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Gas-Liquid Equilibrium of the Oxygen–Carbon Dioxide System

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Gas-liquid equilibrium compositions for the O_2–CO_2 system were determined over the −50° to +10° C. temperature range and from 130 atm. down to the saturation pressure of CO_2. Activity coefficients are calculated, and a thermodynamic consistency test is applied to each isotherm.

THE GAS-LIQUID equilibrium of the oxygen–carbon dioxide system has been studied along a few isotherms (*10, 12, 16*), but until now no isobaric data have been reported. In this work, gas and liquid equilibrium phase compositions were determined for the O_2–CO_2 system at the −50°, −40°, −30°, −20°, −10°, 0°, and +10° C. isotherms at pressures from 130 atm. down to the saturation pressure of CO_2, in 10-atm. increments. Thus, both isothermal and isobaric phase diagrams may be constructed. Activity coefficients based on the unsymmetric normalization are calculated for each isotherm. The activity coefficients for CO_2 are referred to the pure component at the temperature of the system, whereas the activity coefficients for O_2 are referred to the infinitely dilute solution. The activity coefficients are furthermore referred to a constant pressure via the Poynting correction factor, making possible the application of the isothermal-isobaric form of the Gibbs-Duhem equation. This equation, in the form of an area test for thermodynamic consistency, is applied separately to each isotherm.

EXPERIMENTAL

The apparatus used here is of the vapor recirculation type; the gaseous phase is circulated through a stationary liquid phase enclosed in a chamber. The flow diagram of the system is shown in Figure 1, where the main vapor circulation path is indicated by a heavy line. The vapor phase, after leaving the pump (a Lapp model CPS-2 diaphragm compressor), enters the equilibrium cell via cooling coils, both cell and coil being immersed in a constant-temperature bath. The vapor phase bubbles through the liquid phase in the cell and finally goes back to the pump. The design of the cell, which is provided with windows to permit visual observation of the two phases, is given by Fredenslund (*7*).

Before obtaining the gas and liquid phase samples, the lines leading to bypass-valves BP1 and BP2 (Figure 1) and the liquid sample line leading from the bottom of the cell through valve LS2 are flushed. The gas circulation through the liquid is resumed, and the gas and liquid sampling spaces are evacuated. At the time of gas sampling, BP1 is opened. With VS1 and VS2 closed, the gas located in the space between VS1, VS2, VS3, and VS4 is sealed off, while gas circulation continues via BP1. To take the liquid sample, BP2 is opened, MS2 closed, and LS2 opened to transfer about 0.5 cc. of liquid sample into the space between valves LS2, LS3, and LS4, which are all located inside the cryostat. The gas and liquid samples may now be expanded into their respective sample chambers. The liquid sample is pumped through the path LS3-LS4-chamber to ensure that the gas composition in the chamber is the same as that in the lines immersed in the cryostat. From the sample chambers, the samples are sent to a gas chromatograph equipped with a 6-foot silica gel column for analysis.

Refrigeration of the constant-temperature bath is accomplished by forcing a regulated amount of liquid nitrogen through cooling coils located in the bath fluid. A Bayley temperature controller furnishes the final fine control by adding a small amount of heat via six resistance coils located in the bath. It proved possible to control the temperature to within ±0.005° C. for pro-

