. The cell system is suspended in an ethanol bath controlled to ± 0.03°K. A magnetic circulating pump moves fluids through the apparatus.

The cell system is evacuated and purged with gaseous carbon dioxide. Carbon dioxide is introduced at a pressure above its saturated vapor pressure at cell temperature. Liquefaction is allowed to occur until the liquid level is above capacitor II. Capacitors I and II read from 23 to 27 picofarads, depending on the temperature; III and IV read from 15 to 17 picofarads. Helium is admitted until the approximate datum point pressure is reached, and vapor is bubbled through the liquid with the magnetic circulating pump. The pump is stopped after about 15 min., and the system is permitted to stabilize. Pressure, temperature, and capacitances are monitored at intervals of 5 to 20 min. When these measurements are stable for 1 hr., equilibrium is assumed and valves isolating the traps are closed; the rest of the cell system is evacuated. The vapor trap is opened to an evacuated 500 cc. sampling bomb. The cell system is then evacuated, except the liquid trap, so that the liquid-phase sample may be flashed into the entire cell system. The flashed liquid sample is circulated and may be heated, if necessary, until all four capacitors indicate the same dielectric constant ($\epsilon$), and a temperature adjustment produces the same change in each dielectric constant. If this adjustment causes the dielectric constants to change relative to one another, two phases are probably present, with the liquid phase below capacitor I. When the criteria of equal dielectric constants and temperature response indicate a homogeneous single-phase system, the entire cell system is opened to a sampling bomb for analysis.

## CALIBRATION AND ACCURACY

Vapor and liquid sample analyses for both components were made by the Branch of Laboratory Services of the Helium Research Center by means of a calibrated mass spectrometer (*4*). These results are tabulated in Table 1. Estimated accuracies are 3% for the lowest concentration of helium in the liquid phase (0.1 mole %) and at least 0.1% for the highest concentration shown (4.93 mole %). For the carbon dioxide, the mass spectrometer analyses should be accurate to at least 0.1 mole %. The helium used is Bureau of Mines Ultrapure Helium, containing less than 35 p.p.m. total impurities. The carbon dioxide contains less than 20 p.p.m. total impurities, principally nitrogen and oxygen.

The thermocouple, referenced to a ± 0.005°C. electronically controlled temperature bath, is calibrated with a platinum resistance thermometer and a Mueller temperature bridge, each certified by the National Bureau of Standards. Thermocouple temperatures are accurate to ± 0.05°C. The pressure transducer is calibrated with a 0.01% accurate dead weight gauge primary standard and is kept at 35 ± 0.5°C. to minimize pressure errors from thermal resistance changes. The error of the pressure measurements is no more than ± 0.1 atm.

For a parallel plate capacitor, the capacitance $C$ is given by

$$C = \frac{\epsilon k A (n-1)}{4\pi d} \qquad (1)$$

where, by definition, $\epsilon = 1$ for a vacuum. By assuming that the capacitor geometric constants are pressure independent, $\epsilon$ is obtained by dividing the capacitance by the vacuum capacitance value:

---

Diana W. Burfield is with the Shell Chemical Company, Denver, Colorado.

