Multicomponent Vapor-Liquid Equilibria at High Pressures:

Part I. Experimental Study of the Nitrogen—Oxygen—Carbon Dioxide System at 0°C.

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A description is given of a dynamic vapor-liquid equilibrium apparatus in which both phases are recirculated by vane pumps especially designed for high-pressure service. Equilibrium phase compositions as well as vapor and liquid molar volumes up to the critical pressure are reported for the two binary systems nitrogen-carbon dioxide and oxygen-carbon dioxide and for the ternary.

One of the ultimate goals of chemical engineering thermodynamics is the establishment of techniques for predicting the properties of any mixed system from the pure-component properties of its constituents. Lacking such techniques, a secondary, but still very useful, goal in many areas is the development of methods whereby a small amount of binary data may serve as the basis of analytical expressions which can then be used for interpolation and extrapolation of the original data. Such methods can be developed by thermodynamic analysis.

The accomplishment of this secondary goal not only greatly reduces the amount of data which must be taken to define a system, but the thermodynamic analysis involved frequently allows the chemical engineer to narrow greatly the regions and conditions that are of interest to him, eliminating the necessity of experimental exploration of all possible variations of conditions. When multicomponent systems are considered, the economies of thermodynamic analysis are especially important, since the amount of data required to define vapor-liquid equilibria for a ternary system, for example, is manyfold greater than the data needed to define experimentally a binary system.

One of the objectives of this work is the reduction of sets of high-pressure, binary vapor-liquid equilibrium data to basic thermodynamic quantities, and the use of these quantities for the prediction of the vapor-liquid equilibria of a ternary mixture at high pressure. This problem has been considered by numerous authors, but in all previous work the ternary systems under consideration were at low or moderate pressures and contained three components which in their pure state could exist as liquids at the system temperature. This work, however, considers a ternary system wherein two of the components cannot exist as pure liquids at the system temperature. As a result, it is necessary to predict the behavior of the ternary system from data for only two binary systems, since the third binary, consisting of the two light components, cannot exhibit vapor-liquid equilibria at the system temperature.

This work considers the ternary system nitrogen–oxygen–carbon dioxide at 0°C. Part I describes the experimental apparatus and reports experimental results for the two binaries nitrogen–carbon dioxide and oxygen–carbon dioxide and for the ternary. Phase compositions and molar volumes for both phases are reported up to the critical pressure. Part II describes a thermodynamic analysis of the experimental data.

EXPERIMENTAL PHASE EQUILIBRIUM APPARATUS

Of the problems encountered in vapor-liquid equilibria at elevated pressures, two are the most troublesome: the method

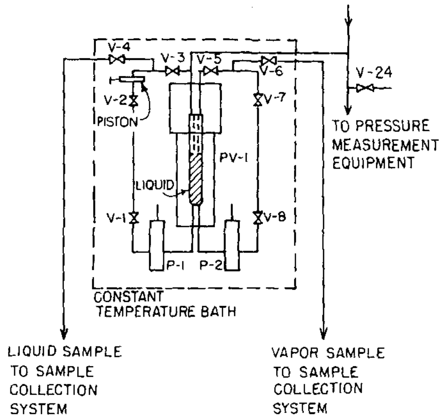

Fig. 1. Flow diagram of equilibrium system.

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of agitating the system to hasten the approach to equilibrium and the withdrawal of samples from the equilibrium phases without disturbing the equilibrium. Usual methods of agitation include shaking, stirring, and circulation of one or both of the phases. Sampling is usually done by cracking valves to release a small portion of the phases into collection equipment. This technique requires the assumption that the samples are withdrawn before the equilibrium is significantly affected by the reduction in pressure. The problems of sampling and of the agitation of the phases were both solved in the equipment described here by the use of a circulation system. Each phase was circulated through tubing external to the equilibrium cell, thus providing ample agitation. Samples were obtained by blocking off sections of the circulation line. The calibration of these sample spaces permitted the determination of the molar volumes of the equilibrium phases as well as their composition.

