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Liquid–Vapor Equilibria of the Hydrogen–Carbon Dioxide System

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The liquid-vapor equilibria of the hydrogen–carbon dioxide system were studied in a vapor recirculation apparatus. Six isotherms were studied, from 219.9° to 289.9° K., up to 200 atm. pressure. The accuracy is believed to be within about ±5% of the reported values. A comparison with other published data is made.

THE liquid-vapor equilibria of the hydrogen–carbon dioxide system were studied because of the lack of data in the literature. Prior to the initiation of the present work, the only available data were those of Abdullayev (1), Mills and Miller (7), and Greco, Casale, and Negri (3). The data of all three investigations were only presented graphically, and therefore were not in a particularly usable form. During the progress of this investigation, Kaminishi and Toriumi (6) published data sparsely covering the entire liquid-vapor region up to 200 atm.

The liquid-vapor equilibria of the hydrogen–carbon dioxide system were studied at six temperatures: 219.9°, 229.9°, 244.9°, 259.9°, 274.9°, and 289.9° K. These isotherms were studied up to 200 atm. pressure. In all, 96 data points were collected and are thought to be accurate within about ±5%. The data are presented in both graphical and tabular form. The data are also compared with those from the literature.

EXPERIMENTAL

The apparatus used was that of Herring and Barrick (5), originally designed for use below 200° K. Since the temperature range required was from 220° to 290° K., a few changes were necessary, but the system remained basically the same.

A diagram of the flow system and of the equilibrium cell are presented (2, 5) with a fairly complete discussion of the apparatus and procedure. The primary changes in the apparatus (for use at the higher temperatures of this investigation) are illustrated in Figure 1. In the previous investigation of Herring and Barrick, the refrigeration was supplied by storing liquid nitrogen beneath the equilibrium cell, and boiling the liquid at a rate sufficient to keep the cell at the desired temperature. Actually, an excess amount of refrigeration was supplied, which was countered by an automatically controlled heater wrapped around the cell. This method was usable for temperatures below 200° K. At temperatures above 200° K., the refrigeration gas was so much colder than the cell temperature that large thermal
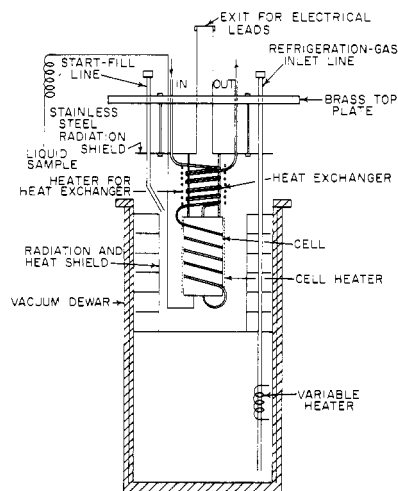

Figure 1. Apparatus modified for high temperature operation

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gradients and cold spots were encountered. The problem was especially bad in the heat exchanger through which the vapor exited from the cell. The problem was solved by making several changes in the refrigeration system. Instead of keeping liquid nitrogen in the Dewar surrounding the cell, it was stored and boiled in an external Dewar and passed into the Dewar surrounding the cell through the refrigeration-gas inlet line shown in Figure 1. A variable heater was placed on this line to preheat the refrigeration gas. To ensure further that the heat exchanger did not develop a cold spot, the Dewar was lowered from the top plate to the position shown in Figure 1, and a heater was placed around the heat exchanger. While heating the heat exchanger in this way destroyed its usefulness, at the high temperatures encountered here, enough heat was exchanged by the part of the vapor-inlet line which was wrapped around the equilibrium cell. Also at these high temperatures, radiation heat transfer was not a problem, as it was at temperatures below 200° K.

The other features of the apparatus and procedure were the same as the previous investigation of Herring and Barrick. The vapor phase was continually recirculated by an electromagnetic pump, and was continually brought into intimate contact with the liquid phase, which remained in the equilibrium cell at the desired temperature. The vapor phase was bubbled into the liquid in this way until equilibrium was reached. By removing samples of liquid and vapor after various lengths of time, equilibrium was usually attained in about 30 minutes of recirculation. After equilibrium was reached, both phases were sampled and analyzed.

