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THE COMPRESSIBILITY OF GASEOUS MIXTURES OF CARBON DIOXIDE AND WATER BETWEEN 0 AND 500 BARS PRESSURE AND 450° AND 800° CENTRIGRADE

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ABSTRACT. The compressibility of gaseous mixtures of carbon dioxide and water has been measured in the pressure range 0 to 500 bars and the temperature range 450 to 800°C. Approximately 1500 points were measured, each utilizing 10 separate physicial measurements. Polynomial functions fitted to each of 8 isotherms were used to compute tables of $Z = PV/RT$ at integral values of pressure and composition. The tables represent the data with a standard deviation of about half a percent and agree well with data for the pure gases taken from other sources.

INTRODUCTION

Full understanding of mineral equilibria involving both carbonate minerals and hydrous minerals requires data on the gaseous materials involved. This paper attempts to fill a gap in existing data in the system H_2O–CO_2 in the low-pressure (0-500 bars) intermediate-temperature (450-800°C) range. This is an important range of conditions for two reasons. First, it coincides with the conditions of formation of many rocks, and second, the calculation of activity coefficients in gas mixtures requires data at low pressure.

The experiments reported upon here are in principle very simple. A pressure vessel of known volume and at a known temperature is injected with a known amount of gas, and the rise in pressure is recorded. A simple calculation then gives the compressibility factor PV/RT where V is the specific molar volume. The compressibility factor, $Z = PV/RT$, is a convenient parameter to report for data of this kind for several reasons: it is dimensionless; it has a smaller range of variation than any one of P, V, or T; it provides an easy way of testing thermodynamic consistency as it must approach 1.00 at very low pressures. In practice, however, these experiments are difficult to do well, chiefly due to the difficulty of knowing the exact volume of the pressure vessel and the exact amount of gas it contains. Most of the text of this paper is concerned with the calibration of the apparatus and with an evaluation of the confidence that may be placed in the results. The final results are presented in tables 1 through 8. The thermodynamics of mixing and derived activities of the components will be reported in a subsequent paper.

EXPERIMENTAL METHOD

The apparatus.—A diagrammatic plan of the apparatus is shown in figure 1. There are basically three parts: one for injection of CO_2, one for injection of H_2O, and the pressure vessel itself. The details of an actual experiment are described in a later section, but an outline of the procedure is given here to draw attention to various parts of the apparatus. The pressure vessel, held at constant temperature in a cylindri-

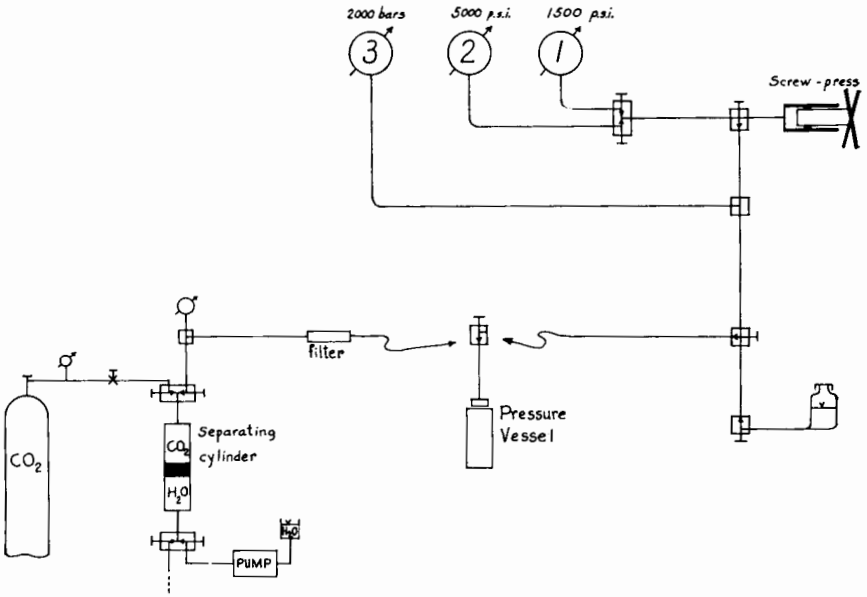

Fig. 1. Diagrammatic plan of the experimental apparatus. The furnace for heating the pressure vessel is not shown.

cal, nichrome-wound, resistance furnace (not shown), was injected with CO_2 from the separating cylinder through a filter of magnesium perchlorate and glass wool. The filter served to trap any H_2O that might have been picked up by the CO_2 from the pressure lines or the separating cylinder. Following the injection of CO_2 and the measurement of its pressure, H_2O was injected from the calibrated screw press and the new pressure measured. The new composition of the gas in the pressure vessel was calculated, and more H_2O was injected to give a new point. In this way an isotherm of P-V-T-x space was traversed in a hyperbolic path (fig. 2) up to a total pressure of 500 bars. Ten such traverses for each isotherm provided the raw data from which the final tables were calculated.