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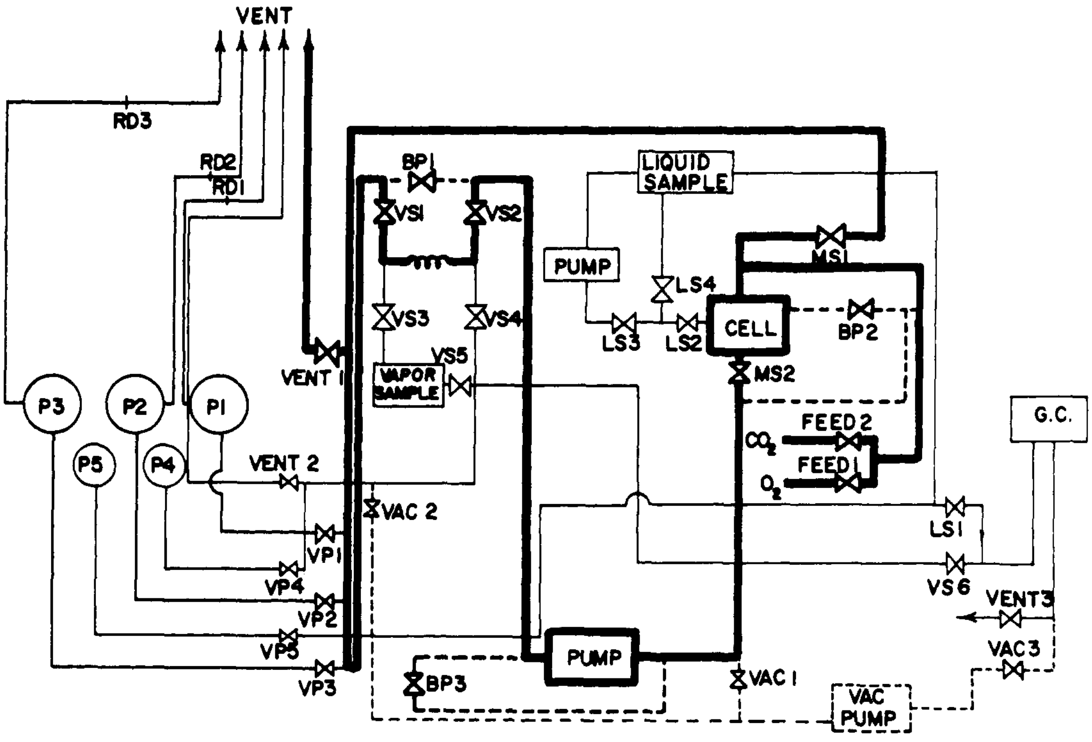

Figure 1. System flow diagram

━━━━ Main system line
———— Sampling or pressure measurement line
- - - - - Vacuum line
P___ Pressure gage number___
RD Rupture disk
G.C. Gas chromatograph

Valves

MS___ Main system valve number___
VP___ Valve for pressure gage number___
VS___ Vapor sampling valve number___
LS___ Liquid sampling valve number___
VAC___ Vacuum system valve number___
BP___ Bypass valve number___
VENT___ Venting valve number___
FEED___ Valve to feed___

longed periods. The absolute temperature is measured to within ±0.02° C., using a Hewlett-Packard Model Dy-2801A quartz thermometer.

Using three Bourdon pressure gages (P1, P2, and P3, Figure 1) of different maximum readings, the pressure was measured to within 0.5% throughout the range of this investigation.

Checks were made for the over-all reproducibility of the phase composition data by completing four runs at −30° C., 100 atm., and −20° C., 40 atm., respectively. The determined compositions were within 0.004 mole fraction for the vapor at −30° C., 100 atm., and within 0.002 mole fraction for the liquid samples and the vapor sample at −20° C., 40 atm.

Entrainment was minimized by using a low vapor circulation rate and by keeping the liquid level in the cell low. Reproducibility tests with the vapor circulation rate increased by a factor of four did not change the vapor composition significantly.

RESULTS

The experimental data for the O_2-CO_2 system are shown in Table I and Figures 2 and 3. The data at 0° C. are in good agreement with those of the previous investigators (*10, 12, 16*), as may be seen from Figure 4. Agreement is closest with the data of Muirbrook and Prausnitz (*12*).

In spite of precautions taken, perhaps entrainment did occur at 0° C., 110 atm., thus accounting for the relatively large deviation from the previous data at that point.

The smooth data from the isothermal and isobaric phase diagrams, Figures 2 and 3, are presented in Table II.

THERMODYNAMIC ANALYSIS

The condition for phase equilibrium is that the fugacity of each component, i, in the gaseous phase is equal to its fugacity in the liquid phase

$$f_i^v = f_i^l, \qquad i = 1, 2, 3, \cdots, n \tag{1}$$

The fugacity coefficient, ϕ_i, is now defined by

$$f_i^v = \phi_i y_i P \tag{2}$$

ϕ_i may be calculated from an equation of state. The activity coefficient, γ_i, is defined by

$$f_i^l = \gamma_i x_i f_i^\circ \tag{3}$$

where f_i° is some (arbitrary) reference fugacity.

