TABLE 1 (Continued)

	110°C			110°C	
bars	liq phase	gas phase	bars	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 CO_2 concentrations than do the isotherms of Todheide. Further, our critical curve lies at about 10 mole percent lower CO_2 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

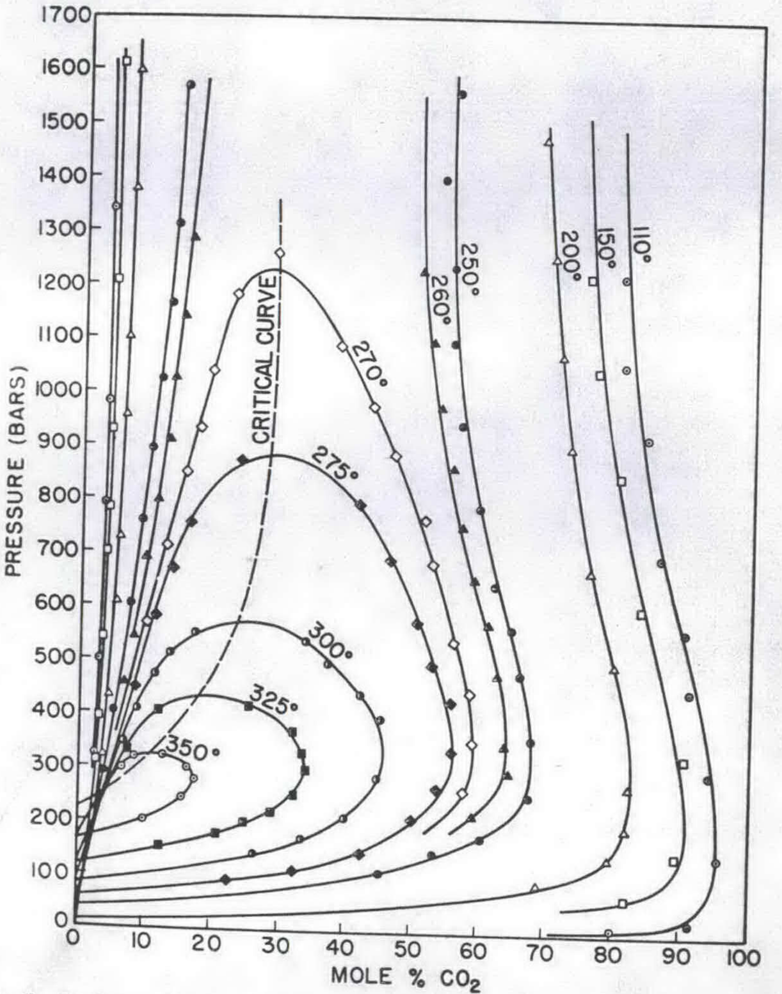


Fig. 2. Isotherms showing the compositions of gas and liquid phases in the system H_2O–CO_2.

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 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.