The detailed procedure.—The most economical method of describing the experiment is to proceed step by step, as follows:

1. The pressure vessel was closed, placed in the furnace, and brought to the constant temperature desired for the run. The vessel was open to the atmosphere at this stage.

2. The separating cylinder was filled with liquid CO_2.

3. The CO_2 line was flushed with CO_2 from the separating cylinder, the gas passing through every part to be connected to the pressure vessel.

4. The valve at the top of the separating cylinder was closed, and the pump operated to bring the pressure of the CO_2 in the cylinder to the desired level of slightly more than the partial pressure of CO_2 needed for the run.

5. The bomb valve was closed, and the CO_2 line connected loosely to it by tightening with the fingers.

6. The valve at the top of the separating cylinder was opened for about 2 seconds to flush the line and the bomb valve further. The connection to the bomb valve was then made tight.

7. The temperature of the pressure vessel was measured, as described in a later section.

8. The valve at the top of the separating cylinder was fully opened, and then the bomb valve was opened. The pressure in the CO_2 dropped to almost zero and recovered its initial value in about 5 seconds.

9. The bleeder valve at the bottom of the separating cylinder was carefully opened to reduce the pressure to that desired for the run.

10. The pressure was measured carefully with the gauge on the CO_2 line, described in detail in the section on pressure calibration.

11. The temperature of the pressure vessel was measured again. Temperature was usually unchanged and never differed from the initial temperature by more than 0.1°C. The pressure measured in step 10 and the temperature measured in this step comprize part of the data for the first data point of the traverse. The amount of CO_2 in the pressure vessel was determined by analysis at the end of the traverse, and the volume of the vessel found by calculation from calibration data.

12. The bomb valve and the valve at the top of the separating cylinder were closed, and the CO_2 line disconnected from the bomb valve.

13. Distilled H_2O was drawn into the screw press from the reservoir bottle, and then about half a gram of H_2O was expelled through the H_2O line to flush it.

14. Compressed air at a pressure of 40 psi was blown into the open side of the bomb valve to ensure the absence of solid CO_2. This valve was invariably warm, about 50°C, and was open to the atmosphere for the duration of steps 12, 13, and 14, a time of about 2 minutes. The valve could not have retained residual CO_2.

15. The H_2O line was connected to the bomb valve and tightened.

16. The valve to the H_2O reservior bottle was closed, and the valves to the gauges and the screw press opened. Gauge 3 was always open to the H_2O line, and either gauge 1 or gauge 2 was open depending on the pressure range.

17. The screw press was advanced until the pressure read on gauge 1, 2, or 3 was equal to the pressure measured on the CO_2 gauge upon inspection of CO_2 (step 10).

18. The bomb valve was opened, and the pressure gauges observed for changes while being manually tapped to reduce frictional hysteresis. Ordinarily there was no pressure change, but in a few instances changes of a maximum of one-half bar were noted. Changes of this order represent a movement of the H_2O–CO_2 interface in the bomb valve of about 2.0 mm. Runs were not terminated under these conditions.

19. The bomb valve was closed, and the screw press advanced to raise the pressure in the H_2O line to that desired for the next data point.

20. The position of the piston in the screw press was recorded by means of the micrometer drum on the barrel of the screw press. The procedure of steps 19 and 20 were followed to cancel out the difference in specific volume of liquid water in the H_2O line caused by the change in pressure between adjacent data points.

21. The temperature was checked.

22. The bomb valve was opened. Pressure transients in the line, as indicated by the gauges, were only momentary and always represented a drop in pressure.

23. The screw press was advanced to inject H_2O into the pressure vessel. This step was performed smoothly and continuously and seldom took as long as 20 seconds. The high velocity of the H_2O as it entered the bomb through the capillary lead-in stem ensured that no back diffusion of CO_2 could occur. The entry of H_2O also had the effect of forcing CO_2 from the lead-in stem into the main part of the pressure vessel. This extra CO_2, and the H_2O taking its place, are discussed under the heading *Stem corrections.*

24. The bomb valve was closed, and the screw press advanced until the pressure was exactly the same as reached in step 19.

25. The second reading of the position of the piston in the screw press was made with the micrometer drum. The difference between the micrometer readings of steps 20 and 25, together with the pressure and the screw press calibration, permits calculation of the amount of H_2O that passed the bomb valve.