Prausnitz *et al.* (*2, 13, 14*) have developed an internally consistent technique for the calculation of liquid phase activity coefficients at high pressures. The activity coefficients of light, supercritical components are referred to the infinitely dilute solutions, whereas the

Table I. Equilibrium Compositions for the O_2–CO_2 System

Mole Fraction Oxygen in Liquid and Vapor Phases

Pressure, Atm.		Temperature, ° C. −50.0 ±0.02	−40.0 ±0.02	−30.0 ±0.02	−20.0 ±0.01	−10.0 ±0.01	0.0 ±0.01	+10.0 ±0.01
10.0	l	0.008	. . .					
±0.03	v	0.312	0.118					
20.0	l	0.025	0.021	0.010	0.006			
±0.2	v	0.617	0.419	0.275	0.061			
30.0	l	0.049	0.041	0.031	0.030	0.009		
±0.3	v	0.712	0.589	0.463	0.302	0.096		
40.0	l	0.071	0.064	0.052	0.042	0.035	0.010	
±0.2	v	0.761	0.651	0.551	0.400	0.263	0.099	
50.0	l	0.096	0.087	0.080	0.062	0.056	0.042	0.028
±0.2	v	0.789	0.695	0.609	0.500	0.346	0.214	0.115
60.0	l	0.117	0.120	0.104	0.092	0.079	0.062	0.040
±0.2	v	0.809	0.723	0.644	0.540	0.417	0.298	0.161
70.0	l	0.150	0.141	0.140	0.125	0.110	0.090	0.071
±0.2	v	0.814	0.741	0.671	0.560	0.463	0.336	0.218
80.0	l	0.189	0.167	0.162	0.141	0.134	0.126	0.087
±0.3	v	0.818	0.757	0.693	0.574	0.493	0.372	0.263
90.0	l	0.220	0.205	0.191	0.170	0.162	0.147	0.115
±0.3	v	0.820	0.766	0.689	0.601	0.495	0.398	0.294
100.0	l	0.267	0.248	0.236	0.220	0.195	0.185	0.187
±0.3	v	0.819	0.767	0.694	0.599	0.500	0.401	0.263
110.0	l	0.293	0.274	0.266	0.255	0.243	0.247	
±0.4	v	0.797	0.760	0.682	0.601	0.498	0.362	
120.0	l	0.334	0.328	0.306	0.300	0.299		
±0.4	v	0.780	0.730	0.671	0.570	0.446		
130.0	l	0.393	0.380					
±0.5	v	0.762	0.702					

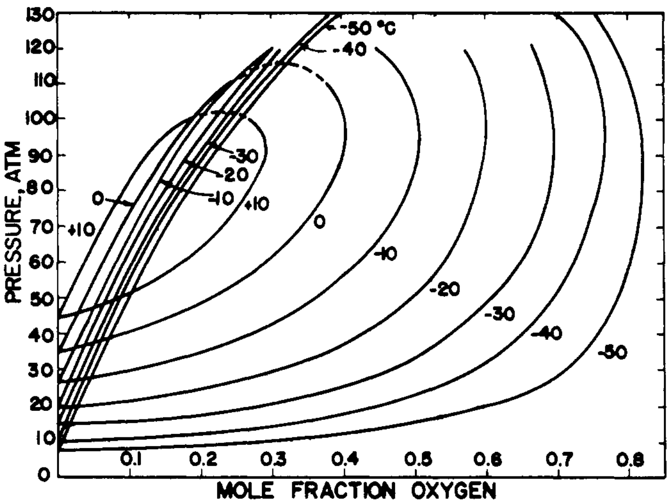

Figure 2. Isotherms for the O_2–CO_2 system

activity coefficients of heavy, condensable components are referred to the pure components.

In the following, component 2 is taken to be a supercritical component (oxygen) and component 1 a condensable component (carbon dioxide). Making use of Equation 3, the reference fugacity of component 2 becomes

$$f_2^\circ = \lim_{x_2 \to 0} (f_2/x_2) \equiv H_2 \tag{4}$$

H_2 is the Henry's law constant at the temperature of the system.