The design and construction of the equipment used in this study was begun by Miner (5). His equipment was designed for the study of the solubility of nitrogen and oxygen in liquid carbon dioxide at temperatures between —40° and +30°C. and at pressures up to 15,000 lb./sq. in.

The equilibrium apparatus is basically a heavy-walled, stainless steel equilibrium cell with circulating lines and pumps, all of which are enclosed in a constant-temperature bath. The tubing and valves used throughout the equilibrium and loading sections are ¼-in. Aminco superpressure equipment.

Figure 1 gives a simplified flow diagram of the equilibrium system. Vapor is pumped out of the top of the equilibrium cell by pump P-2 and then enters the bottom of the cell and bubbles through the liquid. The liquid is pumped out of the bottom of the equilibrium cell by pump P-1 and returned to the top of the cell.

Equilibrium Cell

The equilibrium cell PV-1 (shown in longitudinal section in Figure 2) is a standard Aminco cell, catalogue No. 41-4900. The body is of A.I.S.I. 403 stainless steel, designed for a maximum working pressure of 18,000 lb./sq. in. at 100°F. Wall thickness is 25/16 in. The capacity is approximately 200 cc. The vessel weighs 70 lb.

An outside cap type of closure consists of five parts (Figure 2): outside cap that screws onto the body of the vessel, thrust bolts, hardened-steel thrust ring that keeps the thrust bolts from marring the pressure head, inner pressure head, and stainless steel delta gasket. Vent holes in the cap provide pressure relief in the event of gasket failure or leakage.

The bottom of the cell and the top of the pressure head are each fitted with two standard Aminco tubing fittings which serve as entrance and exit points for the pumped fluids. A piece of tubing attached to the inlet on the pressure head directs the liquid flow against the inner wall of the cell. A baffle was attached to the thermowell to prevent liquid entrainment in the vapor stream. A level indicator has been attached to the thermowell. Two wires, servicing the level indicator, pass through cone-compression electrical fittings in the pressure head.

High-Pressure Vane Pumps

The design of pumps to circulate the vapor and liquid streams was a major design obstacle of this project. Pumps were required which could withstand internal pressures up to 15,000 lb./sq. in. without substantial leaks, pump at a rate of 10 to 100 cc./min., and produce a head of 1 ft. of fluid.

The pumps chosen were designed and developed by J. G. Dorward, Jr., of the Lawrence Radiation Laboratory at Berkeley. The vapor and liquid pumps are identical. The design is a variation of a vane pump with cylindrical rollers acting as vanes moving the fluid from inlet to outlet. The rollers are mounted on an eccentric rotor which is driven by a shaft that passes out of the pump through packing. A blind shaft vented to the external pressure is provided on the other side of the rotor to eliminate a pressure imbalance on the drive shaft.

Teflon V-ring packing was used for packing both ends of the rotor shaft. Internal pressure tends to make the V's straighten out, which forces them more tightly against the shaft. This packing accomplishes its objective quite effectively; however, some problems were caused by the Teflon's tendency to flake off under prolonged use. Some of these flakes worked their way into the pump cavity requiring occasional shutdowns to dismantle and clean the pumps. This flaking was reduced, but not eliminated, by lubricating the shafts with a fluorosilicone lubricant.

One end of the pump is designed with a removable, seal body which is bored to receive the shaft and packing. A Teflon O-ring was used to seal the joint between the seal body and the pump body. Sectional drawings of the pumps are given in Figures 3 and 4.

The bodies of the pumps are 304 stainless steel. The seal body and packing nuts are 303 stainless steel, and the rotor is Monel. The rollers are made of Rulon A (an oxide-impregnated Teflon).