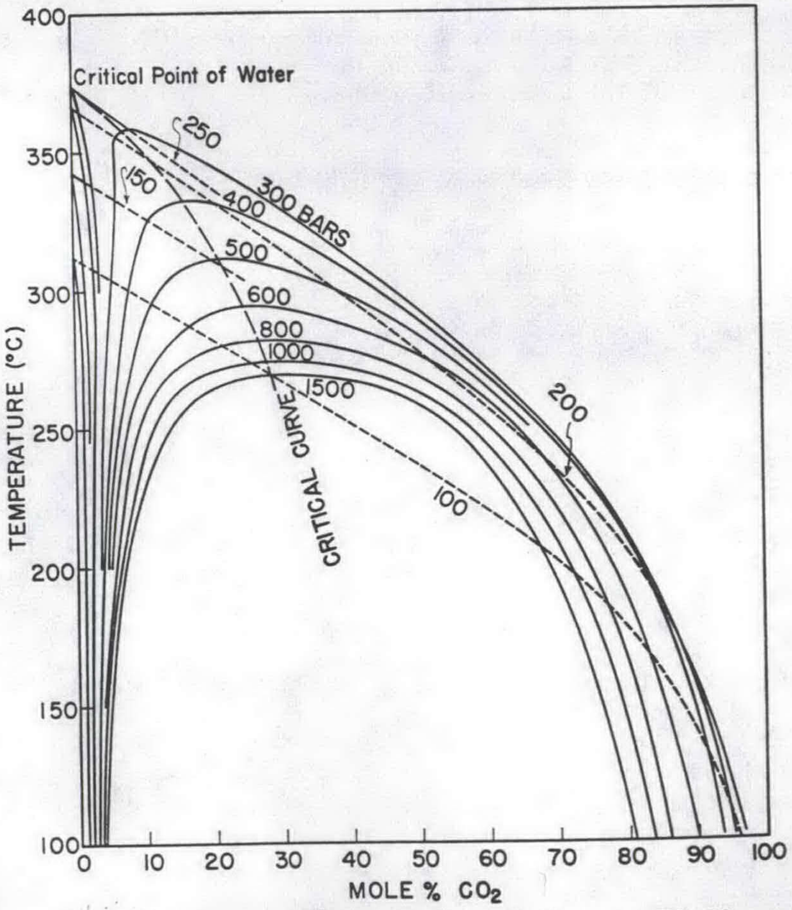


Fig. 3. Isobaric curves with the critical curve for the system H_2O–CO_2.

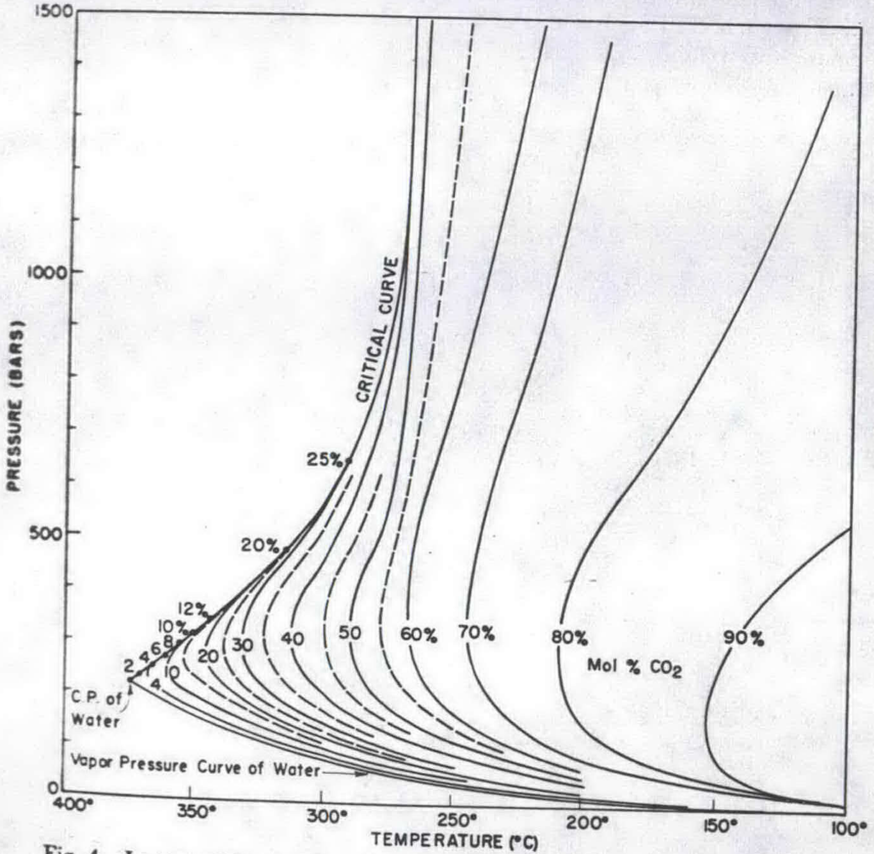


Fig. 4. Isocompositional curves of the gas phase in equilibrium with the liquid phase in the system H_2O–CO_2.

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.

