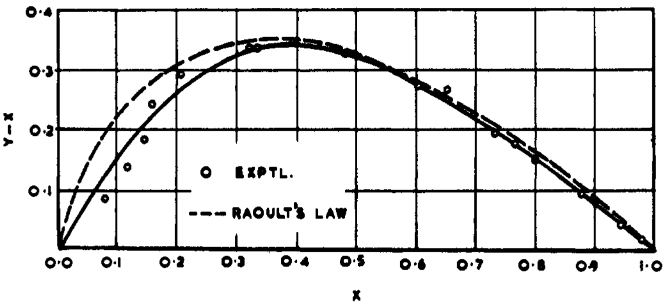

Figure 3. x vs. y-x diagram for 1,2-dichloroethane–ethylbenzene system

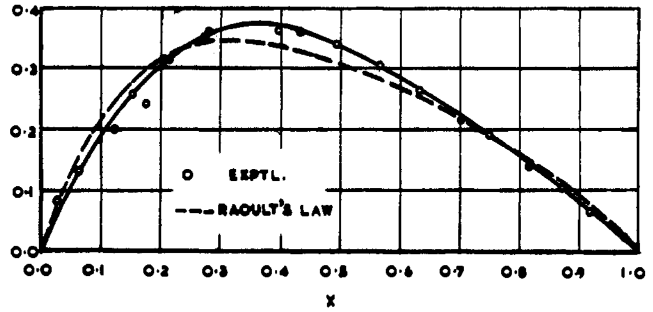

Figure 4. x vs. y-x diagram for 1,2-dichloroethane–p-xylene system

The deviations of the vapor phase from the perfect gas laws were estimated using the following equation:

$$z_i = \exp\left[(\pi - P_i^\circ)(B_i - V_i)/RT\right]$$

For ethylbenzene and p-xylene vapor pressures, second virial coefficients and liquid molar volumes were estimated by the correlations referred to (*2*). Vapor pressures of 1,2-dichloroethane were estimated using the Wrede equation (*5*) with the constants obtained (*1*). The average absolute deviations between the calculated and literature (*3*) vapor pressures for 1,2-dichloroethane over the temperature range 82–184°C were estimated to be 8.29 mm of Hg. The O'Connell and Prausnitz correlation and Yen and Woods correlation (*2*) were used for the estimation of its second virial coefficients and liquid molar volumes, respectively.

The assumption that the vapors follow the ideal gas laws yields errors in the relative volatility up to a maximum of about 6% for the two systems, the values of the relative volatility being higher than the corresponding values for the real vapor phase. This departure from the perfect gas laws is primarily due to the large differences in the boiling points of the constituents of the mixtures. The calculated vapor-phase imperfection coefficients are given in Table III.

ACKNOWLEDGMENT

The authors gratefully acknowledge the encouragement and helpful suggestions of Bimalendu Ghosh.

NOMENCLATURE

z = vapor-phase imperfection coefficient

Nomenclature for the remaining terms appearing in the text is the same as given in ref. *2*.

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Gas-Liquid Equilibrium of Oxygen–Carbon Dioxide System

AAGE FREDENSLUND,[1] JØRGEN MOLLERUP, and OLE PERSSON
Institute of Chemical Technology, The Technical University of Denmark, Building 229, 2800 Lyngby, Denmark

Gas–liquid equilibrium compositions for the O_2–CO_2 system were determined for the −49.4°C isotherm over the complete pressure range from the vapor pressure of CO_2 at −49.4°C, 6.92 atm abs, to the maximum pressure of the system, 142.4 atm abs. Activity coefficients are calculated, and a thermodynamic consistency test is applied.

The gas-liquid equilibrium of the O_2–CO_2 system at low temperatures has been studied in detail previously (*2*, *4*, *6*). Partly to verify and partly to complete the previous work (*2*) where the high-pressure range of the isotherm is missing, a series of gas- and liquid-phase equilibrium compositions were determined at −49.4°C for pressure up to the maximum, 142.4 atm abs. Activity coefficients based on the unsymmetric normalization are calculated, and a thermodynamic consistency test is performed.

EXPERIMENTAL

The apparatus used here is of the vapor-recirculation type and is discussed in detail elsewhere (*1*). The central unit of the vapor-recirculation apparatus is the cell containing a sta-

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[1] To whom correspondence should be addressed.