Table 1. Experimental Data for the Helium-Carbon Dioxide System

| $T$, °K. | $P_{01}$, atm. | $P_T$, atm. | $x_2 \times 100$ | $y_2 \times 100$ | $\epsilon^L$ | $\epsilon^V$ | $Z^L$, calc. | $Z^V$, calc. |
|---|---|---|---|---|---|---|---|---|
| 293.13 | 56.58 | 56.56 | 0.00 | 0.00 | 1.4692 | 1.1039 | 0.134 | 0.542 |
| | | 65.20 | 0.69 | 7.05 | 1.4715 | 1.1039 | 0.153 | 0.583 |
| | | 76.41 | 1.37 | 13.80 | 1.4730 | 1.1043 | 0.178 | 0.635 |
| | | 86.89 | 1.90 | 19.60 | 1.4743 | 1.1047 | 0.200 | 0.675 |
| | | 95.76 | 2.37 | 24.66 | 1.4765 | 1.1050 | 0.219 | 0.699 |
| | | 105.37 | 3.03 | 28.43 | 1.4768 | 1.1056 | 0.239 | 0.730 |
| | | 119.52 | 3.70 | 34.29 | 1.4780 | 1.1065 | 0.269 | 0.759 |
| | | 127.40 | 4.27 | 38.89 | 1.4813 | 1.1046 | 0.284 | 0.772 |
| | | 139.26 | 4.93 | 41.60 | 1.4810 | 1.1071 | 0.308 | 0.793 |
| 273.26 | 34.55 | 34.53 | 0.00 | 0.00 | 1.5796 | 1.0515 | 0.073 | 0.704 |
| | | 37.32 | 0.10 | 4.48 | 1.5799 | 1.0517 | 0.079 | 0.726 |
| | | 40.31 | 0.22 | 9.41 | 1.5806 | 1.0517 | 0.085 | 0.746 |
| | | 48.83 | 0.29 | 14.34 | 1.5802 | 1.0518 | 0.093 | 0.769 |
| | | 51.02 | 0.48 | 22.25 | 1.5817 | 1.0521 | 0.108 | 0.814 |
| | | 60.86 | 0.89 | 31.97 | 1.5826 | 1.0531 | 0.128 | 0.844 |
| | | 66.42 | 1.42 | 36.30 | 1.5837 | 1.0531 | 0.138 | 0.869 |
| | | 74.51 | 1.73 | 42.32 | 1.5852 | 1.0537 | 0.155 | 0.882 |
| | | 80.91 | 1.81 | 45.94 | 1.5849 | 1.0543 | 0.168 | 0.895 |
| | | 87.84 | 2.10 | 49.83 | 1.5860 | 1.0545 | 0.181 | 0.907 |
| | | 106.74 | 2.68 | 57.75 | 1.5879 | 1.0556 | 0.218 | 0.931 |
| | | 127.43 | 2.93 | 63.94 | 1.5897 | 1.0573 | 0.259 | 0.943 |
| | | 134.60 | 3.10 | 65.69 | 1.5908 | 1.0576 | 0.273 | 0.953 |
| 253.11 | 19.46 | 19.58 | 0.00 | 0.00 | 1.6588 | 1.0276 | 0.040 | 0.792 |
| | | 29.45 | 0.20 | 28.60 | 1.6615 | 1.0287 | 0.060 | 0.845 |
| | | 34.91 | 0.41 | 34.94 | 1.6596 | 1.0286 | 0.072 | 0.926 |
| | | 46.74 | 0.55 | 50.70 | 1.6617 | 1.0287 | 0.096 | 0.964 |
| | | 54.64 | 0.70 | 57.23 | 1.6619 | 1.0301 | 0.111 | 0.953 |
| | | 63.23 | 0.80 | 63.00 | 1.6636 | 1.0304 | 0.129 | 0.965 |
| | | 76.42 | 1.02 | 68.36 | 1.6644 | 1.0313 | 0.155 | 0.994 |
| | | 89.51 | 1.34 | 73.23 | 1.6660 | 1.0323 | 0.181 | 0.987 |
| | | 108.76 | 1.61 | 78.76 | 1.6676 | 1.0331 | 0.218 | 0.984 |
| | | 115.66 | 1.90 | 79.91 | 1.6695 | 1.0339 | 0.231 | 0.977 |
| | | 137.06 | 1.73 | 81.83 | 1.6718 | 1.0353 | 0.274 | 1.038 |

$$\frac{C_{T,P}}{C_{T,\mathrm{vacuum}}} = \epsilon_{T,P} \tag{2}$$

If the capacitors are stable within the ± 0.0002 picofarad accuracy of the measuring bridge, dielectric constants can be determined to ± 0.00003. The capacitors are probably accurate to ± 0.0005 picofarad.

## ESTIMATION OF COMPRESSIBILITIES

To compute the compressibilities given in Table 1, the molar densities are first computed from the Clausius-Mosotti (C.M.) function:

$$\text{C.M.} = \left(\frac{\epsilon - 1}{\epsilon + 2}\right)\frac{1}{\rho} \tag{3}$$

Experimental dielectric constants (Table 1) and estimated mixture C.M. values are used in Equation (3).