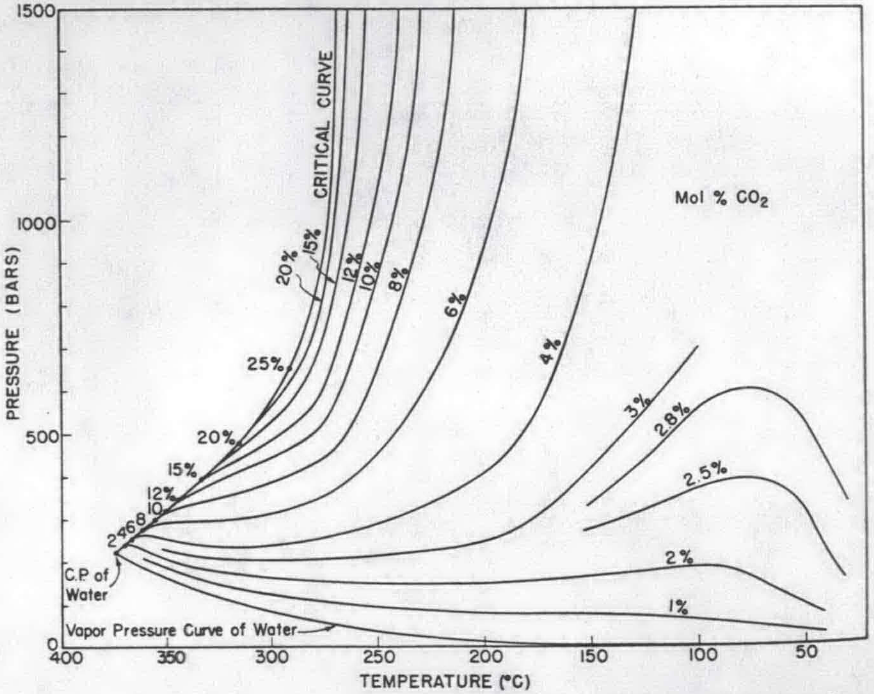


Fig. 5. Isocompositional curves of the liquid phase in equilibrium with the gas phase in the system H_2O–CO_2.

