THE BINARY SYSTEM H₂O–CO₂
AT HIGH TEMPERATURES AND PRESSURES*

SUKUNE TAKENOUCHI and GEORGE C. KENNEDY

Institute of Geophysics and Planetary Physics,

University of California, Los Angeles

ABSTRACT. The system water–carbon dioxide has been studied to pressures of 1600 bars and over a temperature range of 110°C to 350°C. Some preliminary work up to pressures of 3000 bars has been completed. The compositions of coexisting gases and liquids at various temperatures and pressures have been determined by analyses of samples. The critical curve of the binary system has been determined. It has been found that the critical curve of the system trends toward higher pressures at lower temperatures and departs strongly from the critical point of pure water. The critical curve has a minimum temperature at approximately 265° with a pressure of 2150 bars. At low pressures the CO₂ rich phase is the light phase, but at higher pressures an inversion in density takes place and the CO₂ rich phase becomes the denser fluid phase.

INTRODUCTION

The binary system carbon dioxide-water is one of the fundamental geo-chemical binary systems, and results from it may be directly applied to prob-lems of regional metamorphism, contact metamorphism, hydrothermal activity, and the problems of hot springs and ore deposits. Strangely enough, there has been no investigation of this system until recently. Malinin (1959) presented a binary diagram that extended to 600 bars in pressure and to temperatures of 330°C. Malinin's data overlapped some and are in good agreement with early unpublished data on the system H₂O–CO₂ by Knight and Kennedy.

Naturally occurring hydrothermal systems are of course more complicated than the simple system H₂O–CO₂. However, recent studies of the liquid inclu-sions in certain minerals suggest that in some cases the ideal system may not differ too much from the natural one. This investigation represents a continua-tion of a general study of critical phenomena in binary systems of geological interest. The systems H₂O–NaCl and H₂O–SiO₂, through their critical regions, have recently been described by Kennedy and coworkers.

The system H₂O–NaCl belongs to the class of binary systems that has a continuous critical curve extending from the critical point of one of the com-ponents to that of the other component (Sourirajan and Kennedy, 1962). By contrast, the system H₂O–SiO₂ has discontinuous critical curves that end in two critical end points (Kennedy and others, 1962). Results to date show that the system H₂O–CO₂ most probably belongs to the same class of systems as does H₂O–SiO₂; however, the critical curve is not regular, and it is marked by a saddle.

At the present time there is insufficient data to prove conclusively two critical end points in the CO₂ water system. The presence of a minimum tem-perature on the critical curve is shown in the present data. Krichevsky and Ziclis (1943) and Ziclis (1947) have presented the results of their studies on the binary system SO₂–N₂. This system is also one of molecules with and with-out dipole moments. Here the polarization of the components in their mixture

plays a major role in the separation of the gaseous mixture into two phases. The critical curve in this system has a minimum point in the pressure-temperature diagram, the coordinates of which are P = 4300 atm and T = 34.5°C.

The binary system $H_2O–CO_2$ is quite similar to the system $SO_2–N_2$ in that water has a large dipole moment and carbon dioxide does not. In the present data we find a minimum point on the critical curve at about 2150 bars and at a temperature of approximately 265°C. The recent results of Todheide (ms) on the system $H_2O–CO_2$, made available near the completion of this study, show a critical minimum temperature at 266°C and 2450 bars.

PREVIOUS WORK

Pollitzer and Strebel (1924) have studied the relations between saturated water vapor and various gases. They reported values for concentration of water vapor in carbon dioxide gas at temperatures of 50° and 70° and to pressures of 87 atm. The compression of liquid water by CO_2 gas as well as solution of CO_2 in the water causes the partial pressure of water in the vapor phase to increase.

Zel'venskii (1937) has investigated the solubility of carbon dioxide in water at temperatures up to 100°C and up to 100 atm pressure. He has presented an equation of state for this system. He reports that the corrected Henry's law is obeyed by these solutions up to 95 atm at 100°C and 80 atm at 75°C. The formation of a hydrate of carbon dioxide with an equilibrium pressure of approximately 10 bars at 0°C was also reported. Weibe and Gaddy (1939, 1940, 1941) report on the binary system $H_2O–CO_2$. They report on vapor phase compositions up to 100° and at pressures up to 700 atm. Khitarov and Malinin (1958) report preliminary data on the system $H_2O–CO_2$ over the temperature range 200°C to 330°C and to pressures of 600 kg per cm². Malinin (1959) reports detailed data on the binary system. His data is the first that clearly shows the critical temperature of the solution is below the critical temperature of water in the gas–liquid system. Ellis (1959) reports further detailed data on solubility of CO_2 in water in the temperature range of 120°C-350°C and at pressures up to 160 atm. Ellis and Golding (1963) have reported on solubility of carbon dioxide in dilute aqueous sodium chloride solutions, and their study covered the range 170°C to 340°C and a pressure range of 15 to 90 atm. Their value of solubility of CO_2, expressed in Henry's law coefficients, is shown in table 4 along with the results of our measurements.

Franck and Todheide (1959) report on supercritical mixtures of water and carbon dioxide at 750°C and at pressures to 2000 atm. According to their work, the behavior of the system $H_2O–CO_2$ is typical of a binary system composed of a strongly polar and a non-polar component.

Todheide (ms) continued the study of the system $CO_2–H_2O$ up to 3500 bars. His data on liquid phase composition are close to the data of Wiebe, Gaddy, and Malinin, but his gas phase data show generally higher CO_2 concentrations than is shown in Malinin's data (see fig. 8). He found that the critical curve of the binary system $H_2O–CO_2$ extended from the critical point of pure water to a minimum critical temperature at 266°C with a pressure 2450 bars and a critical composition of 41.5 mole percent CO_2. He also ob-

served an inversion in the relative densities of gas and liquid taking place at approximately 800 bars at 50°C, 1250 bars at 100°C, and 2000 bars at 250°C. He estimated the pressure of the upper critical end point to be more than 50,000 bars.

APPARATUS

A schematic diagram of our apparatus is shown in figure 1. The apparatus in general consisted of an autoclave of Haynes stellite no. 25, stainless steel sampling valves, gauges, and pumping and intensifier systems for water and CO_2.

The design of the autoclave used in this work was the same as that previously described (Sourirajan and Kennedy, 1962). The autoclave has approximately 105 cc volume and was sealed with a closure stem and tapered nut and washers of conventional design. Our autoclave had no provision for mechanical and magnetic stirring as was the case of the apparatus used by Malinin (1959) and Todheide (ms). Two Inconel X capillary tubes of 0.125 inches O.D. and 0.020 inches I.D. were welded into the Inconel X closure stem. These capillary tubes extended into the top and into the bottom of the bomb so that samples of either the light or the dense phase could be extracted from the bomb. Unfortunately Inconel X proved peculiarly susceptible to stress corrosion by carbonic acid and was replaced by stainless steel for the higher pressure runs.

The autoclave was heated in an electric furnace which was regulated with a precision of approximate ± 0.8°C.

Temperatures of the autoclave were measured with two chromel-alumel thermocouples and Leeds and Northrop type K potentiometer. A deep thermocouple well, not shown on the schematic drawing, extends almost to the center
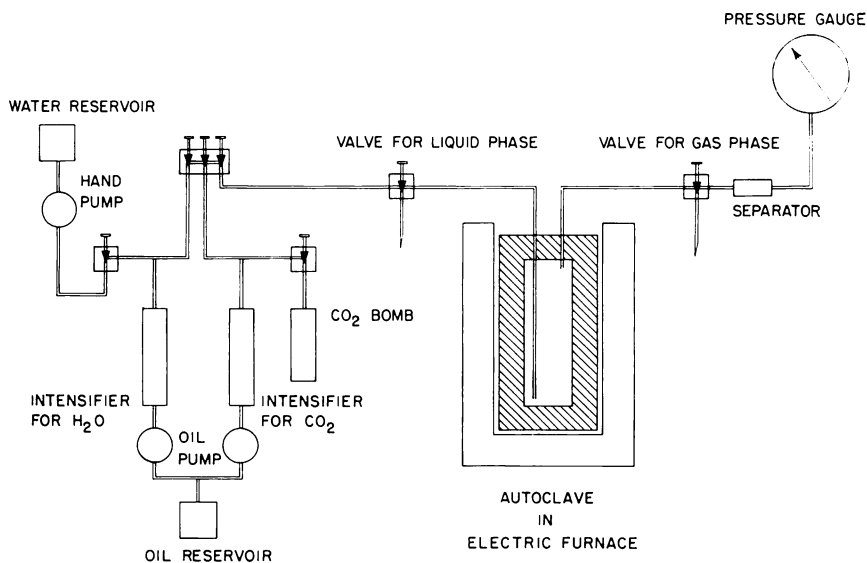

Fig. 1. Schematic diagram of the experimental apparatus.

of the bomb. Temperature is measured both here and at the upper end of the bomb. The difference in the two temperatures normally is less than 0.5°C during an experiment.