The value of C.M. for each helium-carbon dioxide equilibrium composition is computed from the C.M. values for the pure components. Since neither helium nor carbon dioxide has a permanent dipole moment, the C.M. function for these molecules is directly proportional to the molecular polarizabilities and should be independent of temperature (*5, 6, 7*). The C.M. function is not independent of density. However, Keyes and Kirkwood (*8*) show that the C.M. function for liquid carbon dioxide is nearly constant to pressures of 200 atm. at 0°C.; the total deviation in C.M. in going from gas at the lowest density to liquid is 4%. Table 2 gives computed values of the C.M. function for carbon dioxide by using the experimental dielectric constants from Table 1 and densities taken from Quinn and Jones (*9*). For pure carbon dioxide, the value of 7.71 is selected for use in all calculations of mixture C.M. values. For helium, a value of C.M. = 0.52 is taken as representative. Johnston, Oudemans, and Cole (*10*) show that C.M. for helium varies from 0.5220 to 0.5207

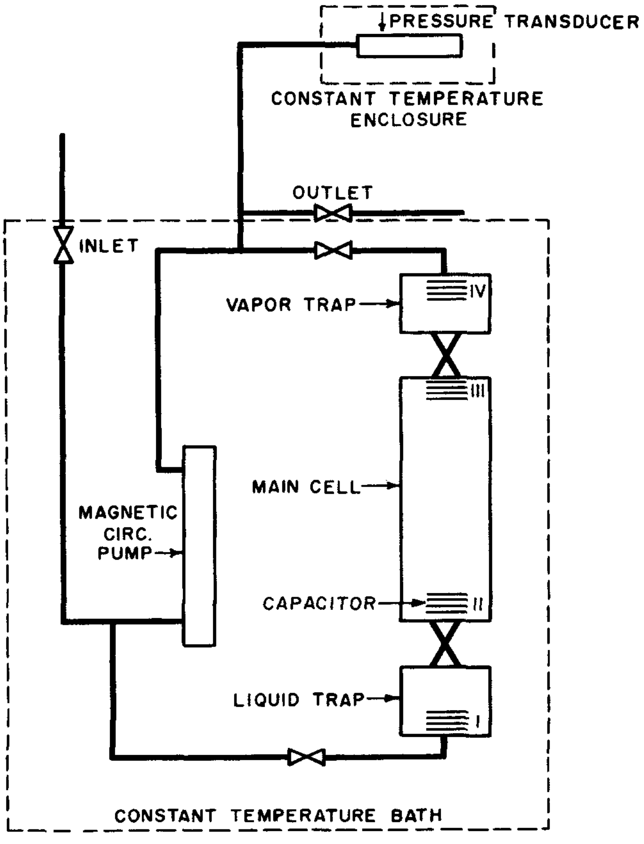

Fig. 1. Equilibrium apparatus.

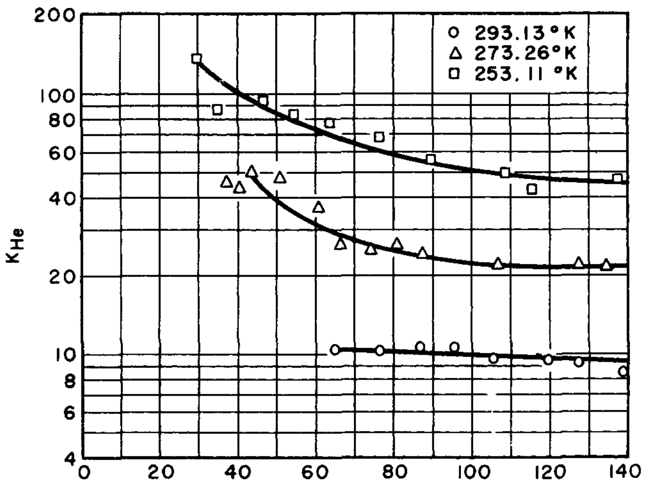

Fig. 2. Helium K factors.

for densities from 0 to 3.7 moles/liter. Pure helium densities at the experimental conditions are in general between 2 and 3 moles/liter.