These pumps were operated with the shafts in a vertical position with the end of the rotor resting on the end of the pump cavity. In this design the only lubrication is that provided by the fluid being pumped. The resulting metal-to-metal friction in the original pump design proved to be quite troublesome, giving rise to considerable abrasion of the rotor and scoring of the end of the pump cavity. This problem was corrected by plating the ends of the rotor with hard chrome and by using a plastic insert in the end of the pump cavity. The insert used was a disk of Fluoroscint about 0.055 in. thick. This material is an impregnated Teflon similar to the material used as the roller vanes in the pump. The Fluoroscint was chosen because of its low thermal coefficient of

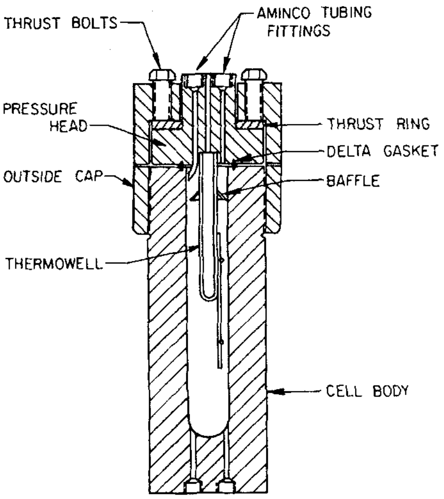

Fig. 2. Equilibrium cell, PV-1, longitudinal section.

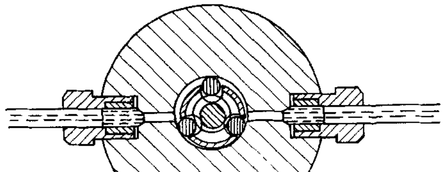

Fig. 3. High-pressure vane pump, section through cavity.

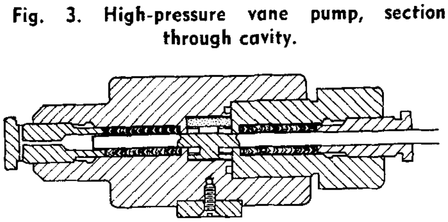

Fig. 4. High-pressure vane pump, longitudinal section.

expansion, inertness, durability, and lubrication properties. Both pumps were driven by Zero-Max variable-speed motors with a speed range of 0 to 400 rev./min. in either a clockwise or counterclockwise direction. Both pumps were operated in the range 12 to 20 rev./min., which produced flow rates of the order of 15 to 20 cc./min.

Constant-Temperature Bath

The equilibrium equipment was enclosed in a constant-temperature bath which was equipped to maintain temperatures ranging from —40° to +30°C. Cooling was provided by a refrigeration unit, and the temperature was controlled by heat input from heaters totaling 2,500 w. The bath fluid was an ethylene glycol–water mixture chosen for its suitable viscosity over the specified temperature range and its nontoxicity.

Because it is extremely difficult to control a refrigeration unit very closely, the temperature control of the bath was by heat input. A "Resistotrol" temperature controller regulated the power input to blade heaters. The manufacturer claims 0.01°C. temperature control. The bath fluid was thoroughly stirred by two stirrers.

GAS LOADING AND PURIFICATION

The equilibrium system has been designed for pressures up to 15,000 lb./sq. in. since gas cylinders normally deliver gas up to only 2,000 or 3,000 lb./sq. in., some means was needed to increase the pressure. Figure 5 illustrates the simple procedure used to do this. The polystyrene casings surrounding the gas-loading vessels were filled with liquid nitrogen. The oxygen or nitrogen at a pressure of 50 to 60 lb./sq. in. gauge was then fed through its purification vessel into its gas-loading vessel where it condensed. At these pressures, approximately 15°C. ΔT was available for condensing the nitrogen and 30°C. ΔT for the oxygen condensation. This was sufficient to fill the vessel in less than 30 min. The loading vessels had a capacity of 11.7 std. cu. ft. of nitrogen or 15.1 std. cu. ft. of oxygen. The approximate amount of gas liquified could be determined from the cylinder regulator gauge.