26. The temperature was measured.

27. Steps 19 to 26 were repeated in sequence for successive incremental additions of H_2O to the pressure vessel. Temperature was checked at every increment, and in all cases it was stable to 0.2°C over the whole of each traverse from low pressure to 500 bars.

28. The run was terminated by analysis of the contents of the bomb. The details of this analysis have been reported elsewhere (Greenwood, 1961, 1967) and will not be repeated here, except to note that the gas mixture is extracted rapidly through a 2-stage cold trap that quantitatively removes the H_2O and into a 10-liter bottle, where a measurement of pressure and temperature together with the calibrated 10-liter volume suffice to calculate the quantity of gas.

29. The H_2O recovered in the analysis was compared with the cumulative total of the H_2O injected. If the disagreement exceeded 0.100 grams the entire run was rejected as inconsistent. This criterion was chosen because repeated tests indicate that the trapping of H_2O is precise to about this level while the screw press is better. Only 5 runs were rejected on this basis. The data used for the calculation of the water content of the pressure vessel were invariably derived from the screw press readings.

30. The gas extracted from the bomb, exclusive of the H_2O, all of which stopped at the cold trap, was measured by means of its pressure in a fixed volume. This pressure was measured with a mercury mano-

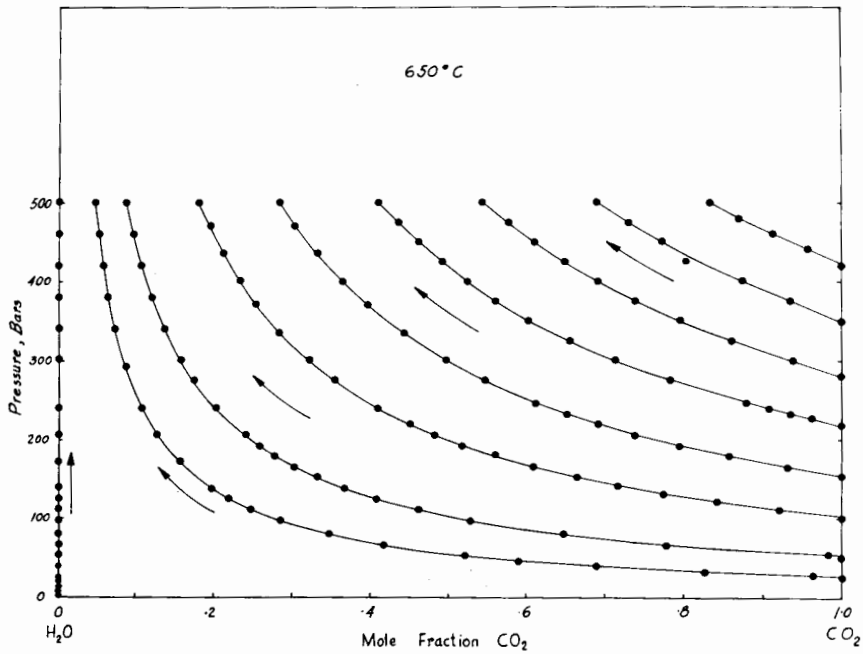

Fig. 2. Pressure-composition plot of data for the 650°C isotherm. Solid circles represent points used in preparing the final tables of compressibility factor. Each line indicates the sequence of incremental additions of H_2O starting from an initial pressure of CO_2.

meter and is discussed under the heading *Gas* analysis. It provided the data for calculating the total CO_2 content of the pressure vessel. Samples of the gas from many experiments were analyzed by gas chromatography for CH_4, H_2, and H_2O. Gases other than CO_2 make up less than one tenth of one percent of the material not trapped by the cold trap.

31. Finally, the volume of the pressure vessel was calculated from the calibrated volume at 0°C, the temperature, and the coefficient of thermal expansion. At every data point were then calculated the total number of moles of each gas in the bomb, the specific molar volume of the gas (V = volume of bomb/total moles of gas), and the compressibility factor Z = PV/RT.

In figure 2 may be seen an example of a pressure-composition plot of data for the 650°C isotherm. The solid dots represent the P-x position of the data points that were used to prepare table 5 and figures 5 and 6. The arrows show the general path followed by pressure and composition as H_2O is injected into the pressure vessel. Runs that had no CO_2 in them initially are aligned on the H_2O ordinate, whereas those that started with an initial pressure of CO_2 trace out hyperbolae convex to the H_2O axis. Each of the points represents an experimental measurement of pressure, mole fraction, specific molar volume, and temperature, from which has been calculated the compressibility factor at that point. The

compressibility fator provides a clear criterion for deviations from the ideal gas law and for deviations from ideal mixing between components that are themselves non-ideal.