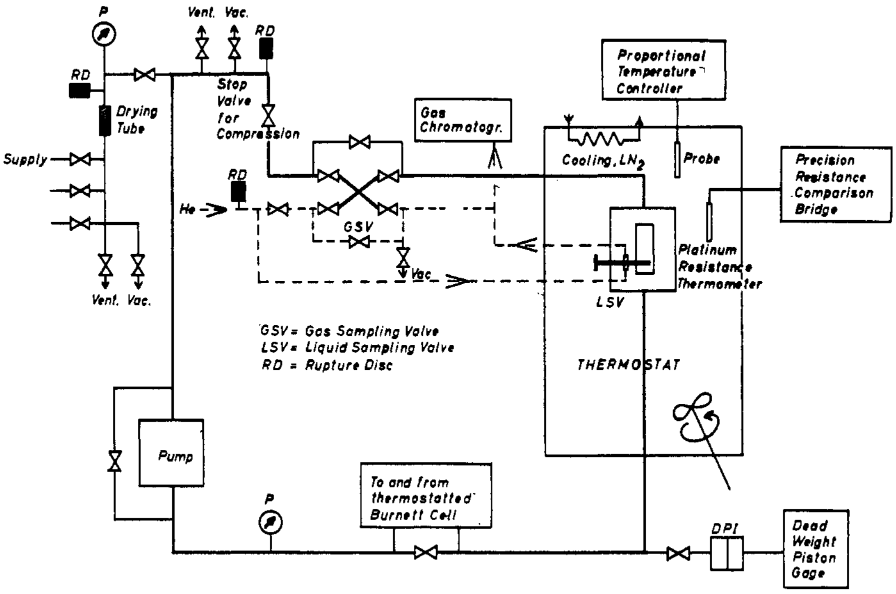

Figure 1. Vapor recirculation apparatus

tionary liquid phase. The gaseous phase is circulated through the liquid using a diaphragm compressor. The gas phase, after leaving the pump, enters the equilibrium cell via a cooling coil, both cell and cooling coil being immersed in a constant-temperature bath. The gas bubble through the liquid in the cell goes through a gas space of volume 75 cm^3 also located in the constant-temperature bath, goes through a gas-sampling unit, and finally returns to the pump (Figure 1). The bath fluid is air.

The range of operating pressure and temperature is 1–750 atm and −150° to 50°C, respectively. The temperature is measured using a platinum resistance thermometer, and the pressure is determined using a deadweight piston gage.

The method of refrigeration and temperature control is similar to the method described (*3*). The temperature is controlled to the nearest ±0.01°C.

Novel to this apparatus are the possible inclusion of the Burnett apparatus in the gas volume of the vapor-recirculation apparatus, which allows direct measurement of the *PVT* properties of the gas phase, and the gas- and liquid-sampling technique. Both the gas and the liquid samples are injected directly into the carrier gas of the gas chromatograph.

SAMPLING PROCEDURE

During normal operation, the space between the four valves of the gas-sampling unit is being flushed by the system gas phase. When a gas sample is to be taken, the system gas-bypass valve is opened. Two of the valves of the gas-sampling unit are closed, the other two opened, which allows the gas-sampling space to be flushed with helium. The helium carries the sample directly to the gas chromatograph for analysis. The volume of the gas-sampling space is about 0.2 cm^3. It is possible to reduce the pressure in the gas-sampling unit before flushing with helium. Before returning to normal operation, the helium occupying the gas-sampling space is evacuated. During normal operation, the helium bypasses the gas-sampling unit following the dotted line in Figure 1. The helium- and gas-sampling system is shown on Figure 2.

Also the liquid sample is injected directly into the carrier gas of the gas chromatograph. The liquid-sampling device is shown in Figure 3. A 5-mm diameter rod protrudes into the liquid phase in the cell. A 3.5-μl hole is drilled vertically through the part of the rod immersed in the liquid. Activation of a piston connected to the rod and mounted outside the thermostat causes the hole containing 3.5 μl of liquid phase to be drawn out into the cell wall. Here the liquid sample comes in contact with the gas chromatograph carrier gas and is carried to the gas chromatograph for analysis.