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

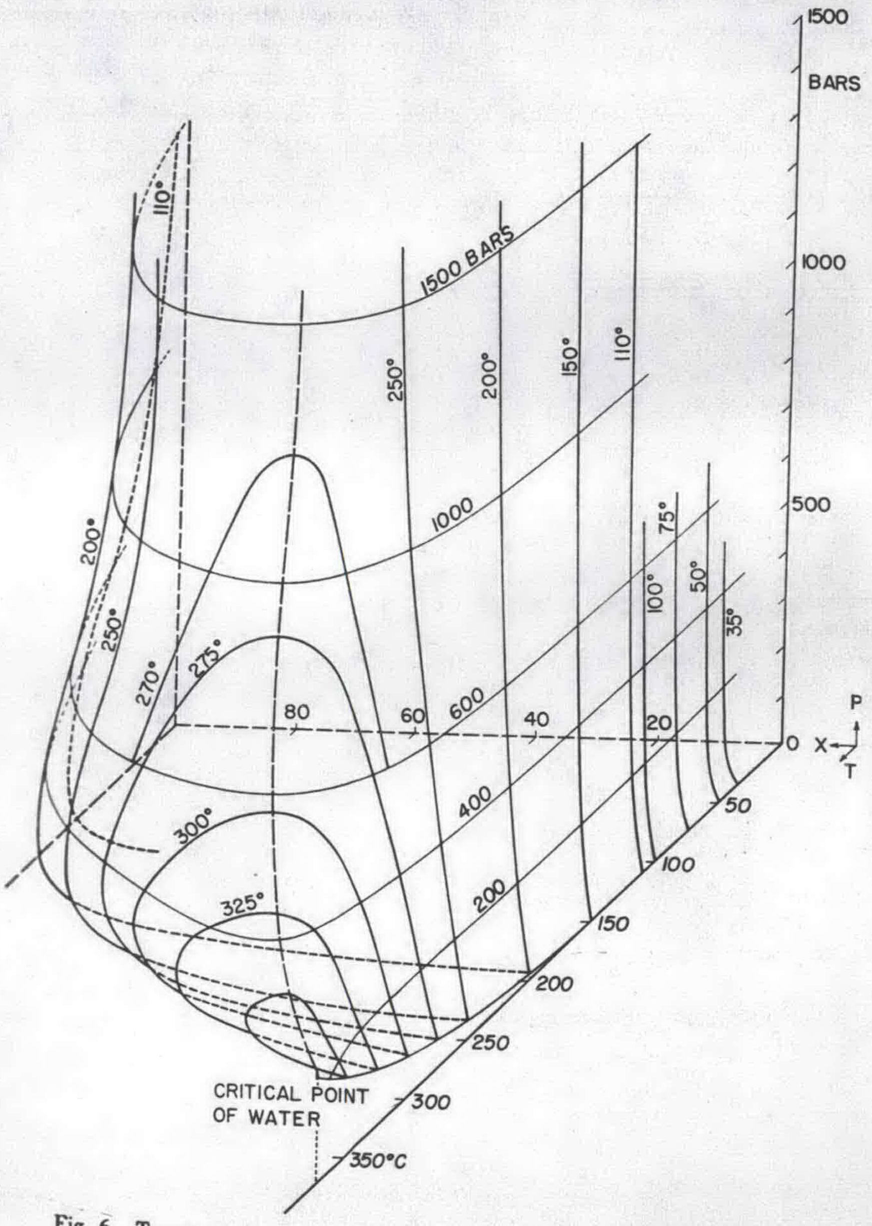


Fig. 6. Temperature-pressure-composition diagram of the system H_2O–CO_2.