CALIBRATION OF THE APPARATUS

Temperature.—Temperature was measured with sheathed chromel-alumel thermocouples that were calibrated against the melting points of lead (327.42°C), zinc (419.50°C), and aluminum (660.0°C), supplied as melting point standards by the U.S. National Bureau of Standards, and against the melting point of analytical grade sodium chloride (801°C). Freezing curves were run on all melting point standards, and the standards were also examined by quench methods after runs in the bomb at atmospheric pressure. The measuring thermocouple during experiments was placed in a well in the outside of the bomb, making it necessary to determine the temperature differences between the well and the inner cavity of the bomb. These gradients were less than 0.2°C on the basis of both melting-point and thermocouple-probe calibrations. Temperatures were read to 0.1°C and are believed to be precise to 0.3°C and accurate to 1°C.

Pressure.—The pressure measurements were made with three bourdon-tube gauges made by the Heise Bourdon Tube Company of Newtown, Connecticut. Three gauges were used to be sure that each was read in its most accurate range. The 2000-bar gauge was calibrated at the factory and certified to be within the division (1 bar) of a Bureau of Standards traceable dead-weight gauge. The 5000-psi gauge (Ser. #H-6161-R) was calibrated with the kind assistance of Professor H. Schamp of The Molecular Physics Laboratory of the University of Maryland. The calibration was made with Pressure Balance #27-503 manufactured by Hart Engineering, Netherlands. This calibration was performed with a precision of one part in one thousand. Measurements with this gauge were precise to 4 psi. The gauge on the CO_2 line, a Heise 500 bar gauge, was calibrated by direct comparison with these two primary standard gauges. The remaining gauge (Heise H-15096) was calibrated with a small deadweight piston gauge at the Geophysical Laboratory. This calibration was precise to 2 psi in the low-pressure range where the gauge was used. The gauges were constantly checked against one another to detect any drift in the calibration, but no drift was detected. All gauges were compensated for atmospheric pressure. Pressure uncertainty in the experiments is conservatively estimated to be about one part in five hundred.

Screw press.—Water was injected into the pressure vessel with a calibrated screw press with micrometer drum, supplied by the High Pressure Equipment Company of Erie, Pennsylvania. The calibration was done at the Geophysical Laboratory by the writer. Eighty measurements were made during the calibration, during which the discharge of the screw press was found by least squares to be linear with pressure and independent of the position of the piston in the cylinder. The calibra-

tion was performed with all the connections in place that were used in actual runs, including the bomb valve and the bomb stem. The same procedure was followed as has been outlined previously in steps 15 to 19, inclusive. The amount of water expelled at a given pressure was collected in a weighing bottle, weighed, and the weight divided by the number of turns of the screw press to give a figure of grams expelled per turn at that pressure. Eight replications were made at each pressure, and ten different pressures between 0 and 500 bars were studied. A regression equation was fitted to the variation of grams expelled per turn as a function of pressure. The dependence is linear with pressure and independent of the position of the piston in the screw press cylinder. The regression equation is (g per turn) $= 0.12768 + 0.54825(10^{-6}) \times P_{bars}$. The standard deviation of the calibration measurements from the regression equation is 0.029 percent and the maximum deviation is 0.085 percent.

Gas analysis.—The analysis of the CO_2 fraction of the bomb contents was performed volumetrically, by measuring the pressure and temperature of the gas in a large glass bottle of known volume. This volume was measured by two independent methods. The first method consisted of weighing a lecture cylinder of CO_2 and expanding a few grams of the gas into the analysis system, and reweighing the cylinder.

The second method consisted of the following experiment. A second smaller vessel of known volume was prepared. This volume was measured by weighing the vessel both full of water and empty of water, taking care to use the specific gravity of water appropriate to the temperature for calculating the volume. This second vessel, dried, was connected with glass tubing to the main analysis vessel of approximately ten liters' volume. The vessel of unknown volume was evacuated to a pressure of 10^{-3} mm Hg and sealed from the other by a stopcock. Air was then expanded from the vessel of known volume into the unknown, and the change in pressure recorded with the mercury manometer. Temperature was measured in both vessels before and after. Ten repeats of this experiment were performed, and three of the CO_2-weighing calibration. The results were identical, giving a volume for the analysis vessel of 9850 ± 20 cm^3. Most of this uncertainty comes from the readability of the manometer, which could not be relied upon to better than 1.5 mm of mercury. This introduced an uncertainty of 1.5 percent in runs where the partial pressure of CO_2 was less than 50 bars, but over most of the data the uncertainty was less than 0.5 percent.