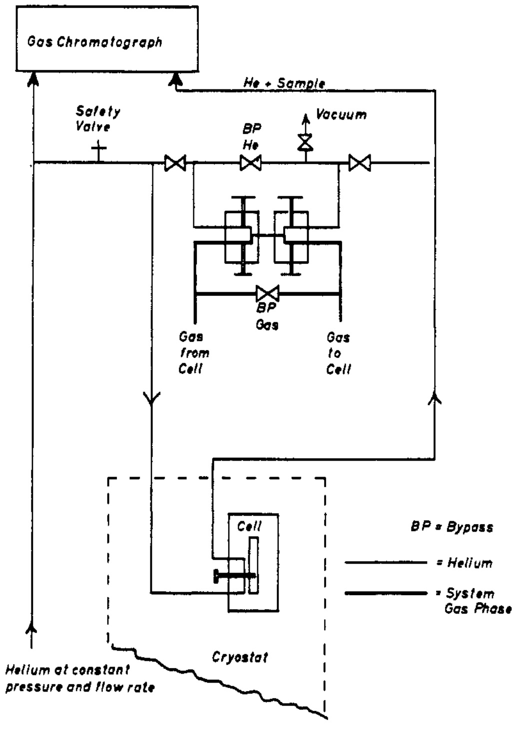

Figure 2. Helium- and gas-sampling system

The packing gland surrounding the rod is constructed of Invar, graphite, and a graphite- and glass-impregnated Teflon. The rings of Teflon and graphite nearest the center of the cell are 0.5 mm thick, and the rings on the other side of the helium ports are 0.7 mm thick. The packing gland is thermally compensated so that the volumetric decrease of the packing gland equals that of the stainless steel hole containing the gland when the temperature goes from room temperature to −100°C.

This method of vapor and liquid sampling has been successfully tested at pressures up to 350 atm and temperatures from −50° to −150°C. The advantages of this method are the small sampling volume, a minimal disturbance of the equilibrium during sampling, and the constant volume of liquid sam-

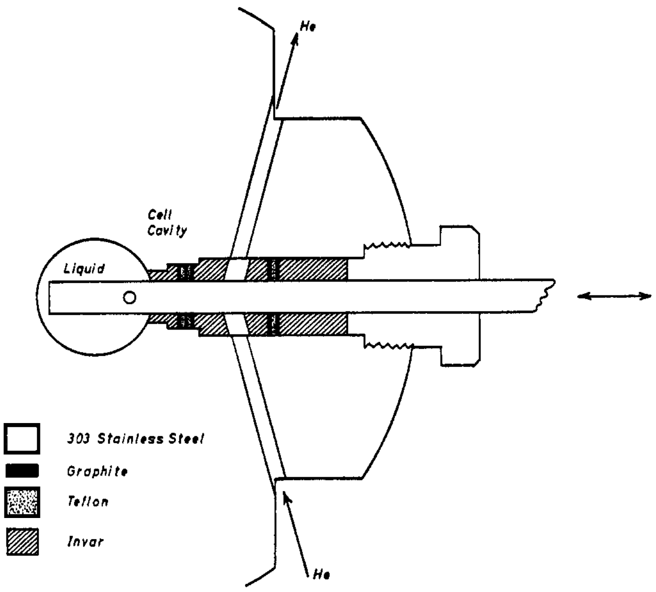

Figure 3. Liquid sampling unit

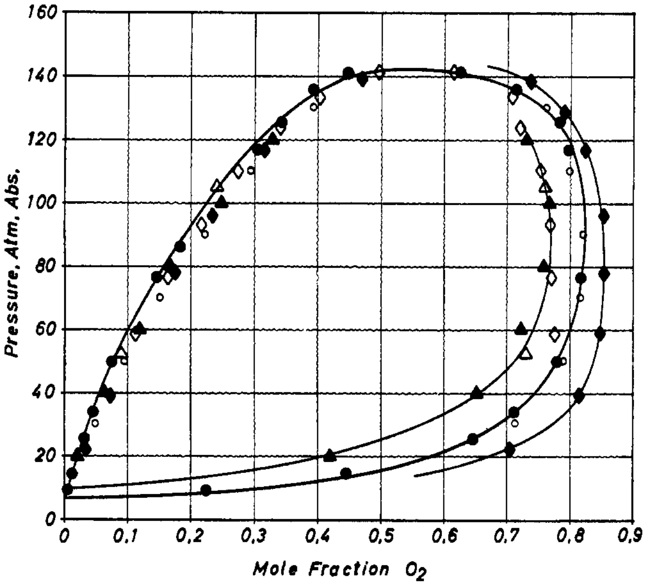

Figure 4. Gas-liquid equilibrium of O_2–CO_2 system

- ● This work, −49.4°C
- ○ Fredenslund and Sather (2), −50°C
- ▲ Fredenslund and Sather (2), −40°C
- △ Kaminishi and Toriumi (4), −40°C
- ◆ Zenner and Dana (6), −55°C
- ◇ Zenner and Dana (6), −40.3°C