The mixture C.M. values are computed from

$$C.M.^L{}_{1-2} = C.M._1x_1 + C.M._2x_2 \tag{4}$$

and

$$C.M.^V{}_{1-2} = C.M._1y_1 + C.M._2y_2 \tag{5}$$

According to Hirschfelder, Curtiss, and Bird (*5*), this method for computing mixture C.M. values is justified for mixtures of molecules with no permanent dipole moments, except at high densities or field intensities.

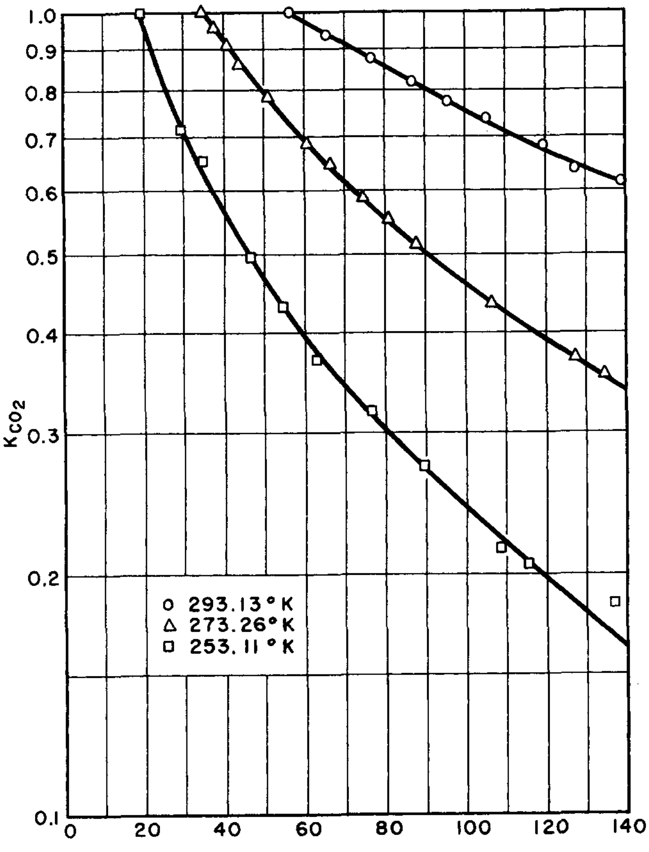

Fig. 3. Carbon dioxide K factors.

TABLE 2. CLAUSIUS-MOSOTTI FUNCTION FOR CARBON DIOXIDE

| $T$, °K. | $\rho_1{}^L$, g./cc. | $\rho_1{}^V$, g./cc. | C.M.$^L$ | C.M.$^V$ |
|---|---|---|---|---|
| 253.11 | 1.031 | 0.0530* | 7.69 | 7.57* |
| 273.26 | 0.924 | 0.0993 | 7.71 | 7.48 |
| 293.13 | 0.772 | 0.1910 | 7.71 | 7.71 |

* An extrapolated value.

Compressibilities for liquid or vapor are computed from the following equations:

$$Z^V = \frac{(P_T)(C.M.^V)(\epsilon^V + 2)}{(\epsilon^V - 1)RT} \tag{6}$$

and

$$Z^L = \frac{(P_T)(C.M.^L)(\epsilon^L + 2)}{(\epsilon^L - 1)RT} \tag{7}$$

The error in the compressibilities caused by the assumption of a constant C.M. value for carbon dioxide is considered negligible for the vapor phase above 50 atm. and for the liquid at all pressures. The maximum vapor compressibility error is 0.04.

## DISCUSSION OF RESULTS

Experimental results are summarized in Table 1. Experimental vapor pressures of pure carbon dioxide are shown with the two-component data. The tabulated value of $P_{01}$ at each temperature is computed from Equation (6) given by Meyers and Van Dusen (*11*); experimental and computed vapor pressures agree within the errors of temperature and pressure measurements. Experimental dielectric constants computed from Equation (2) are given for the liquid and vapor phases. A literature value of 1.583 (*12*) for the dielectric constant of pure liquid carbon dioxide at 0°C. compares favorably with the experimental value of 1.5796 at 273.26°K. Estimated vapor-phase compressibility factors at 293° and 273°K. compare very favorably with those determined by an entirely different (Burnett type of measurements) method (*13*).