The isothermal Gibbs-Duhem equation for binary mixtures is

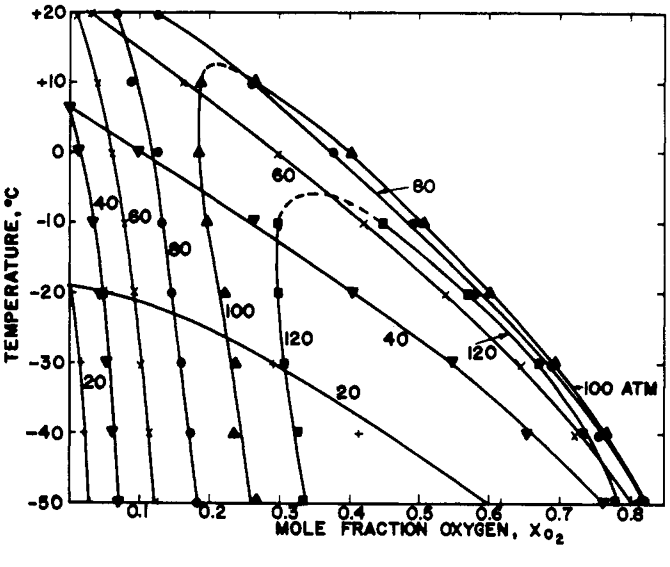

Figure 3. Isobars for the O_2–CO_2 system

+ 20 atm.	× 60 atm.	▲ 100 atm.
▼ 40 atm.	● 80 atm.	■ 120 atm.

$$\left[x_1 \mathrm{d} \ln f_1 + x_2 \mathrm{d} \ln f_2 = \frac{v^l}{RT} \mathrm{d}P\right]_T \tag{5}$$

Since $v^l = x_1\bar{v}_1 + x_2\bar{v}_2$ (the bar indicates a partial molar quantity), it follows that

$$\left[x_1\left(\mathrm{d} \ln f_1 - \frac{\bar{v}_1}{RT} \mathrm{d}P\right) + x_2\left(\mathrm{d} \ln f_2 - \frac{\bar{v}_2}{RT} \mathrm{d}P\right) = 0\right]_T \tag{6}$$

Now one defines an adjusted fugacity, $f_1^{(P^\circ)}$, by

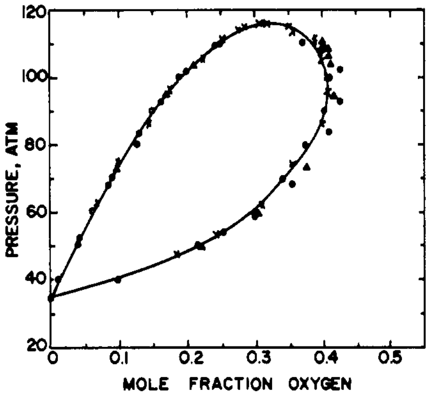

Figure 4. The 0° C. isotherm

○ This work ▲ Zenner and Dana
× Muirbrook ● Kaminishi

$$\left[\mathrm{d}\ln f_1{}^{(P^\circ)} = \mathrm{d}\ln f_1 - \frac{\bar{v}_1}{RT}\,\mathrm{d}P\right]_T \qquad (7)$$

and similarly for component 2.

At pressure P°, $f_i{}^{(P^\circ)} = f_i$, so integrating Equation 7 from pressure P° to any pressure, P, one obtains upon rearrangement

$$f_1{}^{(P^\circ)} = f_1 \exp\left\{-\int_{P^\circ}^{P} (\bar{v}_1/RT)\,\mathrm{d}P\right\} \qquad (8)$$

The pressure-adjusted activity coefficient, $\gamma_i{}^{(P^\circ)}$, is defined by

$$f_1{}^{(P^\circ)} = \gamma_1{}^{(P^\circ)}\, x_1 f_{1\,\mathrm{pure}}{}^{(P^\circ)} \qquad (9)$$

where $f_{1\,\mathrm{pure}}{}^{(P^\circ)}$ is the pure-component reference fugacity. Then Equation 8 becomes, at constant temperature,

$$\left[\gamma_1{}^{(P^\circ)} = \frac{\phi_1 y_1 P}{x_1 f_{1\,\mathrm{pure}}{}^{(P^\circ)}} \exp\left\{-\int_{P^\circ}^{P} \frac{\bar{v}_1}{RT}\,\mathrm{d}P\right\}\right]_T \qquad (10)$$

For component 2,

$$\left[\gamma_2^{*(P^\circ)} = \frac{\phi_2 y_2 P}{x_2 H_2{}^{(P^\circ)}} \exp\left\{-\int_{P^\circ}^{P} \frac{\bar{v}_2}{RT}\,\mathrm{d}P\right\}\right]_T \qquad (11)$$

The reference pressure, P°, is taken to be the vapor pressure of CO_2 at the temperature of the system. $H_2{}^{(P^\circ)}$ is Henry's law constant evaluated at the temperature of the system and the saturation pressure of CO_2.