ple withdrawn. Entrainment was minimized by using a low-vapor circulation rate and keeping the liquid level in the cell low. Deviations from equilibrium were never detected after 2 hr of operation.

RESULTS

The new experimental data for the O_2–CO_2 system are shown in Table I and Figure 4, where data from previous investigations (*2*, *4*, *6*) also are shown. The data of this work are seen to be in good agreement with the previous work at −50°C, and the data appear to be in qualitative agreement with the investigations at −40° and −55°C.

Table I. Vapor- and Liquid-Phase Measurements and Calculations

Press. atm abs	Experimental compositions[a]		"Smoothed" compositions[a]		Activity coefficients	
	Liquid	Gas	Liquid	Gas	Carbon dioxide	Oxygen
9.19	0.0040	0.2222	0.004	0.225	0.996	0.987
14.08	0.0122	0.4461	0.012	0.446	1.034	0.970
25.60	0.0306	0.6453	0.031	0.646	1.067	0.929
33.8	0.0426	0.7101	0.045	0.712	1.042	0.875
49.8	0.0756	0.7771	0.076	0.777	1.026	0.782
76.5	0.1433	0.8137	0.146	0.813	1.012	0.569
86.0	0.1808	...	0.178	0.812	1.037	0.499
117.0	0.3056	0.7970	0.295	0.797	1.121	0.336
125.6	0.3413	0.7808	0.338	0.781	1.205	0.291
136.0	0.3929	0.7113	0.393	0.711	1.427	0.236
140.5	0.4462	0.6240	0.446	0.624	1.760	0.185

$f_{CO_2,\,\mathrm{pure}}$ = 6.92 atm; $H_{O_2}^{(P^\circ)}$ = 523 atm; % inconsistency = 2.5%.

[a] Mole fraction oxygen.

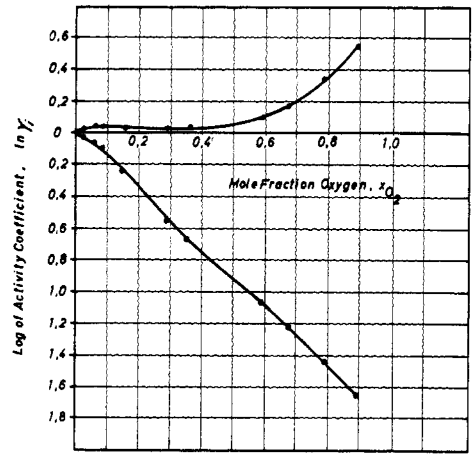

Figure 5. Activity coefficients for O_2–CO_2 system

The maximum pressure of the new isotherm is 142.4 atm abs at $x_{O_2} = 0.538$. The data were smoothed graphically.

Pressure-reduced activity coefficients, $\gamma_i^{(P^\circ)}$, were calculated according to the methods shown (*5*). For carbon dioxide, component 1, the activity coefficient was calculated as

$$\left[\gamma_1^{(P^\circ)} = \frac{\Phi_1 y_1 P}{x_1 f_{1\,\mathrm{pure}}^{(P^\circ)}} \exp\left\{-\int_{P^\circ}^{P} \frac{\bar{v}_1}{RT}\,dP\right\}\right]_T \qquad (1)$$

The reference pressure, P°, is here taken to be the saturation pressure of pure CO_2 at −49.4°C; $f_{1\,\mathrm{pure}}^{(P^\circ)}$ is the fugacity of pure CO_2 at pressure P° and temperature of the system. The fugacity coefficient, Φ_1, and the partial molar volume, $\bar{v}_1$, are calculated using the Redlich-Kwong equation of state as shown in (*5*).