(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

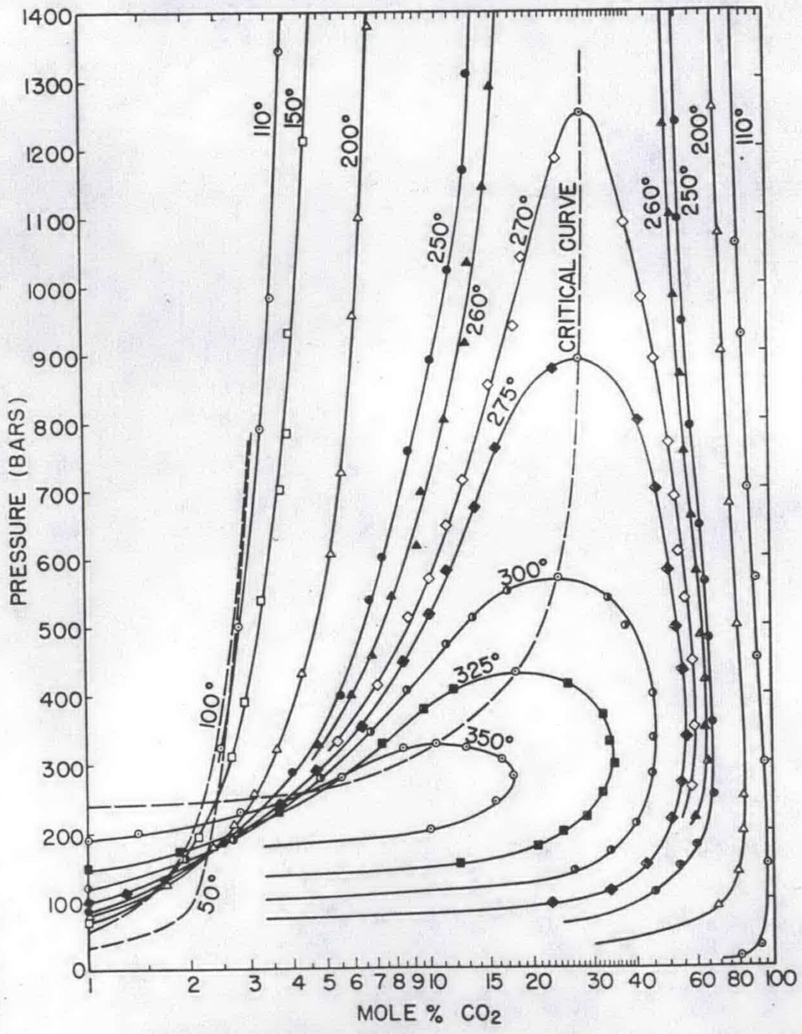
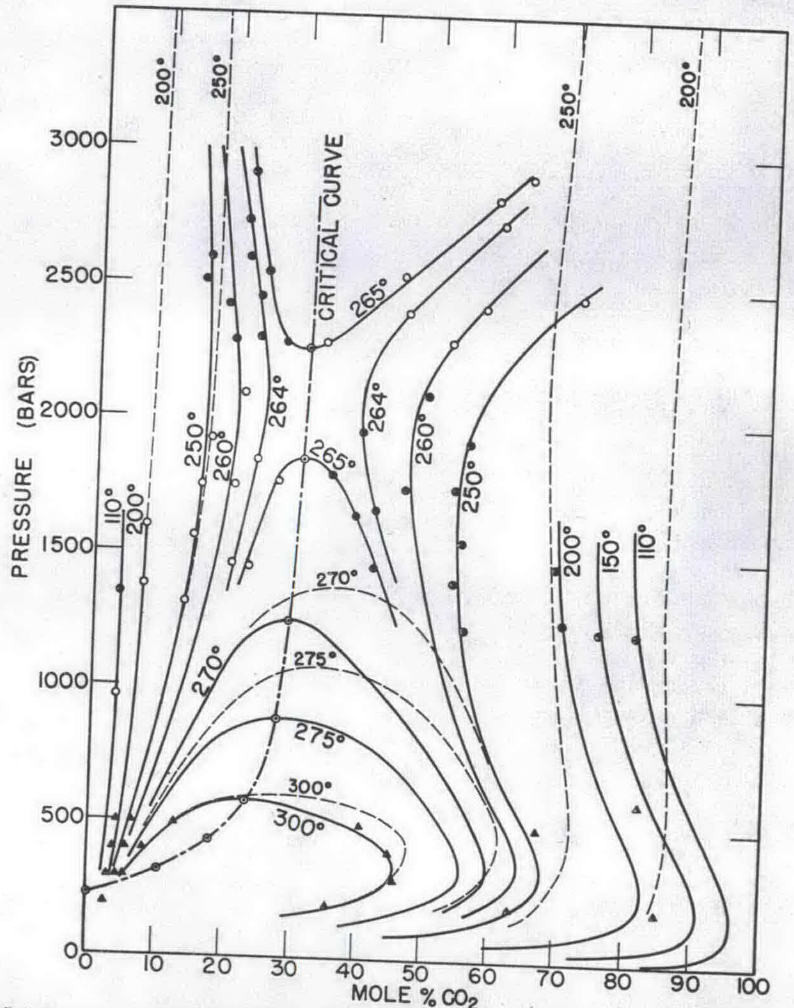


Fig. 7. Semi-logarithmic diagram of isotherms showing the composition of coexisting gases and liquids in the system H_2O–CO_2.

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)

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

where $X_g{}^1$ is the mole fraction of the gas in the liquid solution; P is the total pressure; $\bar{v}_g{}^1$ 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.