The equation of state used for the calculation of the fugacity coefficients and partial molar volumes is a modified version of the Redlich-Kwong equation suggested by Chueh and Prausnitz (*4*). The equation of state is

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v\,(v+b)} \qquad (12)$$

For binary mixtures, the constants a and b are given by

$$a = \sum_i \sum_j y_i y_j a_{ij};\quad a_{ii} = \frac{\Omega_{a_i} R^2 T_{ci}{}^{2\cdot 5}}{P_{ci}}\quad a_{ij} = \frac{\Omega_{a_i} + \Omega_{a_j}}{2}\cdot\frac{R^2 T_{cij}{}^{2\cdot 5}}{P_{cij}}$$
$$b = \sum_i y_i b_i;\qquad b_i = \frac{\Omega_{b_i} R T_{ci}}{P_{ci}}$$

T_{ci} and P_{ci} denote the pure-component critical temperatures and pressures, respectively; T_{cij} and P_{cij} denote the mixture pseudocritical temperature and pressure. Ω_{a_i} and Ω_{b_i} are parameters which are curve-fitted

Table II. Smoothed Compositions for the O_2–CO_2 System

Mole Fraction Oxygen in Liquid and Vapor Phases

Pressure, Atm.		Temperature, ° C.						
		−50	−40	−30	−20	−10	0	+10
10	l	0.006	0.001					
	v	0.300	0.100					
20	l	0.0265	0.0205	0.0105	0.001			
	v	0.617	0.425	0.285	0.050			
30	l	0.0485	0.0415	0.031	0.021	0.009		
	v	0.718	0.585	0.463	0.302	0.097		
40	l	0.071	0.0635	0.053	0.0425	0.033	0.0135	
	v	0.761	0.652	0.550	0.422	0.263	0.099	
50	l	0.0955	0.087	0.0765	0.066	0.056	0.038	0.015
	v	0.789	0.695	0.609	0.495	0.359	0.214	0.087
60	l	0.122	0.112	0.102	0.092	0.080	0.062	0.039
	v	0.806	0.723	0.646	0.537	0.418	0.293	0.170
70	l	0.1515	0.1405	0.129	0.119	0.106	0.089	0.065
	v	0.815	0.744	0.675	0.566	0.463	0.341	0.225
80	l	0.1835	0.170	0.159	0.1465	0.133	0.118	0.092
	v	0.820	0.757	0.691	0.586	0.493	0.377	0.263
90	l	0.2183	0.2035	0.191	0.1765	0.162	0.147	0.119
	v	0.821	0.766	0.696	0.598	0.504	0.398	0.294
100	l	0.255	0.2385	0.226	0.209	0.195	0.184	0.187
	v	0.817	0.767	0.695	0.600	0.505	0.401	0.263
110	l	0.294	0.276	0.2635	0.247	0.243	0.247	
	v	0.805	0.758	0.685	0.595	0.493	0.380	
120	l	0.338	0.320	0.306	0.300	0.299		
	v	0.785	0.738	0.665	0.570	0.446		
130	l	0.393	0.380					
	v	0.758	0.698					

from saturated vapor or liquid P-v-T data for each of the pure components. Note that the liquid phase parameters are not necessarily equal to those of the gas phase. For liquid phase calculations, x_i is substituted for y_i in the above combining rules.

The suggested mixing rules for P_{cij} and T_{cij} are

$$P_{cij} = \frac{z_{cij} R T_{cij}}{v_{cij}} \tag{13}$$

$$T_{cij} = (T_{ci}\, T_{cj})^{1/2}\,(1 - \kappa_{ij}) \tag{14}$$

where $v_{cij} = \frac{1}{8}\,(v_{ci}{}^{1/3} + v_{cj}{}^{1/3})^3$

and $z_{cij} = 0.291 - 0.04\,(\omega_i + \omega_j)$

ω_i and ω_j are the acentric factors for components i and j. κ_{ij} is a measure of the deviation of T_{cij} from the geometric mean for the given system. It is the only parameter entering into the equation of state, Equation 12, which depends on binary interactions. It may be obtained from independent sources such as the second cross-virial coefficient, B_{ij}, and is relatively independent of temperature, pressure, and composition (*5*). On the basis of B_{ij} data from references (*5, 8, 11*), it was found that κ_{ij} for the O_2–CO_2 system is 0.03.