For oxygen, component 2, which is noncondensable,

$$\left[\gamma_2^{*(P^\circ)} = \frac{\Phi_2 y_2 P}{x_2 H_2^{(P^\circ)}} \exp\left\{-\int_{P^\circ}^{P} \frac{\bar{v}_2}{RT}\,dP\right\}\right] \qquad (2)$$

This is the so-called unsymmetrical convention, where $H_2^{(P^\circ)}$ is Henry's constant for infinite dilution of O_2 in CO_2 at the temperature of the system and the pressure P°.

The calculated activity coefficients are shown in Table I and Figure 5.

The data and overall calculation may be tested for internal consistency, since the isothermal-isobaric Gibbs-Duhem equation applies to $\gamma_1^{(P°)}$. The thermodynamic consistency test becomes

$$\left[(x_1 \ln \gamma_1^{(P°)} + x_2 \ln \gamma_2^{*(P°)})\Big|_{x_{2,\max}} = - \int_0^{x_{2,\max}} \ln \frac{\gamma_1^{(P)°}}{\gamma_2^{*(P°)}}\, dx_2 \right]_T \qquad (3)$$

where $x_{2,\max}$ is the maximum value of x_{O_2} for which data were taken. The left-hand side of Equation 3 is defined as area$_1$ and the right-hand side as area$_2$. Percent inconsistency is then defined as

$$\% \text{ inconsistency} = 100\, \frac{\text{area}_1 - \text{area}_2}{\text{area}_1}$$

These data show an inconsistency of 2.5%. This is considerably better than the data for the −50°C isotherm (*2*) which exhibit an inconsistency of 9.5%.

NOMENCLATURE

f = fugacity, atm
H = Henry's law constant, atm
P = pressure, atm
R = gas constant
T = temp, °C
v = molar volume, cc/g-mol
x = liquid-phase mole fraction
y = vapor-phase mole fraction
γ = activity coefficient
Φ = fugacity coefficient
$(P°)$ = evaluated at $P°$
$*$ = unsymmetrical convention used
1 = carbon dioxide
2 = oxygen

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Thermodynamic and Physical Properties of Ammonia–Lithium Thiocyanate System

ROBERT A. MACRISS,[1] DHARAMVIR PUNWANI, WILLIAM F. RUSH, and WENDELL J. BIERMANN[2]
Institute of Gas Technology, Chicago, Ill. 60616

Vapor pressure data obtained in the concentration range of 40 to about 60 wt % lithium thiocyanate in ammonia and for pressures of 15–200 psia show extremely high negative deviations from Raoult's law. The data were used to compute heats of vaporization from these solutions. Viscosity data were obtained over a temperature range of 75–200°F and concentrations to about 60 wt % salt. The data fit Andrade's equation and produce straight lines amenable to extrapolation to higher temperatures. The densities of the solutions were also measured.

Most of the investigations of thiocyanate salts in the literature involve aqueous or molten solutions. Progress in formulating theoretical descriptions of concentrated nonaqueous electrolytic solutions requires the availability of experimental data presently in meager supply in the literature. Such measurements have been reported earlier by the authors for concentrated monomethylamine solutions of lithium (*4*) and sodium thiocyanate (*5*) and by Blytas (*1*) for ammonia–sodium thiocyanate solutions. The present work reports on such measurements for ammonia–lithium thiocyanate solutions. Experimental data on vapor pressures, solubility, density, and viscosity are given between 75° and 250°F, from 60–40 wt % ammonia, and at pressures from 1–200 psia. These solutions exhibit high negative deviations from Raoult's law. This particular system was chosen because of its possible application to absorption cooling in a gas-fueled air-cooled absorption system.

Most of the literature studies involving ammonia have been carried out at or near its normal boiling point to avoid experimentation at high pressures. Because the present work was carried out in a range of temperatures extending much above room temperature, special equipment was constructed to facilitate measurements at high pressures.

DISCUSSION

Vapor Pressures. Vapor pressure data were obtained utilizing equipment and procedures described by the authors in a recent publication (*4*). The pressure of the mixtures at low- and high-pressure ranges was read with a manometer or a deadweight tester, depending on the pressure range.

The 1000-psi deadweight tester was supplied with a calibration accurate to ±0.1 psia. Measurements, however, were

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[1] To whom correspondence should be addressed.
[2] Present address, Research Division, Carrier Corp., Syracuse, N.Y.