Figure 2 shows the helium $K$ factor data. The smooth curves give the very low pressure data less weight than the other data. Helium $K$ factors at infinite dilution ($K_2{}^\infty$) were computed from Table 2 densities and graphs of $P_T$ vs. $x_2$ for each isotherm by using the following equation (14):

$$\left(\frac{dx}{dP}\right)^\infty_{T,x=0} = \frac{v_1{}^V - v_1{}^L}{RT(K_2{}^\infty - 1)} \tag{8}$$

The $K_2{}^\infty$ values are 9.5 at 293°K. and 51.7 at 273°K. and fit well in Figure 2; the $K_2{}^\infty$ value at 253°K. is 8,566, where $v_1{}^V$ is obtained from the extrapolated density. Figure 3 gives the carbon dioxide $K$ factors.

The enhancement factor $\phi$, as defined by Dokoupil et al. (*15*), is plotted in Figure 4 and gives reasonably smooth curves with similar trends for the three isotherms, indicating the internal consistency of the data and the deviations from ideality of the vapor phase. Based on best least-square curve fits, the standard errors of the carbon dioxide vapor-phase data are 0.68, 1.60, and 2.02 mole %, respectively, for the 293°, 273°, and 253°K. isotherms. The scatter in the 253°K. isotherm data at higher pressures indicates the probable need for further experimental work in this area.

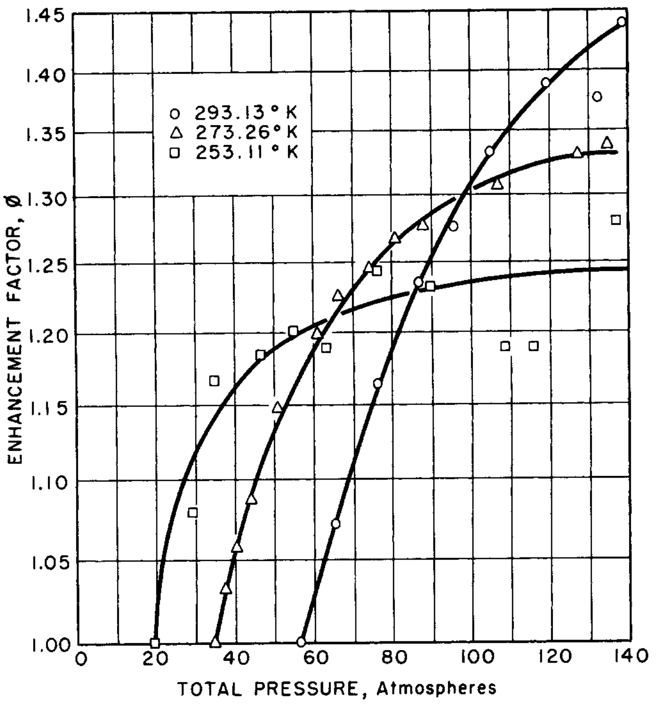

Fig. 4. Enhancement factors.

The helium composition data of Barrick et al. (2), at 244°, 260°, 275°, and 290°K., were smoothed by two-variable, least-square curve fits (second order in pressure and second order in temperature for the liquid phase and third order in pressure and second order in temperature for the vapor phase). Based on the curve fits, the standard errors of their experimental data were 0.018 (liquid) and 2.922 (vapor) mole %; the maximum, single-point deviations were 0.5 (liquid) and 6.7 (vapor) mole %. The two empirical equations are used to compute hypothetical helium compositions at the temperatures and pressures of this investigation. Based on these hypothetical values, estimates for standard deviations (*16*) of our data are 0.340 (liquid) and 2.057 (vapor) mole %; maximum single deviations are 0.67 (liquid) and 6.64 (vapor) mole %. Comparatively good agreement is indicated. Also, Porter's data (*1*) at 0° and −19.07°C, are consistent with our experimental results. (Two other points are reported by Porter: one at −50°C, and 58.8 atm., $x_2 = 0.00490$ and $y_2 = 0.869$; one at −34.94°C. and 58.8 atm., $x_2 = 0.00656$ and $y_2 = 0.757$.)