When the vessels were allowed to warm up to room temperature, considerable pressure was developed. If the vessels were completely full of liquid, this pressure would have been about 39,000 lb./sq. in. The loading vessels were hydrostatically tested to 40,000 lb./sq. in.; however, this much pressure was not needed, and the vessels were never completely filled with liquid.

The nitrogen, oxygen, and carbon dioxide (Coleman grade) had a specified purity of at least 99.99%.

Carbon dioxide was loaded directly into the equilibrium cell, passing through the purification vessel. The carbon dioxide is collected as a liquid; this requires only that the equilibrium cell be at a lower temperature than that of the carbon dioxide cylinder during the loading operation. Each gas passed through a purification vessel containing activated silica gel and "Drierite."

TEMPERATURE AND PRESSURE MEASUREMENT

The temperature of the constant-temperature bath surrounding the equilibrium cell was determined with a thermometer calibrated by the National Bureau of Standards. It was assumed that this temperature was the same as that inside the equilibrium cell. The only eventuality likely to negate this assumption would be the addition of sufficient energy by the circulation pumps to raise the temperature inside the equilibrium cell. The thermowell that reaches into the interior of the equilibrium cell offered an opportunity to check this possibility as well as a check of the temperature at a location closer to the equilibrium mixture than the constant-temperature bath. A thermocouple in this thermowell showed no discernible temperature difference with the pumps off for extended periods of time and with the pumps on. Thus it is assumed that the material within the equilibrium cell was at the same temperature as that of the constant temperature bath.

The equilibrium pressure was measured with an Aminco pressure balance. This instrument is a very accurate pressure measuring device of the floating-piston type. The model used was accurate to 0.1% over its entire range of 35 to 20,000 lb./sq. in. gauge.

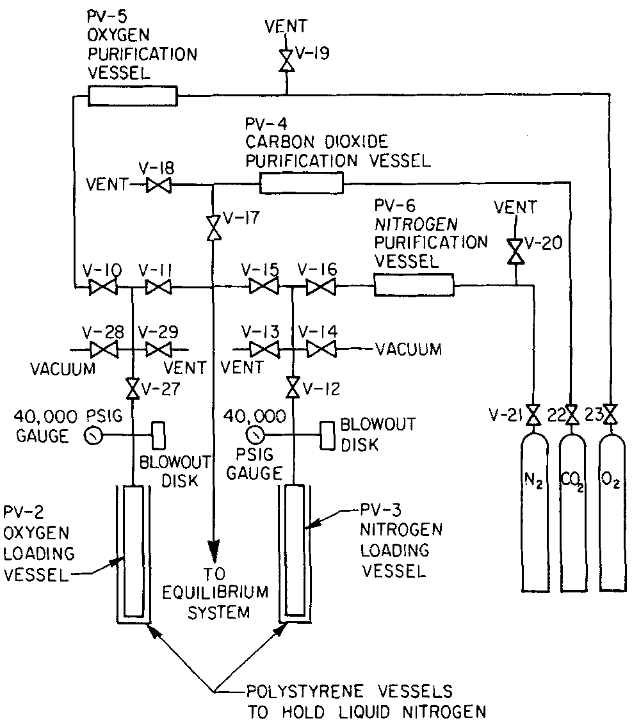

Fig. 5. Gas loading and purification system.

SAMPLE COLLECTION

The vapor sample is isolated between valves V-8 and V-7 and drawn off through valve V-6 after the space between valves V-5, V-7, and the sample collection system have been evacuated. The liquid sample is trapped between valves V-1 and V-2 and treated in a manner similar to that used for the vapor sample.

During vapor sampling, the vapor pump was operated at the lowest rate in order to prevent liquid entrainment. The condensation of saturated vapor on the wall of the sample space (which affects the vapor molar volume but not the equilibrium composition) was eliminated by a heating tape which maintained the outer wall of the sampling space at about 1°C. higher during vapor sampling.