The calculation of the fugacity coefficients is performed as described by Chueh and Prausnitz (*4*):

$$\ln\phi_k = \ln\frac{v}{v-b} + \frac{b_k}{v-b} - \frac{2\sum_i y_i a_{ik}}{RT^{3/2} b}\ln\frac{v+b}{v} + \frac{ab_k}{RT^{3/2} b^2}\left(\ln\frac{v+b}{v} - \frac{b}{v+b}\right) - \ln\frac{Pv}{RT} \tag{15}$$

The volume, v, of the saturated vapor mixture was calculated from Equation 12 after $\Omega_{a_{CO_2}}$ and $\Omega_{b_{CO_2}}$ were obtained from (*4*), and $\Omega_{a_{O_2}}$ and $\Omega_{b_{O_2}}$ were determined by a nonlinear least squares fit of Equation 12 to pure, saturated vapor P-v-T data obtained from (*15*). The resulting fugacity coefficients are given in Table III. Only calculated results for the 0° C. isotherm are presented here. The complete Table III may be obtained from the American Society for Information Science.

In the calculation of partial molar volumes in the liquid phase, the first problem is to obtain v, the molar volume of the liquid mixture. Fortunately, data are available on the molar volumes of the saturated liquid mixture at 0° C. as a function of pressure (*12*). These data were fitted to the modified Redlich-Kwong equation of state, again using a nonlinear least squares procedure, and leaving Ω_{a_i} and Ω_{b_i} for O_2 and CO_2 as parameters to be determined. The saturated liquid mixture molar volumes were then determined at all the temperatures and pressures of interest from the modified Redlich-Kwong equation of state, with the new Ω_{a_i} and Ω_{b_i} incorporated in the coefficients of Equation 12.

Once the molar volume is known, the partial molar volumes may be determined using the equation of state, Equation 12, as discussed by Chueh and Prausnitz (*3*):

$$\bar{v}_k = \frac{\dfrac{RT}{v-b}\left(1 + \dfrac{b_k}{v-b}\right) - \dfrac{2\sum_i x_i a_{ik} - \dfrac{ab_k}{v+b}}{v(v+b)\,T^{1/2}}}{\dfrac{RT}{(v-b)^2} - \dfrac{a}{T^{1/2}}\left(\dfrac{2v+b}{v^2(v+b)^2}\right)} \tag{16}$$

$\Omega_{a_{CO_2}}$ and $\Omega_{b_{CO_2}}$ for this calculation are given in (*3*), and $\Omega_{a_{O_2}}$ and $\Omega_{b_{O_2}}$ were obtained from the pure-component, saturated-liquid P-v-T data given in references (*1, 15*).

In the calculation of the Poynting correction factors,

$$\left(PCF_i = \exp\int_{P^\circ}^{P}\frac{\bar{v}_i}{RT}\,dP\right)_T \tag{17}$$

it is assumed that $\bar{v}_i$ is a function of temperature and composition, but not pressure. The partial molar volumes and Poynting correction factors are shown in Table III.

The reference fugacity for CO_2 was calculated at each temperature by the generalized methods discussed by Hougen *et al.* (*9*). Comparison with the data available at 0°, 10°, and 20° C. (*6*) was satisfactory.

The reference fugacity for O_2 is Henry's law constant, evaluated at the temperature of the system and the saturation pressure of CO_2. The details of the graphical determination of $H_2^{(P^\circ)}$ in accordance with Equation 4 are given in (*7*).

All of the information needed to calculate the activity coefficients according to Equations 10 and 11 is now

Table III. Vapor and Liquid Phase Calculations

$T = 0°$ C. [a,b]

	Fugacity Coefficients		Liquid Partial Molar Volumes, Cc./Gram-Mole		Poynting Correction Factors		Activity Coefficients	
Pressure, P	ϕ_{O_2}	ϕ_{CO_2}	$\bar{v}_{O_2}$	$\bar{v}_{CO_2}$	PCF_{O_2}	PCF_{CO_2}	$\gamma_{O_2}^*$	γ_{CO_2}
40.0	1.1010	0.7404	87.96	47.25	1.0222	1.0119	1.0094	0.9997
50.0	1.0923	0.6827	91.30	46.76	1.0656	1.0331	0.9221	1.0096
60.0	1.0871	0.6301	94.74	46.12	1.1143	1.0541	0.8838	1.0110
70.0	1.0933	0.5791	99.58	45.19	1.1713	1.0744	0.7997	1.0208
80.0	1.1016	0.5314	105.83	43.83	1.2402	1.0933	0.7253	1.0272
90.0	1.1205	0.4845	112.82	41.98	1.3229	1.1097	0.6594	1.0370
100.0	1.1641	0.4353	125.86	38.36	1.4453	1.1188	0.5608	1.0682
110.0	1.2600	0.3815	171.24	23.71	1.7817	1.0832	0.3824	1.1929