Pressures were determined by a 15 inch face-diameter Heise Bourdon Tube gauge with a range of 0-3000 bars and a scale interval of 4 bars. This gauge has previously been calibrated against a dead weight free piston gauge. Hysteresis of the gauge was approximately 2 bars. Our pressure gauge was connected to the gas phase sampling line by a separator which served to isolate the mixture of kerosene in the pressure gauge from $H_2O–CO_2$ in our sampling line. The capillary tube. used to introduce water and CO_2 in the autoclave, was coupled to the liquid phase sampling line. Hypodermic needles formed the points of each sampling line through which samples were taken into polyethylene bottles. Our sampling lines were heated to the same approximate temperatures as those obtaining in the bomb by impressing a low voltage electric current on them. This prevented condensation of water in the lines during sampling activity. The valve outlet of the gas phase line was heated by an external nichrome wire heater to prevent the freezing of water caused by the sudden expansion of compressed carbon dioxide (Saddington and Krase. 1934; Ellis and Fyfe, 1957).

EXPERIMENTAL METHOD

All determinations of coexisting gas–liquid compositions in this study were made along isotherms. We found it relatively easy to keep the temperature of the system constant and to take samples at various pressures beginning with the highest pressure at a given isotherm and extending to lower pressures.

The following procedures were normally employed in the course of a run. The autoclave was first filled with distilled water and then brought to temperature, allowing some of the water to escape as it expanded. This procedure largely eliminated the problem of air in the autoclave. Once the desired temperature was reached and the required amount of water extracted, carbon dioxide was pumped into the system to bring the total composition to nearly the critical composition of the intended isotherm. Samples were then alternately withdrawn from the top and the bottom of the autoclave. At supercritical temperatures and pressures both top and bottom samples were the same. Under conditions lower than the critical, the compositions of coexisting fluid phases were thus determined. At each new pressure the gas phase was sampled first. The liquids apparently reached equilibrium more rapidly than gas after a pressure drop owing to exsolution of bubbles and mechanical segregation of the two phases, whereas diffusion equilibrium is very slow.

Samples were taken in weighed polyethylene bottles of about 50 cc volume. The polyethylene bottles contained a solution of one normal sodium hydroxide which immediately reacted with the carbon dioxide upon sampling. The content of carbon dioxide was determined by the titration method (Kolthoff and Sandell, 1952). The weight of the sample was determined directly. The content of sodium carbonate in the sodium hydroxide solution was determined by titration with the standardized hydrochloric acid solution using phenolphthalene and bromcresol green as indicators.

TABLE 1

Equilibrium concentration of carbon dioxide in liquid phase and gas phase of binary system water-carbon dioxide at various temperatures and pressures. Concentration of carbon dioxide is shown by mole percent. P_c shows critical pressure, and X_c shows critical concentration of carbon dioxide.

bars	350°C liq phase	350°C gas phase	325°C liq phase	325°C gas phase	300°C liq phase	300°C gas phase
100	—	—	—	—	0.4	8.0
150	—	—	1.0	10.6	1.6	29.0
200	1.5	9.0	2.6	24.6	2.9	39.0
250	4.0	16.2	4.3	32.1	4.1	43.4
300	6.4	16.6	6.1	34.2	5.4	45.4
350			8.2	33.4	6.8	45.6
400	$P_c = 325^{bars}$		11.2	28.6	8.4	44.8
450	$X_c = 10.5\%$				10.4	42.2
500			$P_c = 435^{bars}$		12.7	38.0
550			$X_c = 18.0\%$		17.0	32.0
					$P_c = 575^{bars}$	
					$X_c = 23.6\%$	

bars	275° liq phase	275° gas phase	270°C liq phase	270°C gas phase	260°C liq phase	260°C gas phase
100	1.0	25.6				
150	1.9	42.6				
200	2.8	50.0	2.7	53.0	2.7	57.2
250	3.8	54.0	3.6	57.0	3.5	62.0
300	4.9	55.8	4.6	59.0	4.4	64.0
400	7.2	55.8	6.7	59.0	5.9	64.2
500	9.6	53.0	8.7	57.0	7.3	62.4
600	12.0	49.6	10.6	54.6	8.7	60.4
700	14.4	46.0	12.5	52.0	10.0	58.0
800	17.5	42.0	14.5	49.6	11.3	56.0
900			16.6	46.2	12.5	54.8
	$P_c = 885^{bars}$					
1000			19.0	42.4	13.5	53.6
	$X_c = 27.0\%$					
1100			21.5	38.2	14.5	52.4
1200			25.0	34.0	15.5	51.0
1300					16.0	50.4
1400			$P_c = 1230^{bars}$		16.5	50.2
1500			$X_c = 28.8\%$		17.5	50.0

bars	250°C liq phase	250°C gas phase	200°C liq phase	200°C gas phase	150°C liq phase	150°C gas phase
100	1.2	41.0	1.3	71.5	1.35	88.0
200	2.7	63.6	2.6	82.0	2.15	91.0
300	4.2	68.0	3.4	82.5	2.60	90.0
400	5.5	67.6	4.1	81.6	2.90	88.2
500	6.4	66.0	4.7	80.0	3.20	86.2
600	7.4	63.6	5.2	78.0	3.45	84.0
700	8.4	61.3	5.6	76.0	3.70	82.4
800	9.4	59.3	5.8	74.5	3.90	80.8
900	10.4	58.0	6.1	73.2	4.05	79.4
1000	11.5	56.7	6.3	72.0	4.20	78.0
1100	12.5	55.5	6.5	71.6	4.40	77.0
1200	13.2	54.8	6.7	70.6	4.50	76.4
1300	13.6	54 2	6.9	70.0	4.60	75.8
1400	14.0	54.0	7.0	69.4	4.70	75.4
1500	14.4	54.0	7.2	69.0	4.80	75.2

TABLE 1 (Continued)

bars	110°C liq phase	gas phase	bars	110°C liq phase	gas phase
100	1.40	95.6	900	3.45	84.0
200	2.10	95.8	1000	3.60	83.0
300	2.40	94.8	1100	3.70	82.2
400	2.60	93.2	1200	3.75	81.6
500	2.80	91.4	1300	3.85	81.0
600	3.00	89.3	1400	3.90	80.4
700	3.15	87.2	1500	4.00	80.0
800	3.30	85.4			

In general, samples were taken at intervals of from 6 hours to 7 days depending on temperature and pressure. Approximately 0.1-0.3 grams of sample were taken for determination of the gas phase, and 0.4-1.5 grams were taken for the liquid phase.

Three or four samples were taken at each sampling period. The first part of the sample flow was discarded. This part of the sample was normally contaminated by residual material in the capillary tubes and sampling block. The volume of our lines and blocks was approximately 0.4 cc, thus generally 0.3-1.0 gram of sample was discarded with each sampling. A pressure drop of between 4 and 100 bars took place during the sampling. However, the values are recorded at the pressure prior to sampling. Temperature drop during sampling was normally less than 1°C. In general duplicate determinations of liquid phase composition agreed within the error of titration and weighing. However, in the case of the gas phase, deviation from sample to sample under presumably duplicate conditions was considerably larger and much beyond the error in titration. The scatter of results in the sampling of the gas phase is believed to be owing to condensation in the sample lines and sample block. The deviation of results in the gas phase was reduced by sampling at very low rates.