A liquid phase at high pressure and at low temperature is usually considered to be difficult to sample. The method used here was to extract a sample of the liquid from the bottom of the cell through a capillary line (10 feet long × 0.006 inch I.D.). The use of a capillary made it easy to sample at high pressures, and also involved little dead space. The liquid sample, as it passed out through the sample line, underwent a reduction in pressure and a rise in temperature. As it did so, at some point in the sample line, it vaporized. The vapor produced at this point did not necessarily have the same composition as the liquid sample. However, after a short period of time, the composition of the vapor passing out of the line must be the same as the composition of the liquid entering it. This is the result of a material balance made at steady-state. Steady-state was reached experimentally after about 1 minute of sample removal. The amount of liquid lost from the cell in this way was essentially negligible.

The samples were analyzed with two Beckman GC-1 gas chromatographs using the peak area method. The peak areas were measured using a voltage-to-frequency converter (Dymec, DY-2211 AR-M17) in conjunction with a frequency counter (Hewlett-Packard 5512A), which served as a digital-integrating voltmeter. One chromatograph was used to measure each component in the gas mixtures. On each chromatograph the other component of the binary mixture was used as the carrier gas, so that only the desired component gave a peak, and a separation column was therefore unnecessary. The chromatographs were calibrated using gas mixtures obtained from and analyzed by a commercial supplier. The sample analyses were reproducible within about ±1%, except at the lowest concentrations encountered, where the reproducibility was only within 2 or 3%.

The temperatures were controlled to within ±0.1° K. of the values reported. The temperature was measured with a platinum resistance thermometer (Leeds and Northrup 8164), placed at the top of the cell, with a K-3 potentiometer (Leeds and Northrup 7553-5) and a null detector (Leeds and Northrup 9834). The thermometer was calibrated by the National Bureau of Standards using the 1955 NBS temperature scale. The small temperature differences in

the cell were measured with differential thermocouples. The pressures were measured with one of two Heise gages. One gage read from 0 to 100 atm. and was used to measure the pressures in that region. The other read from 0 to 300 atm. and was used for pressures above 100 atm. The rated accuracy of the gages was ±0.1% of full scale. The carbon dioxide used had maximum impurities of 100 p.p.m. The hydrogen used had maximum impurities of 10 p.p.m.

RESULTS

The data are presented in Table I. The liquid and vapor phases were always analyzed for the minor component com-

Table I. Liquid-Vapor Equilibria of H_2–CO_2 System

Temp., ° K.	Pressure, Atm.	Liquid, Mole % H_2	Vapor, Mole % CO_2
219.9	10.7	0.13	57.2
	21.3	0.44	30.7
	35.4	0.81	20.0
	52.1	1.28	14.8
	69.7	1.75	. . .
	72.2	. . .	11.5
	101.5	2.58	9.10
	152.4	3.85	7.33
	195.7	4.87	6.65
229.9	16.4	. . .	58.0
	25.5	0.56	38.6
	31.4	0.77	. . .
	36.0	0.92	. . .
	45.1	1.21	. . .
	45.9	. . .	23.5
	65.7	. . .	17.8
	72.3	2.16	16.8
	86.0	. . .	15.0
	105.5	. . .	13.6
	120.0	3.65	12.2
	159.5	4.77	10.4
	200.3	5.86	9.54
244.9	20.5	0.27	. . .
	21.5	. . .	73.5
	37.5	1.00	47.7
	51.9	1.59	36.6
	79.4	2.76	26.7
	111.5	4.07	21.1
	159.0	5.89	17.4
	163.0	6.05	17.2
	198.5	7.27	16.1
	200.5	7.32	15.9
259.9	30.6	. . .	82.6
	32.3	0.47	79.4
	50.0	1.46	58.0
	72.9	2.69	45.0
	91.4	3.63	38.2
	121.6	. . .	32.5
	133.2	5.98	30.5
	151.5	6.88	28.9
	154.7	7.00	28.8
	200.5	9.27	25.5
274.9	49.2	0.97	82.0
	65.2	2.13	70.0
	93.8	4.05	55.8
	121.5	5.88	48.2
	158.4	8.60	. . .
	163.8	. . .	41.2
	175.0	10.00	. . .
	189.5	. . .	39.0
	198.0	11.5	. . .
289.9	64.9	1.30	89.8
	88.8	2.58	82.4
	101.0	4.90	72.0
	151.7	11.0	60.9
	160.0	12.1	60.0
	173.0	13.9	57.8
	180.5	. . .	57.5

position. The vapor phase data are reported as mole per cent carbon dioxide, and the liquid phase data are reported as mole per cent hydrogen. In the few cases where the compositions reported are above 50%, they were obtained by subtraction of the minor component composition from 100%. The compositions are believed to be accurate to within ±5% of the minor component composition, except for the lowest concentration levels, where the errors may be slightly higher than this value.