During liquid sampling, the vapor pump was turned off, and the liquid pump was operated at the lowest rate in order to prevent entrainment of vapor into the liquid sample. Small vapor bubbles formed from the saturated liquid in passing the liquid pump (which affects liquid molar volume but not the equilibrium composition) were eliminated in the following manner. Valves V-3 and V-1 were closed, isolating a large portion of the liquid. The piston was then turned in compressing the fluid in the liquid sample line until increased resistance was felt. Any overcompression was released by cracking valve V-3. Valve V-2 was then closed, isolating the liquid sample which was then removed for analysis.

To analyze the high-pressure liquid and vapor samples from the equilibrium system, they had to be moved to glassware at less than atmospheric pressure where both samples are gases. Before analysis, the entire sample was moved into a calibrated glass collection vessel for a pressure, volume, and temperature measurement from which the density of the sample at equilibrium conditions was calculated.

Four or five cycles of the Toepler pump were found to be sufficient to move the last of the gas from the tubing into the collection vessel. During the original adiabatic expansion of the sample it is possible that some carbon dioxide solidified in the sample tubing. However, if this did occur, the carbon dioxide revaporized quickly (at least during the time required for Toepler pump operation) because further cycles of the Toepler pump after a long pause did not produce a significant quantity of gas.

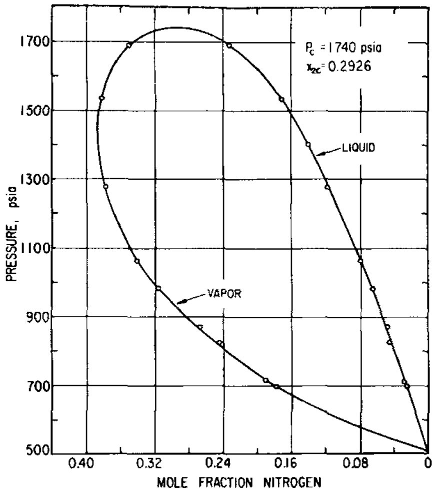

Fig. 6. Pressure vs. composition for the nitrogen-carbon dioxide system at 0°C.

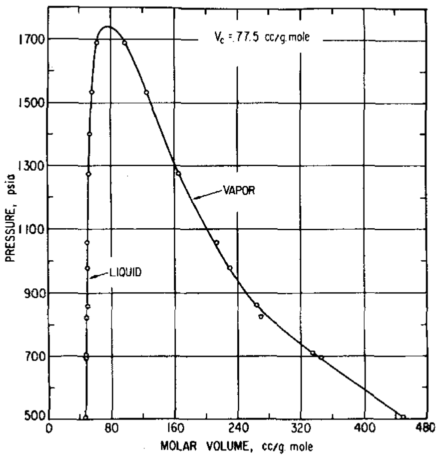

Fig. 7. Pressure vs. liquid and vapor molar volumes for the nitrogen-carbon dioxide system at 0°C.

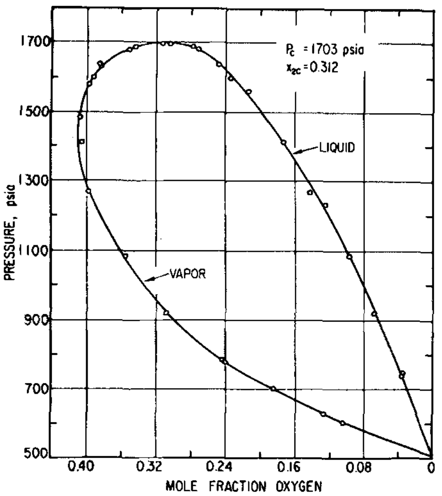

Fig. 8. Pressure vs. composition for the oxygen-carbon dioxide system at 0°C.

MOLAR VOLUME DETERMINATION

One of the advantages of this experimental apparatus was the relative ease with which the molar volumes of the equilibrium phases were determined. This was done by measuring volumetrically at low pressure the amount of material withdrawn from the calibrated sample space.