The carbon dioxide used during the course of this investigation was analyzed by the same means as that used in the determination of composition of the samples. Seven samples taken directly from our CO_2 supply tank showed a mean concentration of carbon dioxide of 99.84 mole percent. Standard deviation of the mean was ± 0.18 mole percent.

RESULTS

Results obtained in the present experiment program are shown in table 1. Compositions of the gas and liquid phases are expressed in mole percent carbon dioxide. These coexisting compositions are taken from smoothed plots of the experimental results. The pressure-composition diagrams and temperature-composition diagrams are shown in figures 2, 3, 4, 5 respectively.

A three dimensional view of the CO_2-H_2O system showing pressure, temperature, and composition is shown in figure 6. A pressure-composition diagram in which composition is shown on a log scale is presented in figure 7. The detailed relationships in the regions of low carbon dioxide concentration, a region of interest to geologists, are better displayed in this plot. Data for the 50° and 100° isotherms shown in figure 7 have been taken from the work of Wiebe and Gaddy (1939). Figure 8 shows the results of some recent work at

very high pressures and also shows a comparison between our data and the data of Todheide (ms) and Malinin (1959). Our data, the data of Todheide. and the data of Malinin are all in almost exact agreement where our experimental ranges overlap in the liquid region. Our data in the gas region is in reasonably good agreement with that of Malinin even though the area of overlap of the two sets of data is small. Unfortunately our data are not in accord with the results of Todheide especially at lower temperatures. In general our isotherms lie at lower CO₂ concentrations than do the isotherms of Todheide. Further, our critical curve lies at about 10 mole percent lower CO₂ concentration than does the critical curve of Todheide. We believe that the difference between our results and the results of Todheide lies in a fundamental difference
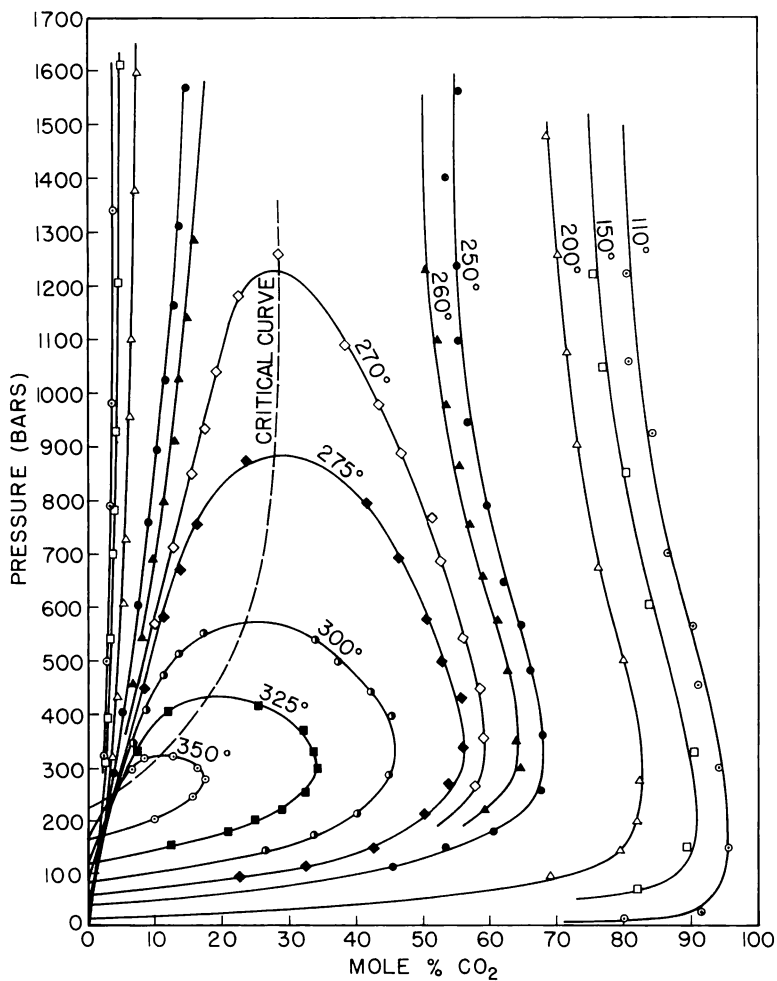
Fig. 2. Isotherms showing the compositions of gas and liquid phases in the system H₂O–CO₂.

in experimental technique. This difference is discussed in a later section of this paper. In general, however, the form of the phase diagrams and the phenomenology reported is the same in our work and the work of Todheide.

Figure 8 shows data obtained at pressures above 1600 bars. Our data points are shown by means of filled and opened circles. Samples represented by filled circles were taken from the upper part of the bomb, and samples represented by open circles are from the bottom part of the bomb. It is interesting to note that inversion takes place in the system. At high pressures the water rich phase floats on top of the carbon-dioxide rich phase, whereas at lower pressures the carbon dioxide rich phase floats on top of the water rich phase. Along each isotherm there is a pressure at which the density of the two coexisting phases is the same even though the bulk composition of the coexisting phases may be grossly different. The pointlessness of continuing the normal 1 atm distinction between the gas and liquid on to higher pressures is strikingly evident here. For instance, consider the 260° isotherm. At low pressures there
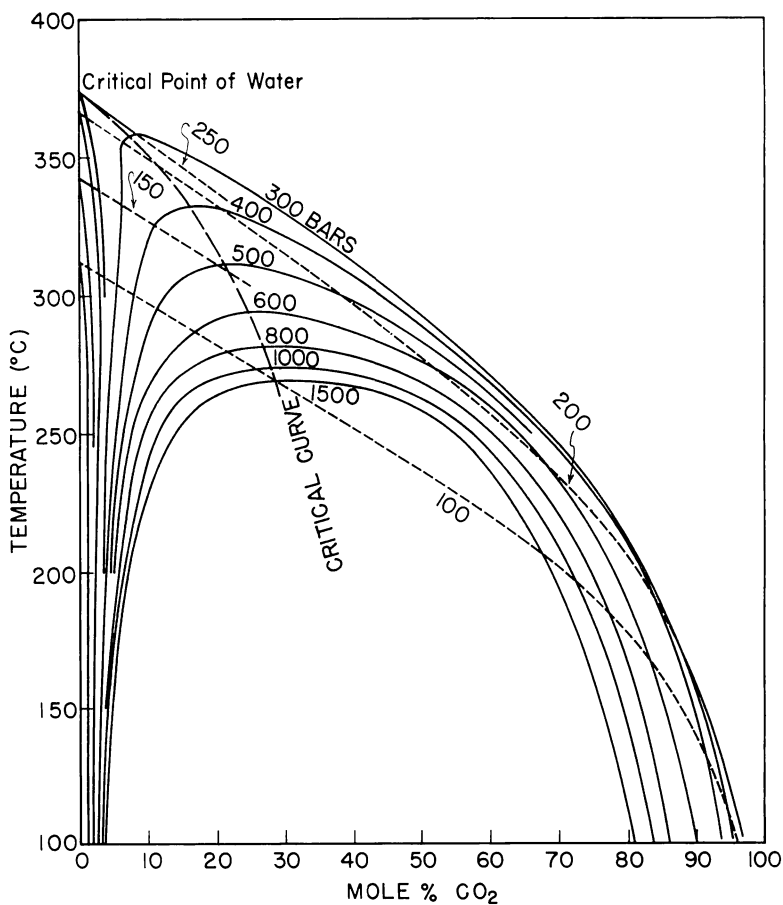

Fig. 3.   Isobaric curves with the critical curve for the system H_2O–CO_2.

is a very sharp density distinction between the water-rich phase and the CO_2-rich gaseous phase, whereas if one follows the carbon dioxide rich gas phase along the 260° isotherm, at a pressure of approximately 2200 atm this gas is now heavier than its coexisting liquid, and it sinks through the liquid to pond on the bottom of the bomb. Temperatures and pressures where the two fluid phases are of essentially the same density range from approximately 1300 bars at 110° to 2200 bars at 260°.