The data are presented graphically in Figures 2 and 3. The vapor phase data are shown as a function of total pressure in Figure 2. The liquid phase data are shown as a function of total pressure in Figure 3.

It is sometimes useful to have simple equations which represent the experimental data within experimental accuracy. This was done here for both phases for each isotherm. Heck and Hiza (4) have shown that a particularly revealing way to plot vapor phase data is in terms of the enhancement factors. This type of plot shows any internal inconsistencies in the data and has the additional advantage of being easier to fit with an equation than the actual vapor data. The enhancement factor is defined as the ratio of the partial pressure of the heavy component in the vapor phase to the vapor pressure of that same component. The enhancement factors for the vapor phase data of this investigation were fit by the method of least squares using the equation

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

for each isotherm. The values of a_1, a_2, and a_3 determined for each isotherm are presented in Table II with the standard per cent error and the maximum absolute per cent error (SPE and MAPE). The standard per cent error used here is defined by the following equation:

$$SPE = \left| \Sigma[(Calcd - Exp)/Exp]^2 \right\}^{1/2} \quad (2)$$

The SPE and the MAPE give some idea of the precision of the data.

Each liquid phase isotherm was fitted in terms of the Henry's law constant, defined as

$$H = (P - p^\circ)/x_2 \quad (3)$$

The equation used to fit the data was

$$\ln H = a_1 + a_2(P - p^\circ) + a_3(P - p^\circ)^2 \quad (4)$$

The values of a_1, a_2, and a_3 determined for each isotherm are presented in Table III, with the SPE and the MAPE.

The vapor phase data were all fitted with a SPE of less than 1.6 and a MAPE of less than 3.2. The liquid phase data were all fitted with a SPE of less than 2.5 and a MAPE of less than 6. Most of the liquid phase data were fitted much better than these values.

The only tabulated data which have been published for the hydrogen–carbon dioxide system in the liquid-vapor region are those of Kaminishi and Toriumi (6). They
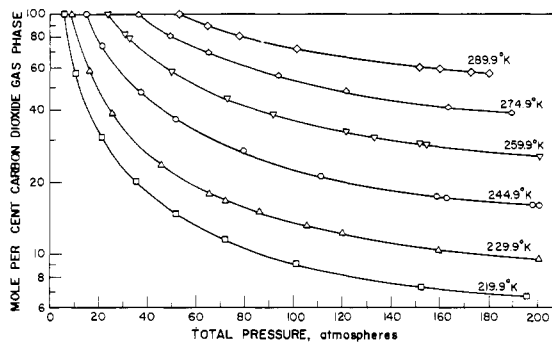
obtained data at six temperatures: 233.15°, 253.15°, 273.15°, 283.15°, 293.15°, and 298.15° K. The accuracy of these data was claimed to be within ±1%. The actual accuracy of the data of Kaminishi and Toriumi is probably somewhat less than this value. These data were fitted by the same equations as were the data of this investigation. Most of the data were represented by the equations within 3%. In some cases, only three data were obtained on an isotherm, so that an equation with three parameters represented the data exactly.

The data of Kaminishi and Toriumi were compared with the data of this investigation by comparing the enhancement factors (for the vapor phase) and the Henry's law constants (for the liquid phase). The smoothed equations were compared, rather than the actual data, for the sake of clarity, and because the smoothed equations probably represent the true isotherms more closely. The vapor phase enhancement factors for both investigations are plotted as a function of total pressure in Figure 4. The data for this investigation are plotted as solid lines, and the data of Kaminishi and Toriumi are plotted as dashed lines. The temperatures of each isotherm are not indicated on the graph since the curves are so close together. The curves for the lowest temperatures intercept the abscissa at the lowest pressures. The curves show fairly good agreement, in that they all originate at the vapor pressure of carbon dioxide and increase in a smooth manner. In some cases, the isotherms
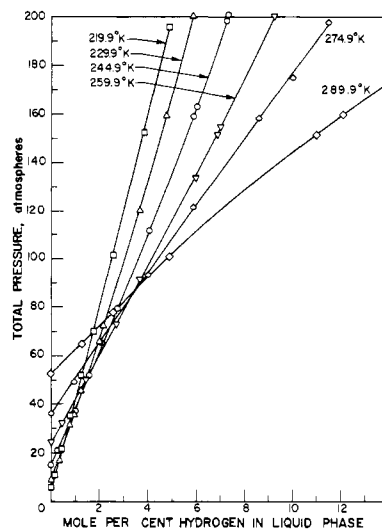
Figure 3. Liquid phase hydrogen composition vs. pressure