[a] At 0° C., $f_{CO_2\ pure}{}^{P^\circ} = 26.74$ atm., $H_{O_2}{}^{(P^\circ)} = 313$ atm., % inconsistency = −2.1 %.

[b] Calculated results at other temperatures are available from ASIS. Per cent inconsistency at other temperatures were: −50° C., +9.5%; −40° C., +14.5%; −30° C., +11.9%; −20° C., −8.5%; −10° C., −2.9%; +10° C., −15.4%.

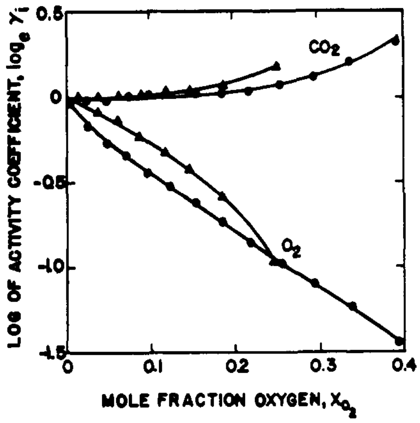

Figure 5. Activity coefficients at the 0° C. and −50° C. isotherms

▲ 0° C.
● −50° C.

available, and the results are given in Table III. Figure 5 shows the activity coefficients at −50° and 0° C. as a function of the composition.

The data and over-all calculation may be tested for internal consistency, since the isothermal-isobaric Gibbs-Duhem equation applies to $\gamma_i^{(P^\circ)}$. The thermodynamic consistency test (*2*) becomes

$$\left[\left(x_1 \ln \gamma_1^{(P^\circ)} + x_2 \ln \gamma_2^{*(P^\circ)}\right)\Big|_{x_{2,\max}} = \int_0^{x_{2,\max}} \ln \frac{\gamma_1^{(P^\circ)}}{\gamma_2^{*(P^\circ)}}\, dx_2\right]_T \qquad (18)$$

where $x_{2,\max}$ is the maximum value of x_{O_2} for which data were taken. Let

$$\mathrm{AREA}_1 = \left(x_1 \ln \gamma_1^{(P^\circ)} + x_2 \ln \gamma_2^{*(P^\circ)}\right)\Big|_{x_{2,\max}}$$

$$\mathrm{AREA}_2 = \int_0^{x_{2,\max}} \ln \frac{\gamma_1^{(P^\circ)}}{\gamma_2^{*(P^\circ)}}\, dx_2 \qquad (19)$$

and

$$\%\ \text{inconsistency} = 100\ \frac{\mathrm{AREA}_1 - \mathrm{AREA}_2}{\mathrm{AREA}_1}$$

The trapezoidal rule is used in the integration to obtain AREA_2. The calculated per cent inconsistencies are given in Table III for each isotherm. Considering the difficulty in obtaining accurate data for high-pressure gas-liquid equilibria in the critical region and the uncertainties in the calculations, these results are quite satisfactory.

NOMENCLATURE

a = constant in Redlich-Kwong equation of state
b = constant in Redlich-Kwong equation of state
B = second virial coefficient
f = fugacity, atm.
H = Henry's law constant, atm.
P = pressure, atm.
PCF = Poynting correction factor
R = gas constant
T = temp., ° C.
v = molar volume, cc. per gram-mole
x = liquid phase mole fraction
y = vapor phase mole fraction
z = compressibility factor

Greek Letters

γ = activity coefficient
κ = deviation from geometric mean
ϕ = fugacity coefficient
Ω = parameter in Redlich-Kwong equation of state
ω = acentric factor

Subscripts

i, j, k = components of a mixture
c = critical property

Superscripts

$^\circ$ = reference property
$-$ = partial molar property
l = liquid
v = vapor
(P°) = evaluated at P°
$*$ = unsymmetrical convention used

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