The volumes of the liquid and vapor sample spaces were determined from pure carbon dioxide vapor at 0°C. The equilibrium cell was filled with carbon dioxide vapor at a pressure less than its saturation pressure of 505.5 lb./sq. in. abs. The pressure in the cell was measured with the pressure balance. The sample space valves were then closed and the sample withdrawn. The sample pressure and volume were then measured as described above. With the virial coefficients determined by Michels and Michels (*4*) used, the number of moles of gas withdrawn from the sample space was calculated. These coefficients were also used to calculate the molar volume of the gas at the measured cell pressure. From the molar volume of the gas and the number of moles of gas, the volume of the sample space was calculated.

The calibration of the sample spaces was checked by measuring the molar volume of pure, two-phase carbon dioxide at the bath temperature (0°C.). The correct molar volume of the vapor was calculated from the virial coefficients, while the molar volume of the liquid used was taken from Din (*2*).

ANALYTICAL PROCEDURE

The chemical analysis of both liquid and vapor samples is carried out in the vapor phase. The analytical procedure involves the successive removal of the carbon dioxide and oxygen by dry reactants. The gas remaining after these reactions is assumed to be nitrogen. The carbon dioxide is removed by absorption with "Ascarite," a sodium hydroxide on asbestos absorbent. Oxygen is removed by reaction with active copper at 200°C. The active copper is prepared by the reduction of cupric oxide with hydrogen in accordance with the method described by Meyer and Rounge (*3*).

Numerous analyses of samples of known composition indicated that the mole fractions determined were accurate to 0.001 or 0.002. It was deemed advisable to check the completeness of the removal of the reaction gases; frequently, therefore, following an absorption step, the sample was passed through the reaction vessel a second time and a PVT reading again taken. A decrease in the amount of gas at this point indicates incomplete removal of a component during the previous step. This problem was only encountered if the Ascarite (carbon dioxide absorbent) was not replaced frequently. This material seemed to lose some of its efficiency before its color change indicated that it had been used up. This second absorption step also served the purpose of checking for leaks, since an increase in the amount of gas measured indicates a leak in the analytical system.

A digital computer program was written to calculate the composition of the gas sample from the set of PVT measurements described. The virial equation was used to compute the number of moles of gas in each measurement. This equation was used in the form

$$PV = n_T RT \left[1 + \frac{n_T B_m}{V} \right] \qquad (1)$$

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \qquad (2)$$

The equation of Pitzer and Curl (*7*) was used to calculate the virial coefficients B_{ij}. After the composition of the sample had been computed, the program calculated the molar volume of the sample.

Further details on the equipment, as well as a complete description of the experimental procedure, are available elsewhere (*6*).

RESULTS

The critical pressures of the binaries were determined by extrapolating $(y - x)^2$ to zero on a plot vs. pressure. The critical compositions and molar volumes were determined by the application of the law of rectilinear diameters, whereby the plots of pressure vs. $(y + x)/2$ and pressure vs. $(v^L + v^V)/2$ were extrapolated to the critical pressure. The critical constants thus determined are

	N_2—CO_2	O_2—CO_2
Composition, mole fraction of light component	0.2926	0.3120
Pressure, lb./sq.in.abs.	1,740	1,703
Molar volume, cc./mole	77.5	76.0

Plots of the phase compositions and of the volumetric data* are given in Figures 6 to 9.

Some phase-composition data for these two binary systems have been reported previously by Zenner and Dana (*9*), Pollitzer and Strebel (*8*), and Abdullaev (*1*). The liquid-phase compositions as a function of pressure from all of these workers agree quite well with those of this work. The vapor-phase agreement is fair; however, the variation of the previously published sets of data among themselves and from that of this study is much greater than the experimental error claimed by any of the authors.