Table II. Least Square Fit of Enhancement Factor

Temp., °K.	$a_1 \times 10^3$	$a_2 \times 10^5$	$a_3 \times 10^8$	SPE	MAPE
219.9	6.90941	−2.98338	8.17198	0.70	1.04
229.9	6.39449	−2.13631	4.76284	1.57	3.16
244.9	7.88353	−4.35425	12.5750	1.12	2.29
259.9	8.16801	−4.09348	10.9457	0.94	1.55
274.9	9.36224	−5.84986	18.3104	0.51	0.88
289.9	8.73218	−4.40271	13.6346	0.51	0.81

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

Temp., °K.	a_1	$a_2 \times 10^3$	$a_3 \times 10^6$	SPE	MAPE
219.9	8.18255	4.14735	0	1.44	3.03
229.9	7.97623	5.39393	0	1.30	2.44
244.9	7.68433	8.44517	0	2.49	5.99
259.9	7.49424	2.92934	0	0.89	1.55
274.9	7.19377	15.3631	−7.73813	1.19	2.11
289.9	6.85778	16.7846	−20.9599	0.84	1.22

Figure 2. Vapor phase carbon dioxide composition vs. pressure

cross at several points, which probably does not actually occur; however, in all cases it amounts to small errors. The manner in which the data are plotted shows any errors or inconsistencies as large deviations. For example, consider that the total spread of all of the curves at 160 atm. represents a total deviation of 2.2%. So in general, it can be said that the vapor phase data of the two investigations agree fairly well.

The liquid phase data of both investigations are compared in the same way in Figure 5. Here, the Henry's law constants are plotted as a function of total pressure. Each isotherm is labeled with its temperature, followed in paren-
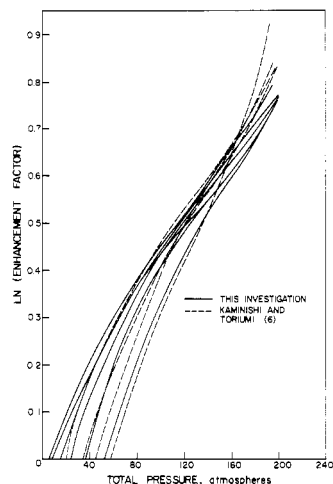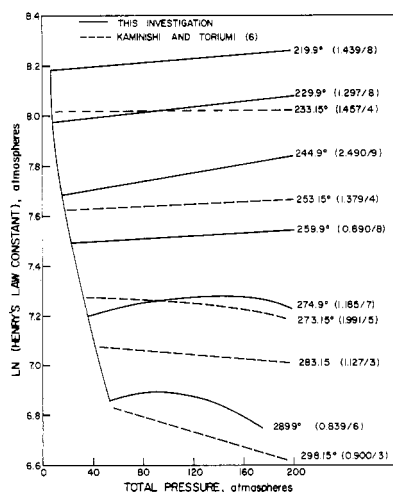

Figure 4. Comparison of vapor phase data

Figure 5. Comparison of liquid phase data

theses by the SPE and the number of data points on which the equation for the data was based. The liquid phase data for both investigations agree fairly well. The curve for 233.15° K. crosses the curve for 229.9° K., but the errors are not large. At 10 atm., the 233.15° curve should be slightly lower than the 229.9° curve, but is 4.1% higher. Similarly, at 190 atm., the 273.15° curve should be above the 274.9° curve, but is 4.6% below it. From this plot, it can not be determined which data are more in error, however, neither set is very far wrong. In conclusion, between the sparse data of Kaminishi and Toriumi and the more complete data of this investigation the vapor-liquid equilibria of the hydrogen–carbon dioxide system has been thoroughly covered up to 200 atm.

NOMENCLATURE

a_1, a_2, a_3	=	parameters fitted to data
Calcd	=	value of variable calculated by equation
Exp	=	experimental value of variable
H	=	Henry's law constant, atm.
P	=	total pressure, atm.
$p°$	=	vapor pressure of carbon dioxide, atm.
x_2	=	mole fraction of hydrogen in liquid phase
y_1	=	mole fraction of carbon dioxide in vapor phase
ϕ	=	enhancement factor $\equiv y_1 P/p°$

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