The critical curve of the system H_2O–CO_2 has a minimum critical temperature at about 265°C at a pressure of approximately 2150 bars. The composition near the minimum critical temperature is approximately 31 mole percent carbon dioxide. Thus, in this system, increasing pressure tends to increase solubility of CO_2 in water and solubility of water in CO_2 gas until a pressure of 2150 bars is reached. At pressures above this the effect of increasing pressure is to cause the two fluid phases to diverge more and more widely in composition as CO_2 segregates out in the dense fluid phase and water segregates into the lighter fluid phase.
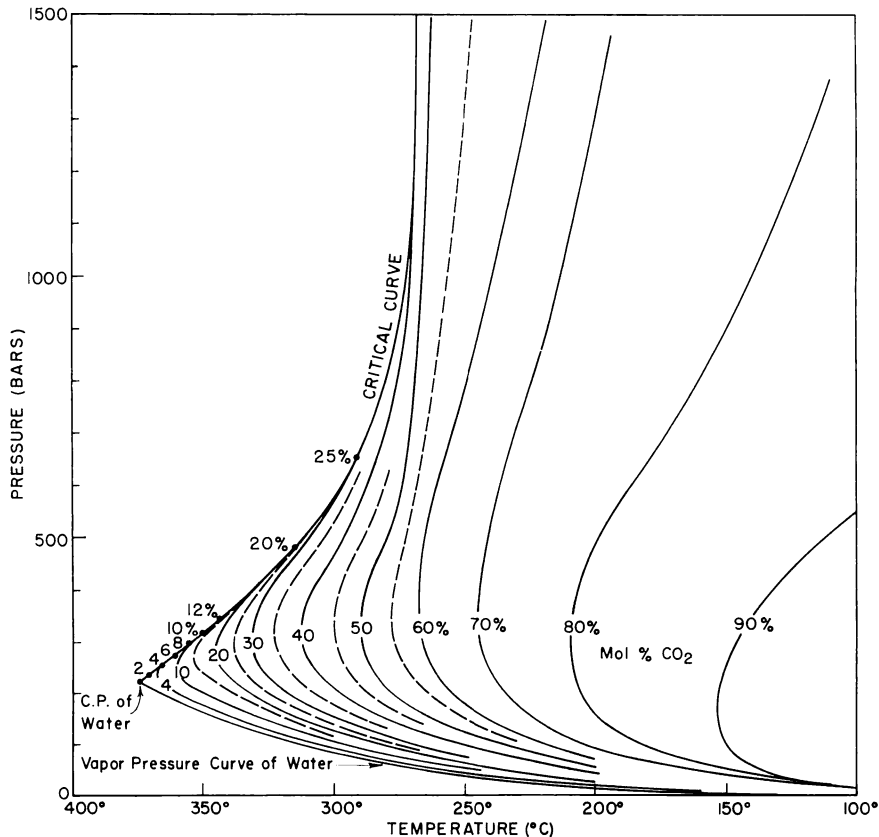

Fig. 4. Isocompositional curves of the gas phase in equilibrium with the liquid phase in the system H_2O–CO_2.

Precise determination of the minimum on the critical curve is most difficult as very slight changes in temperature bring about drastic changes in the composition of the coexisting fluids.

DISCUSSION

Our data as shown in figure 8 are in good agreement with the results of Malinin but depart sharply from the results of Todheide.

Ellis and Golding (1963) state that at least 24 hours were required before equilibrium between water and CO_2 was obtained. Malinin (1959) does not report the time required for attainment of equilibrium in his runs. Todheide, on the other hand, states that the time to reach equilibrium was only 1 hour. However, Todheide fitted his bombs with internal stirrers. In our study we found that at high tempeartures and low pressures, that is, temperatures above 270°C and below 700 bars, 24 hours were sufficient for complete mixture of water and carbon dioxide. However, at higher pressures and lower temperatures where the system was heterogeneous, substantially longer times were required for equilibrium. We assume this to be a result of increasing viscosity and decreasing diffusion speeds of this system at the higher pressures and lower temperatures (Quinn and Jones, 1936; Keyes. 1950; Walton, 1960). Our investigation showed that at least 3 days were required for equilibrium at a temperature of 200°C and substantially more than 1 week was required at 110°C.
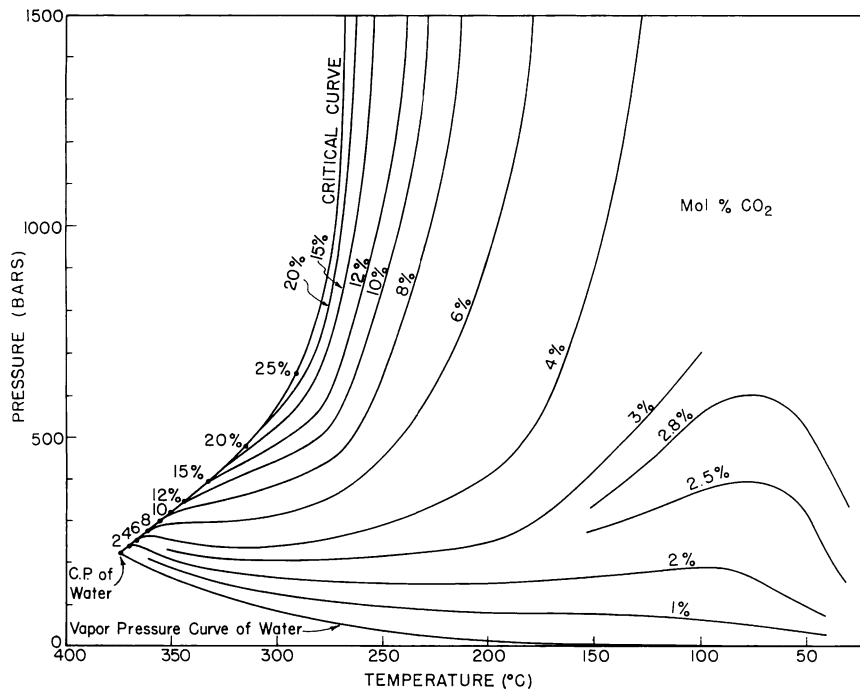

Fig. 5.   Isocompositional curves of the liquid phase in equilibrium with the gas phase in the system $H_2O–CO_2$.