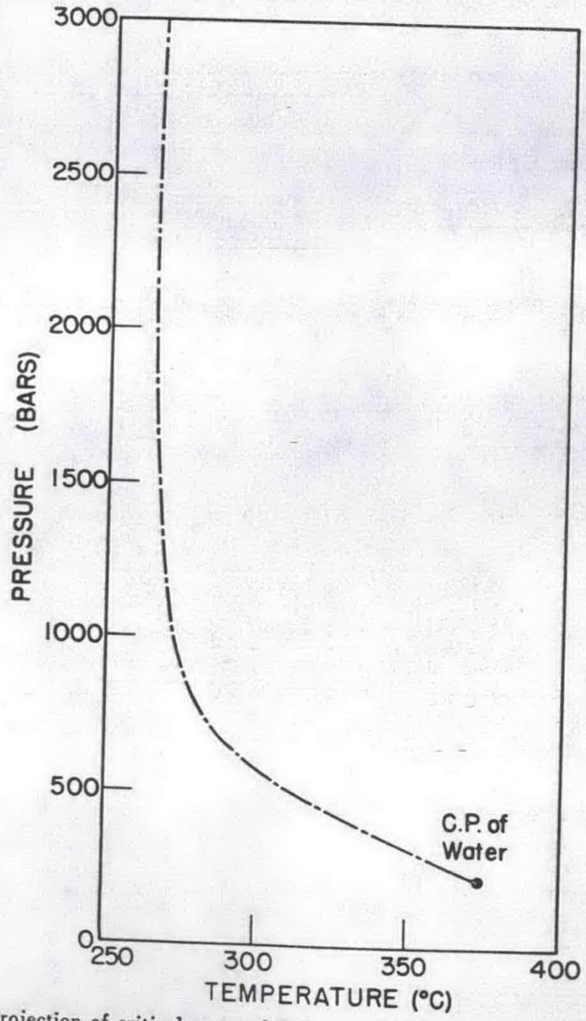


Fig. 9. Projection of critical curve of the system H_2O–CO_2 on a pressure-temperature plane.

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° 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 $\log \frac{f_g^\circ \cdot X_g^g}{X_g^l}$ 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 $\frac{\bar{v}_g^l}{2.303\,RT}$, 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 $\log \frac{f_g^\circ \cdot X_g^g}{X_g^l}$ versus (P-pw), drawn

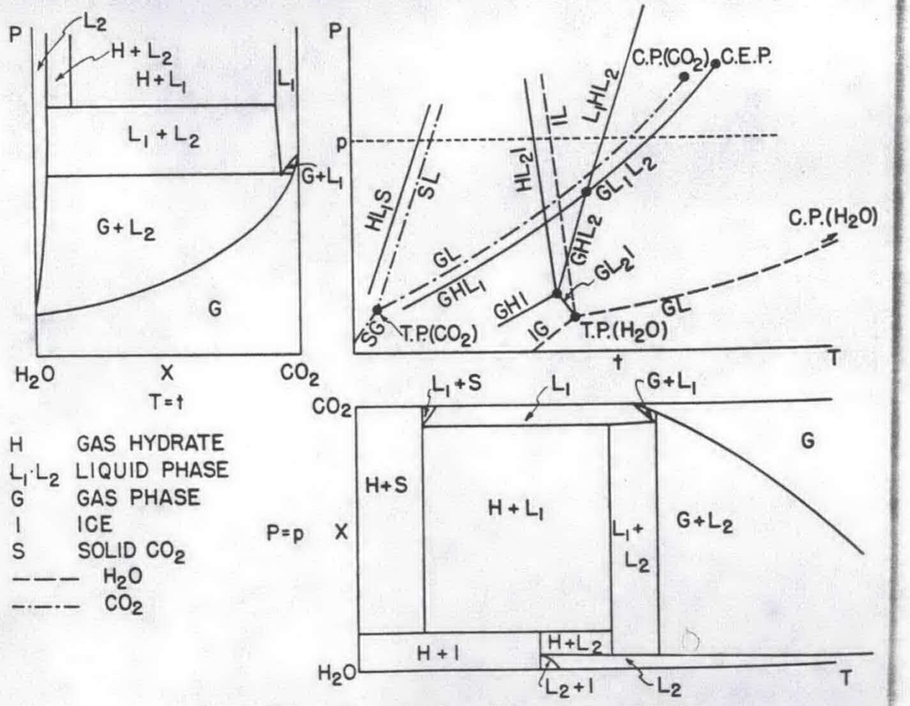


Fig. 10. Schematic projection of the system H_2O–CO_2.