## CONCLUSIONS

The experimental apparatus and methods give reasonably consistent and accurate phase equilibria data, plus new, two-phase dielectric constant data, from which two-phase compressibilities are estimated. Vapor-phase compressibilities are in very good agreement with those determined by an independent method and strongly indicate the validity of the assumptions made concerning the C.M. function. The liquid-phase compressibilities also need to be checked by an independent method. The enhancement factor shows the nonideality that can be expected with the presence of helium in the liquid-vapor systems.

## ACKNOWLEDGMENT

The authors appreciate the assistance of John L. Gordon and Paul W. Woodward of the Helium Research Center for valuable suggestions concerning the C.M. treatment and for experimental work on the lowest isotherm, respectively.

## NOTATION

$A$ = area of capacitor plates, sq. cm.
$C$ = capacitance, picofarads
C.M. = Clausius-Mosotti function, cc./mole
$d$ = distance between capacitor plates, cm.
$k$ = conversion constant to change capacitance from electrostatic units to picofarads
$K$ = ratio of mole fraction in vapor phase to mole fraction in liquid phase, $y/x$
$n$ = number of plates in capacitor
$P$ = pressure
$P_0$ = vapor pressure, atm.
$P_T$ = total pressure, atm.
$R$ = universal gas constant
$T$ = temperature, °K.
$v$ = molar volume, cc./mole
$x$ = mole fraction in liquid phase
$y$ = mole fraction in vapor phase
$Z$ = compressibility
$\epsilon$ = dielectric constant
$\phi$ = enhancement factor, $y_1 P_T / P_{01}$
$\rho$ = density, moles/cc.

### Subscripts

1 = carbon dioxide
2 = helium

### Superscripts

$L$ = liquid phase
$V$ = vapor phase

## LITERATURE CITED

1. Porter, Frank, unpublished data on file at the U.S. Bureau of Mines Helium Research Center (1925).
2. Barrick, P. L., C. K. Heck, and R. F. MacKendrick, *Air Force Materials Laboratory Technical Rept. AFML-TR-67-160* (1967).
3. Hersch, J. F., *General Radio Experimenter,* **37,** No. 8, 1-8 (1963).
4. Miller, J. E., A. J. Carroll, and D. E. Emerson, *U.S. Bureau of Mines Report of Investigations 6674* (1965).
5. Hirschfelder, Joseph O., Charles F. Curtiss, and R. Byron Bird, "Molecular Theory of Gases and Liquids," pp. 857-861, Wiley, New York (1964).
6. Smyth, Charles Phelps, "Dielectric Behavior and Structure," Chapt. 1, McGraw-Hill, New York (1955).
7. Moore, Walter J., "Physical Chemistry," 3 ed., p. 557, Prentice Hall, Englewood Cliffs, N. J. (1962).
8. Keyes, Frederick G., and John G. Kirkwood, *Phys. Rev.,* **36,** 754 (1930).
9. Quinn, Elton L., and Charles L. Jones, "Carbon Dioxide," pp. 38-39, Reinhold, New York (1936).
10. Johnston, D. R., G. J. Oudemans, and R. H. Cole, *J. Chem. Phys.,* **33,** No. 5, 1310 (1960).
11. Meyers, C. H., and M. S. Van Dusen, *J. Res. Natl. Bur. Std.,* **10,** 381 (1933).
12. Quinn, Elton L., and Charles L. Jones, *op cit.,* p. 79.
13. Weems, G. W., and N. L. Miller, *U.S. Bureau of Mines Helium Research Center Internal Rept. 109* (1967).
14. Barieau, Robert E., *U.S. Bureau of Mines Helium Research Center Memo. Rept.* **36** (1964)
15. Dokoupil, Z., G. van Soest, and M. D. P. Swenker, *Appl. Sci. Res.,* **A5,** 192 (1955).
16. Alder, Henry L., and Edward B. Roessler, "Introduction to Probability and Statistics," pp. 123-124, W. H. Freeman, San Francisco, Calif. (1964).

*Manuscript received January 26, 1968; revision received August 5, 1968; paper accepted August 7, 1968.*