Our critical curve shown in figure 9 decreases steadily toward a minimum temperature and then increases in temperature at higher pressures. Such characteristics of a critical curve have been shown by Krichevsky and Ziclis
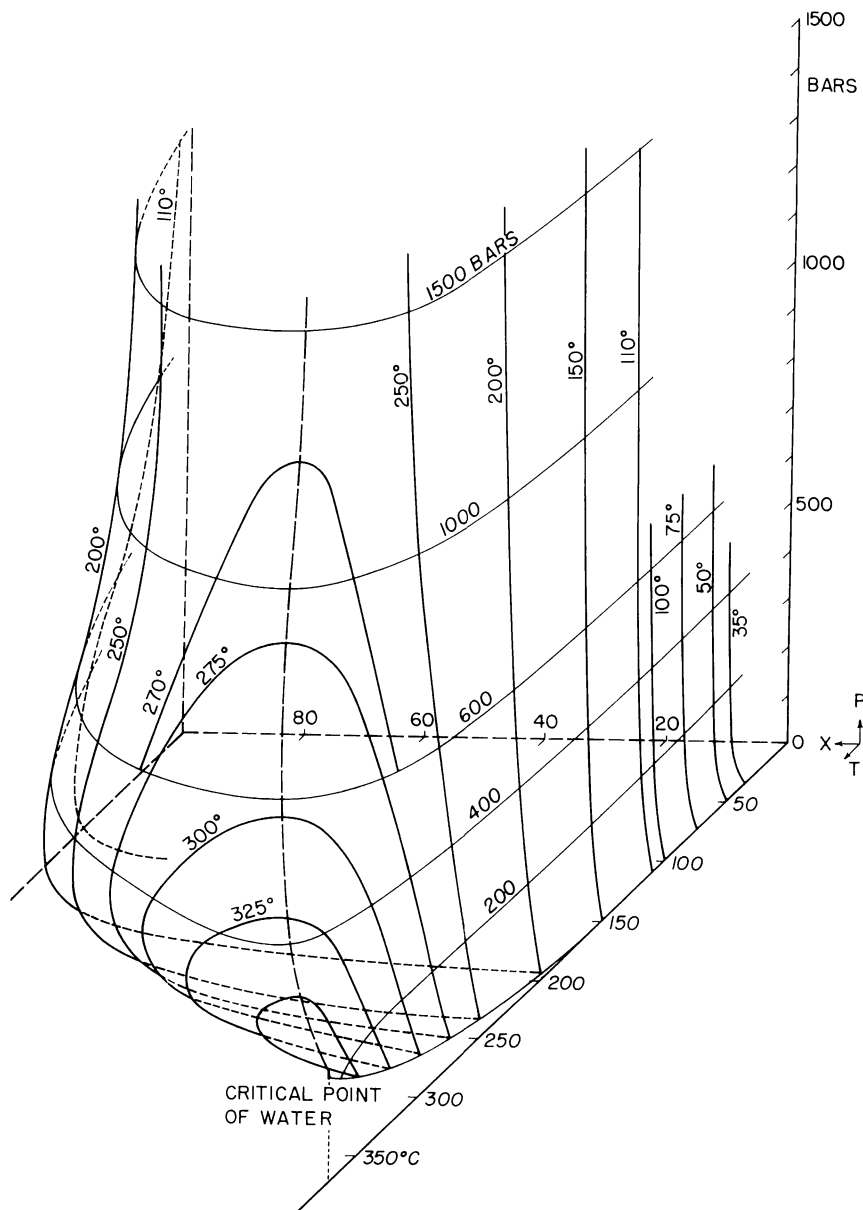

Fig. 6. Temperature-pressure-composition diagram of the system H₂O–CO₂.

(1943) and Ziclis (1947) to be characteristic of binary systems such as nitrogen-sulphur dioxide. nitrogen-ammonia, and methane-ammonia. These systems, like the one we have studied, consist of binary systems at which one molecule has a strong dipole moment and the other molecule has none. We do not know that the isotherms in this system, diverging at the highest pressures we have used. will close again at higher pressures. Ziclis has studied the binary system nitrogen-ammonia to 15,000 bars, but his upper isotherms are still diverging. Todheide inferred the presence of an upper critical end point in the system with pressures above 50,000 bars. Available data (Weibe and Gaddy, 1941; Larson. 1955) suggest that the second critical curve, which extends from the
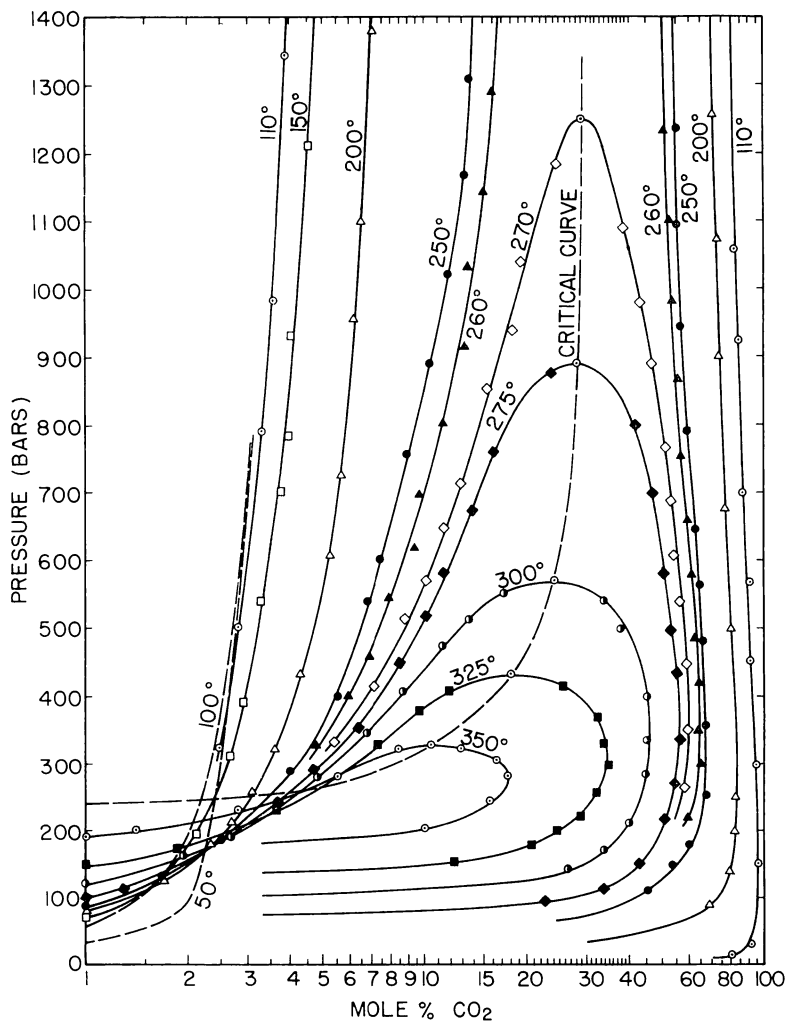

Fig. 7. Semi-logarithmic diagram of isotherms showing the composition of coexisting gases and liquids in the system H_2O-CO_2.

critical temperature and pressure of carbon dioxide, terminates very close to the critical point of carbon dioxide. The general phase relations are shown in figure 10.

One of the more unusual aspects of the system H_2O–CO_2 is the inversion in density where the CO_2-rich phase at low pressures is the lightest and at high pressures the densest of the two coexisting phases. A glance at the densities of water and carbon dioxide as a function of temperature and pressure shows why such inversion should take place (Kennedy, 1954; Holser and Kennedy, 1958).
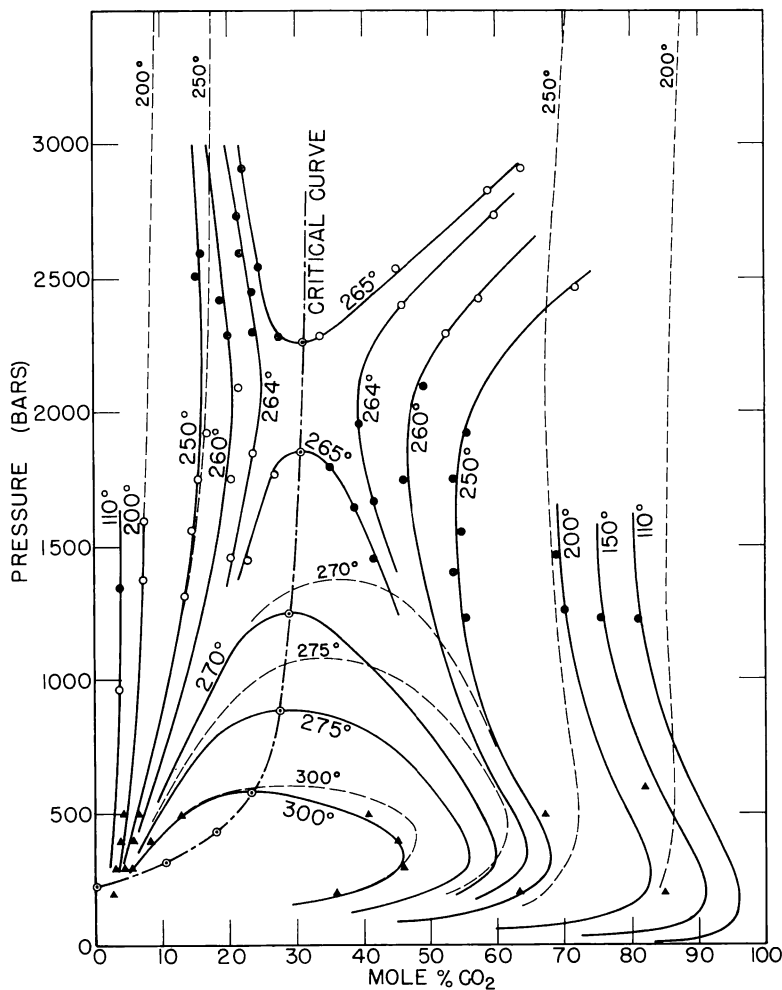

Full line = present data; Dashed line = Tödheide's data; Triangle = Malinin's data

Fig. 8. Isotherms showing the results of preliminary work up to 3000 bars in the system H_2O–CO_2. The results of Malinin and Todheide are shown for comparison. Filled circles show the composition of samples taken from the upper part of autoclave, and open circles show the samples from the lower part.