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

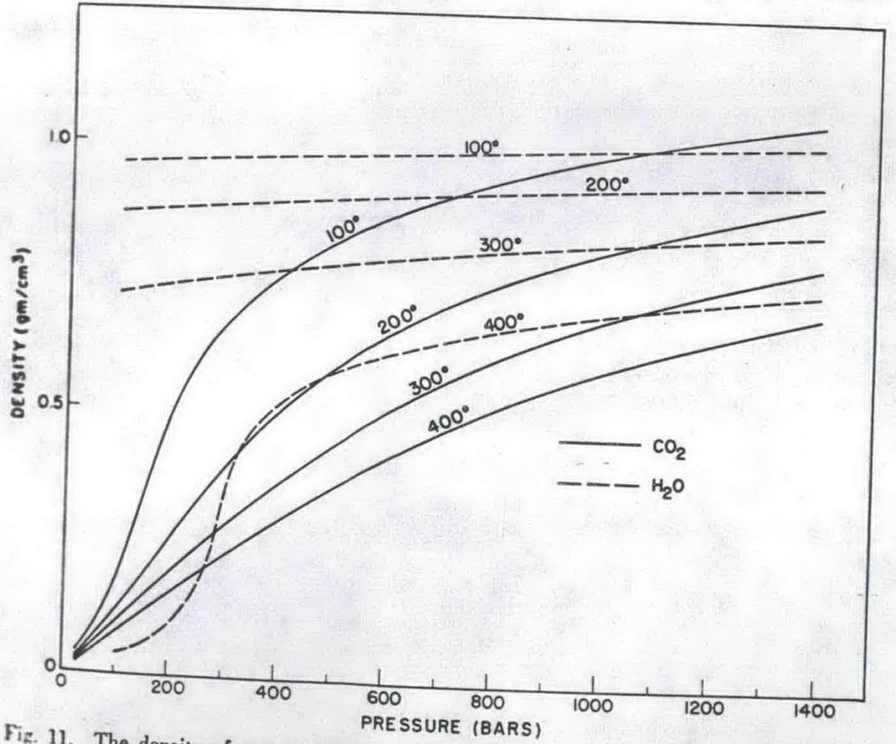


Fig. 11. The density of water and carbon dioxide at various temperatures and pressures.

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).

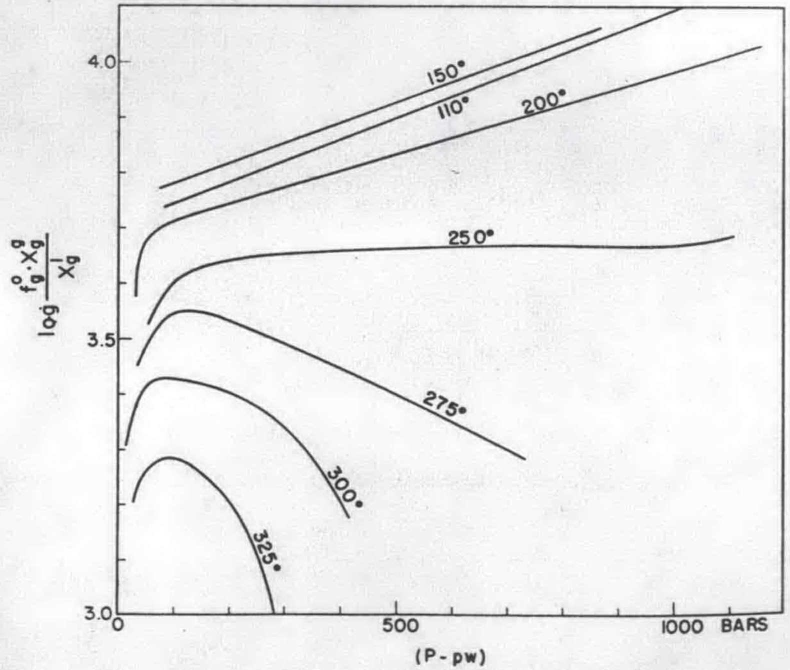


Fig. 12. Solubility curves of carbon dioxide in water.

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.

ACKNOWLEDGMENTS

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