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* Complete data have been deposited as document 8566 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

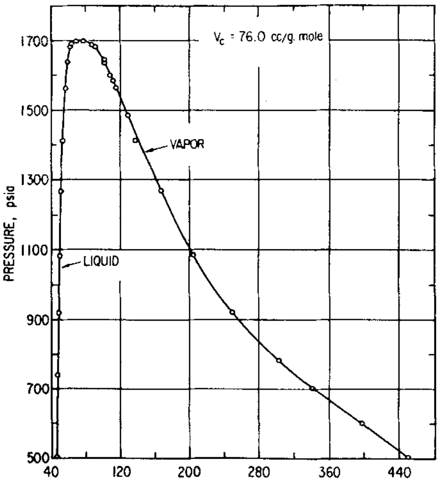

Fig. 9. Pressure vs. liquid and vapor molar volumes for the oxygen-carbon dioxide system at 0°C.

Most of the previously reported data show a higher concentration of the light gas in the vapor phase than those determined by this study. This observation might suggest that despite the precautions taken, entrainment might have occurred, the entrained liquid increasing the amount of carbon dioxide in the vapor sample. A number of tests involving variations in the sampling procedure were performed to check this possibility. These tests involved venting the sample space and then cracking the valve to the equilibrium cell to withdraw a sample. Some samples were taken immediately in this manner, while others were withdrawn after a few minutes operation of the vapor-phase pump. This procedure was followed both with the sample heater on and off. These tests showed excellent agreement with the data taken in the normal manner.

The only data published which allow the determination of the critical constants for the binaries are those of Zenner and Dana (9). The nitrogen–carbon dioxide critical pressure determined from their data is 1,740 lb./sq.in. abs., the same as reported in this work. However, for the oxygen–carbon dioxide system, their data yield a critical pressure of 1,688 lb./sq.in.abs. compared with 1,703 lb./sq.in.abs. from this study. In an effort to resolve this discrepancy, several data points were taken as close as possible to the critical point. Data were taken at 1,684, 1,690, and 1,699 lb./sq.in.abs. Both the composition and molar volume determinations for these points showed two distinct phases and verified the critical pressure of 1,703 lb./sq.in.abs. reported in this work.

TABLE 1. EXPERIMENTAL PHASE EQUILIBRIA FOR THE NITROGEN-OXYGEN-CARBON DIOXIDE SYSTEM AT 0°C.

Total pressure, lb./sq. in. abs	x_{CO_2}	x_{O_2}	y_{CO_2}	y_{O_2}	v^{vapor}, cc./mole	v^{liquid}, cc./mole
755	0.963	0.031	0.778	0.174	315	48.8
822	0.951	0.042	0.737	0.220	289	49.0
974	0.928	0.040	0.679	0.170	234	50.4
952	0.933	0.036	0.688	0.154	241	49.5
1,064	0.917	0.033	0.656	0.127	211	50.7
1,035	0.921	0.028	0.662	0.110	218	50.6
1,174	0.891	0.062	0.627	0.207	188	51.7
1,104	0.905	0.055	0.646	0.200	199	51.1
1,185	0.891	0.058	0.625	0.189	185	51.5
1,340	0.865	0.055	0.607	0.151	—	52.9
1,440	0.837	0.081	0.603	0.183	139	54.9
1,535	0.808	0.105	0.607	0.207	123	56.2

TERNARY SYSTEM

The original (unsmoothed) experimental data for the ternary system at 0°C. are given in Table 1. Ternary data can be most efficiently smoothed and best represented in a simple manner through data reduction based on thermodynamic analysis. Such an analysis is of interest in showing the relationship between the behavior of the ternary system and that of the constituent binary systems; in particular, it would be desirable to establish a thermodynamically sound procedure for predicting with reasonable confidence the ternary equilibria with only binary data. The thermodynamic representation of multicomponent vapor-liquid equilibria at high pressure is considered in Part II.

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NOTATION

B_m = second virial coefficient for gas mixture
B_{ij} = second virial coefficient characteristic of the interaction between molecule i and molecule j
n_T = total number of moles
P = total pressure
T = absolute temperature
v = molar volume
V = total volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Superscripts

L = liquid phase
v = vapor phase

Subscripts

c = critical
2 = light component (oxygen or nitrogen)

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