TABLE 2

Coexisting compositions in the critical region of the system CO_2-H_2O

| Temperature | 265° | | 264° | | 260° | |
Pressure	H_2O rich phase	CO_2 rich phase	H_2O rich phase	CO_2 rich phase	H_2O rich phase	CO_2 rich phase
1400[bars]	21.8	43.0	20.0	45.0	17.2	49.0
1600	24.0	39.6	21.8	42.5	18.6	47.4
1800	27.0	35.0	23.4	40.5	20.0	46.4
2000	—	—	24.8	39.5	20.8	47.2
2200	—	—	24.6	40.5	20.5	50.2
2400	26.0	40.0	23.6	45.5	19.6	56.4
2600	24.2	48.6	22.4	53.6	18.8	63.8
2800	22.8	57.8	21.0	58.0	18.0	72.0
3000	21.8	67.0	19.6	66.0		

$P_c = 1850$ bars

$X_c = 30.8\%$

$P_c = 2260$ bars

$X_c = 31.2\%$

Density curves at various temperatures and pressures for water and carbon dioxide are shown in figure 11. From this it can be noted that the relative densities of water and carbon dioxide become equal and then cross at 100°C and at about 1100 bars. Figure 11 also shows that at 200° and at 300° the relative densities of water and carbon dioxide should become the same at approximately 2000 bars. Unfortunately we do not have any data on the density of mixtures of water and carbon dioxide, but when the compositions of both phases are low in the other component, deviation of the density of these mixtures and the density of the pure component will not be large. It is thus possible to infer the pressure of density inversion. Surprisingly the pressure of density inversion as shown in figure 8 is remarkably close to that estimated if the relative densities of the two components are as shown in figure 11.

TABLE 3

Critical point and dipole moment of components and minimum critical temperature and its pressure of binary systems

| | Component of Binary System | | | Binary System | |
Component	Critical temp	Critical pressure	Dipole moment	Min critical temp	Pressure
H_2O	374.2°C	221.3[bars]	1.87[Debye]	265°C	2150[bar]
CO_2	31.1	73.8	—		
SO_2	157.5	78.7	1.61	34.5	4300
N_2	–147.1	33.9	—		
NH_3	132.4	113.0	1.47	86	1000
N_2	–147.1	33.9	—		
NH_3	132.4	113.0	1.47	43	1100
CH_4	–82.5	46.4	—		

The solubility of ideal gases in an ideal solution is expressed by the following equation (Lewis and Randall, 1961)

$$\left(\frac{d \ln X_g^1}{dP}\right)_T = \frac{\overline{v}_g^1 - v_g}{RT}$$ 1.

where X_g^1 is the mole fraction of the gas in the liquid solution; P is the total pressure; $\overline{v}_g^1$ is the partial molal volume of the gas in solution; v_g is the molal volume of the gas: R is the gas constant (82.06 cc atm/deg); T is the temperature in °K. This equation was derived from the assumption that the solution and the gas are ideal and that the solvent is non-volatile. This equation is not suitable for the calculation of solubility of carbon dioxide in water solution at high temperatures and high pressures.
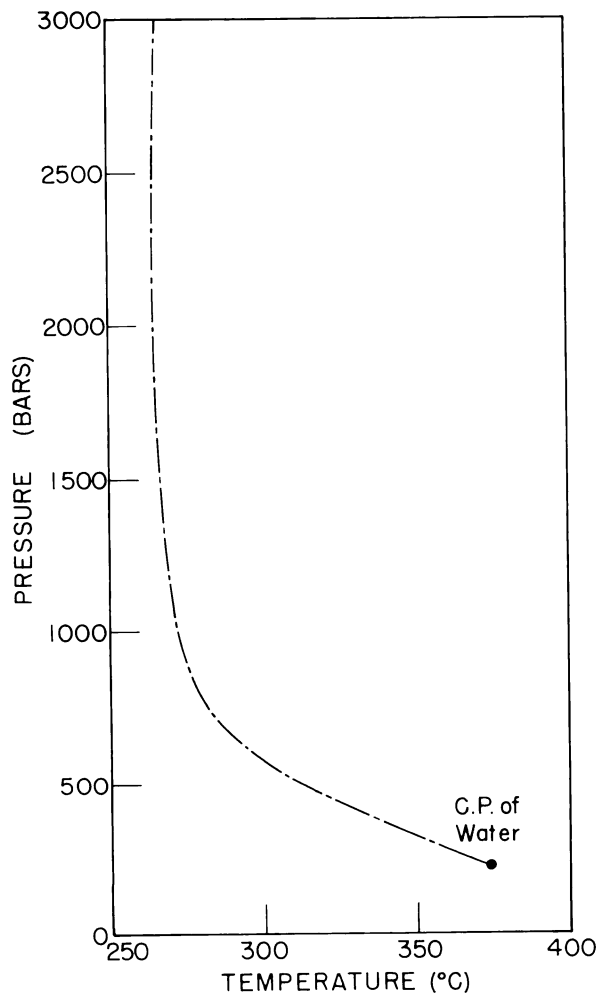
Fig. 9. Projection of critical curve of the system H₂O–CO₂ on a pressure-temperature plane.

The equations of solubility of slightly soluble gases in volatile solvents were reported by Krichevsky and Kasarnovsky (1935) and by Dodge and Newton (1939) separately. According to their results the equation of solubility of gas is expressed as follows:

$$\ln \frac{f_g{}^\circ \cdot X_g{}^g}{X_g{}^l} = \ln K + \frac{\bar{v}_g{}^l (P - p_w)}{RT} \qquad 2,$$

where $f_g{}^\circ$ is the fugacity of the gas at pressure P: $X_g{}^g$ is the mole fraction of the gas in the gas phase; P is the total pressure: p_w is the vapor pressure of the solvent: K is the Henry's law constant: the other symbols are the same as the equation (1). In this equation $\bar{v}_g{}^l$ is not the true partial molal volume of the gas but the apparent molal volume of the dissolved gas in solution at various temperatures. When the solubility data of the system are plotted on the diagram which is expressed by $\log \dfrac{f_g{}^\circ \cdot X_g{}^g}{X_g{}^l}$ as the ordinate and by (P-pw) as the abscissa, the points at the same temperature should lie on a straight line if equation (2) is applicable to the conditions of the system. In this case, the tangent of the line corresponds to the value of $\dfrac{\bar{v}_g{}^l}{2.303\,RT}$, and the values of the ordinate intersected by this line give the Henry's law constant at various temperatures. Figure 12 shows the value of $\log \dfrac{f_g{}^\circ \cdot X_g{}^g}{X_g{}^l}$ versus (P-pw), drawn
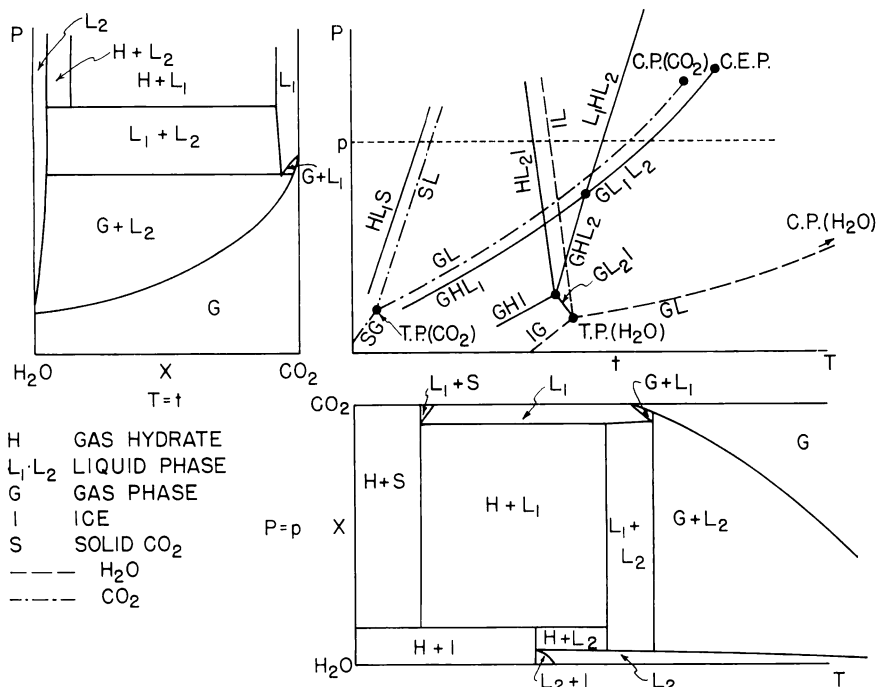

H   GAS HYDRATE
$L_l \cdot L_2$ LIQUID PHASE
G   GAS PHASE
I   ICE
S   SOLID CO_2
— — — H_2O
—·—·— CO_2

Fig. 10.   Schematic projection of the system H_2O–CO_2.

from the data of this investigation. The Henry's law constant and the apparent molal volume of the dissolved carbon dioxide at various temperatures are presented on table 4. The Henry's law constant calculated by the formula $f_c = K \cdot X$ is also presented for comparison. The values of fugacity of carbon dioxide which were necessary for the calculation of these formulae were taken from the diagram of Majumdar and Roy (1956).

It is clear from figure 12 that equation (2) is applicable for a wide range of pressures in this binary system at temperatures below 250°C. At higher temperatures than 250°C. as the solubility of carbon dioxide in the liquid phase and the solubility of water vapor in the gas phase increases, the conditions of the system deviate too much from the assumptions on which equation (2) is based. and the results can no longer be expressed by straight lines. The apparent molal volume and the Henry's law constant determined from figure 12 are shown in table 4. Generally. the Henry's law constant gained by the equation (2) is much lower than the value gained by the equation $f_c = K \cdot X$. The apparent molal volume calculated from the equation (2) is 27–30 cc/mole at temperature between 110° and 200°C, but the value at 250°C is only 4 cc/mole. The reason for the small value of partial molal volume at 250°C may be explained by the supposition that the intermolecular space of the liquid phase at this temperature is large enough to take in molecules of carbon dioxide without a great expansion of volume of the liquid phase. The
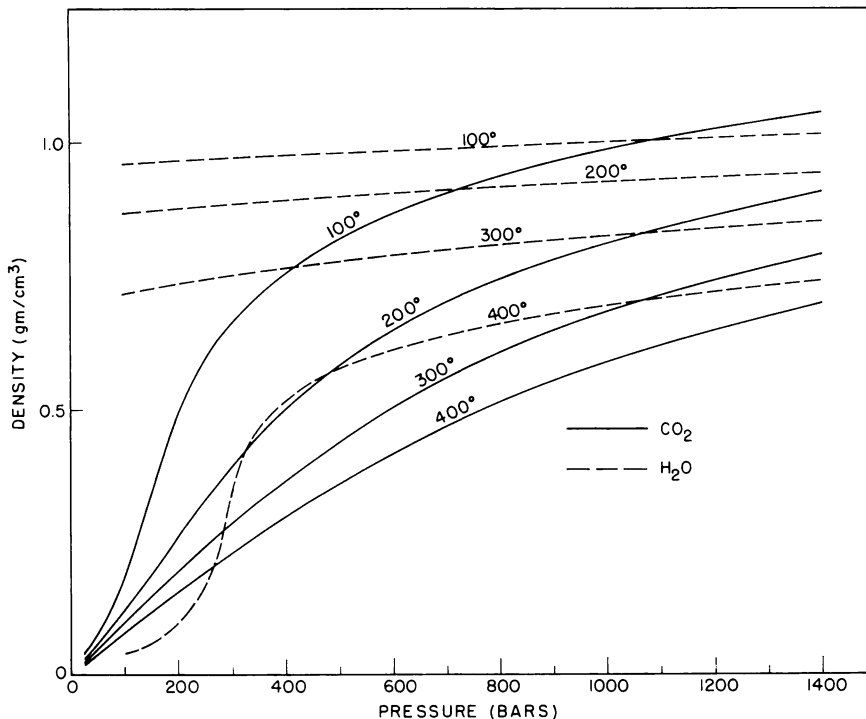

Fig. 11. The density of water and carbon dioxide at various temperatures and pressures.

TABLE 4

Henry's law constant of the system H_2O–CO_2 at various temperatures and partial molal volume of carbon dioxide in water solution gained from figure 11

Temperature °C		100	110	150	200	250	275	300	325
K_E	atm	5200		6600	6400	5300	4600	3900	3100
K_I	atm		5500	6300	6000	5250	4400	3800	2950
K_{II}	atm			5010	5560	4840	4170		
$\bar{v}_g^1$	cc/mole			28.4	30.0	27.0	4.0		

K_E : Data of Ellis and Golding (1963).

K_I : Data gained from the equation $f_c = K \cdot \gamma$.

K_{II} : Data gained from the equation (2).

$\bar{v}_g^1$: Partial molal volume.

conditions at this temperature are already unsuitable for the assumptions of equation (2). At temperatures higher than about 250°C, equation (2) has no significance for this system.

Studies of vacuoles and low temperature hydrothermal liquids suggest that residual ore depositing solutions may be rich in water, CO_2, and dissolved salts, thus the simple binary system H_2O–CO_2 cannot be directly applied. The solubility of carbon dioxide in calcium chloride solutions was investigated by Prutton and Savage (1945) and by Malinin (1959). The solubility of carbon dioxide in sodium chloride solutions was reported on by Ellis and Golding (1963).
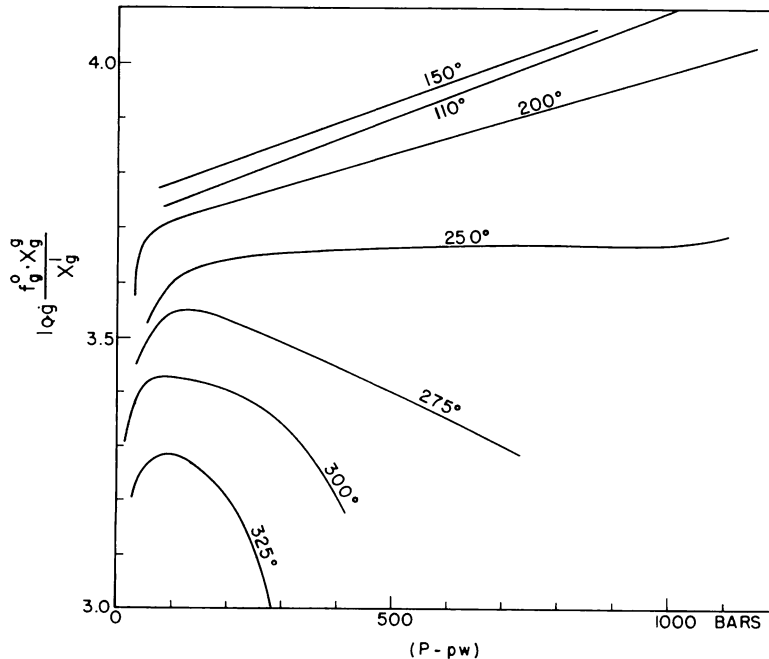

Fig. 12. Solubility curves of carbon dioxide in water.

The results of these investigations show that the solubility of carbon dioxide is sharply decreased by the addition of salts. However, the general trend of the solubility curves of carbon dioxide in the liquid is essentially the same as in the system pure water-carbon dioxide. Unfortunately no data about the gas phase composition of the systems are available at the present time. It is certain however that the heterogeneous region in the system water-carbon dioxide-salt, projected on a pressure composition diagram, will be broader than in the simple binary system. Further, the critical pressure of the system containing salt will be higher than in the pure system.

In general a naturally occurring solution of water and carbon dioxide will remain homogeneous to a temperature lower than the critical temperature of water during its ascent to the earth surface. At medium to very low temperatures the concentration of carbon dioxide in homogeneous solutions will be limited and can scarcely exceed 24 mole percent at any pressure below 265°C.

SUMMARY

1. Phase equilibria in the binary system H_2O–CO_2 has been studied in detail up to 350°C and at pressures up to 1600 bars.

2. Preliminary experiments have been carried on to pressures of 3000 bars and approximately delineate the position of the critical curve.

3. The critical curve in this system starts from the critical point of water. A minimum critical temperature is found at 265°C a pressure of approximately 2150 bars with composition 31 mole percent carbon dioxide.

4. A density inversion in the two phases has been found at high pressures. The pressure of density inversion depends upon the temperature of the system and increases with the temperature.

5. In a natural system complete miscibility in the system H_2O–CO_2 will not be found at temperatures under 265°C. At higher temperatures a completely mixed supercritical fluid may exist, but at lower temperatures this fluid will segregate into two fluid phases.

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REFERENCES

Dodge, B. F., and Newton, R. H., 1937, Calculation of pressure effect on liquid-vapor equilibrium in binary systems: Ind. Eng. Chemistry, v. 29, p. 718-724.
Ellis, A. J., 1959, The solubility of carbon dioxide in water at high temperatures: Am. Jour. Sci., v. 257, p. 217-234.
Ellis, A. J., and Fyfe, W. S., 1957, Hydrothermal Chemistry: Rev. Pure Appl. Chemistry, v. 7, p. 261-316.
Ellis, A. J., and Golding, R. M., 1963, The solubility of carbon dioxide above 100°C in water and in sodium chloride solutions: Am. Jour. Sci , v. 261, p. 47-60.
Franck, E. U., and Todheide, K., 1959, Thermische Eigenshaften uberkritischer Mischungen von Kohlendioxyd und Wasser bis zu 750°C und 2000 atm: Zeitschr. Phys. Chemie, N.F., v. 22, p. 232-245.

Holser, W. T., and Kennedy, G. C., 1958, Properties of water. Part IV: Pressure-volume-temperature relations of water in the range 100-400°C and 100-1400 bars: Am. Jour. Sci., v. 256, p. 744-754.

Kennedy, G. C., 1954, Pressure-volume-temperature relations in CO_2 at elevated temperatures and pressure: Am. Jour. Sci., v. 252, p. 225-241.

Kennedy, G. C., Wasserburg, G. J., Heard, H. C., and Newton, R. C., 1962, The upper three-phase region in the system SiO_2–H_2O: Am. Jour. Sci., v. 260, p. 501-521.

Keyes, F. G., 1950, The viscosity and heat conductivity of steam: Am. Chem. Soc. Jour., v. 72, p. 433-436.

Khitarov, N. I., and Malinin, S. D., 1958, Phase equilibria in the system H_2O–CO_2: Geochemistry, no. 7, p. 846-848.

Kirillin, V. A., and Scheindlin, A. E., 1956, Thermodynamics of solutions [in Russian]: Moscow, Gosudarst. Energet. Izdatel., 272 p.

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis, 3rd ed.: New York, Macmillan Co., 759 p.

Krichevsky, I. R., and Bolshakov, P., 1941, Die heterogenen Gleichgewichte in Ammoniak-Stickstoff-System bei hohen Drucken: Acta Physicochimia U.R.S.S.: v. 14, p. 353-364.

Krichevsky, I. R., and Hasanova, N. E., 1939, Solutions gas-vapor at high pressures: Acta Physicochimia U.R.S.S., v. 10, p. 199-216.

Krichevsky, I. R., and Kasarnovsky, J. S., 1935, Thermodynamical calculations of solubilities of nitrogen and hydrogen in water at high pressures: Am. Chem. Soc. Jour., v. 57, p. 2168-2171.

Krichevsky, I. R., and Ziclis, D., 1943, Gas-gas equilibrium and phase equilibria in binary systems: Acta Physicochimia U.R.S.S., v. 18, p. 264-274.

Larson, S. D., 1956, Phase studies of the two component carbon dioxide-water system involving the carbon dioxide hydrate: Univ. Microfilms No. 15,235, Ann Arbor, Mich., diss. abs. (1956), v. 16, p. 248.

Lewis, G. N., and Randall, M., 1961, Thermodynamics, 2nd ed.: New York, McGraw-Hill Book Co., 723 p.

Majumdar, A. J., and Roy, Rustum, 1956, Fugacities and free energies of CO_2 at high pressures and temperatures: Geochim. et Cosmochim. Acta, v. 10, p. 311-315.

Malinin, S. D., 1959, The system water-carbon dioxide at high temperatures and pressures: Geochemistry, no. 3, p. 292-306.

Pollitzer, F., and Strebel, E., 1924, Uber den Einfluss indifferenter Gase auf die Sattigungs-Dampfkonzentration von Flussigkeiten: Zeitschr. Phys. Chemie, v. 110, p. 768-785.

Prutton, C. F., and Savage, R. L., 1945, The solubility of carbon dioxide in calcium chloride-water solutions at 75, 100, 120° and high pressures: Am. Chem. Soc. Jour., v. 67, p. 1550-1554.

Quinn, E. L., and Jones, C. L., 1936, Carbon dioxide: Am. Chem. Soc. Mon. no. 72, New York, Reinhold Pupl. Corp., 294 p.

Saddington, A. W., and Krase, N. W., 1934, Vapour-liquid equilibria in the system nitrogen–water: Am. Chem. Soc. Jour., v. 56, p. 353-361.

Sourirajan, S., and Kennedy, G. C., 1962, The system H_2O–NaCl at elevated temperatures and pressures: Am. Jour. Sci., v. 260, p. 115-141.

Todheide, K., ms, 1963, Das Zweiphasengebiet und die kritische Kurve im System Kohlendioxyd–Wasser bis zu Drucken von 3500 bar: Ph.D. thesis, George August University, Gottingen, 54 p.

Walton, Matt, 1960, Molecular diffusion rates in supercritical water vapor estimated from viscosity data: Am. Jour. Sci., v. 258, p. 385-401.

Wiebe, R., 1941, The binary system carbon dioxide–water under pressure: Chem. Rev., v. 29, p. 475-481.

Wiebe, R., and Gaddy, V. L., 1939, The solubility in water of carbon dioxide at 50°, 75°, and 100° at pressures to 700 atm.: Am. Chem. Soc. Jour., v. 61, p. 315-318.

————— 1940, The solubility of carbon dioxide in water at various temperatures from 12 to 40° and at pressures to 500 atm.: Am. Chem. Soc. Jour., v. 62, p. 815-817.

————— 1941, Vapor phase composition of carbon dioxide-water mixtures at various temperatures and at pressures to 700 atm.: Am. Chem. Soc. Jour., v. 63, p. 475-477.

Zel'venskii, Ya. D., 1937, The solubility of carbon dioxide under pressure: Jour. Chem. Industry [U.S.S.R.], v. 14, p. 1250-1257 [Chem. Abs., 1938, v. 32, p. 852].

Ziclis, D. S., 1947, The limited mutual solubility of gases at high pressures (system SO_2–N_2) [in Russian]: Jour. Phys. Chem., v. 21, p. 349-354.