Volume of the pressure vessel.—Numerous methods were applied to the problem of determining the volume of the pressure vessel. In spite of considerable effort, uncertainty in this quantity remains the greatest single contributor to inaccuracy in this study. The five methods of calibration follow with all volumes recalculated to 0°C.

1. The bomb was filled with mercury at room temperature, and the mercury emptied out and weighed. Five repeats of this method resulted in a volume of 56.39 ± 0.01 cm^3 (0°C).

2. The bomb was filled with CO_2 at a pressure of 147 bars and a temperature of 148°C. The volume was then calculated from the amount of gas extracted into the gas analysis apparatus, using the data of Michels, Michels, and Wouters (1935). Seven experiments resulted in a volume of 57.23 ± 0.2 cm³ (0°C).

3. The same procedure as in method 2, above, was followed with argon (data from Michels, Wijker, and Wijker, 1949) at 193 bars and 146°C. Seven determinations gave a volume of 57.09 ± 0.2 cm³ (0°C).

4. Water at 150°C and 1000 psi was also used in the same way. The water content of the bomb was measured both with the calibrated screw press and with the cold trap. Both kinds of measurement agreed with one another to better than 0.2 percent. Three repeats of the water calibration under these conditions with the data of Keys, Smith, and Gerry (1936) gave a volume of 56.98 ± 0.3 cm³ (0°C).

5. The fifth method consisted of the following experiment: A cylindrical glass cylinder was prepared, circular in cross-section, with an internal volume of slightly less than that of the bomb. This vessel narrowed down at either end to tubes of 4 mm internal diameter. A fiducial mark was made on one of these tubes, and the vessel clamped vertically with the marked tube down. A manometer tube was attached by glass blowing so that it was vertical, parallel to, and longer than the vessel plus end-tubes. Mercury was admitted to the lower end of the assembly up to the fiducial mark. The bomb was evacuated, and the bomb valve closed. The tube from the top of the glass vessel was connected to the bomb valve, and the bomb valve opened, thus drawing mercury into the glass vessel. The mercury level was adjusted with a levelling bottle until the level in the upper tube of the gass vessel was exactly level with the mercury in the attached manometer tube, thus equalizing the air pressure in the bomb with the atmospheric pressure. A mark was then placed on the upper end of the glass vessel at the height of the mercury. This procedure was repeated five times with five different glass vessels, and each time the glass parts were dismantled. The volume was then found by weighing the vessels empty and full of mercury up to the fiducial marks. Five determinations gave a volume of 56.74 ± 0.2 cm³ (0°C).

The value finally adopted was 56.85 ± 0.2 cm³ at 0°C as this is within the limits of the calibrations and produces the best agreement of the present data with other data on pure H_2O and CO_2. In general, the calibrations by each method were more consistent than intercomparisons between methods, and one must conclude that establishment of the volume of the pressure vessel even at room temperature and pressure is the most difficult single part of measuring the specific volume of gases. The calibration made directly with mercury in the bomb is significantly lower than the others. I believe this to be due to trapped air bubbles, and this method was not given weight in assigning a volume to the bomb.

The volume of the pressure vessel at elevated temperatures was calculated using the coefficient of thermal expansion provided by the manu-

facturer of the alloy, Allegeny-Ludlum S-816. Use of this coefficient resulted in good agreement with literature data on the pure gases at high temperature. Deformation of the bomb by the pressure of the gas was less than other uncertainties in the volume, and corrections were not applied for this effect. This deformation was estimated from the formula

$$r = \frac{r^2P}{(b^2 - r^2)E} \times \left\{ (1 + \mu) \frac{b^2}{r} + (1 - \mu)r \right\}$$

where

r	= internal radius of the bomb	(1 in.)
b	= external radius of the bomb	(3.5 in.)
P	= pressure inside the bomb	
μ	= Poisson's ratio	(0.29)
E	= Youngs modulus	(29.6 (10^6) lbs in^{-2})

Application of this formula indicates a maximum volume change of 0.14 percent at the highest pressures. Actual volume changes would be less than this by an unknown amount due to constraint by the ends of the bomb.

Stem corrections.—Injection of water from the screw press into the bomb had the effect of displacing CO_2 from the stem into the bomb and of leaving some H_2O in its place. Corrections were applied for these effects. The volumes of the stem and bomb valve were established by evacuating them and filling them with mercury and weighing the mercury. Ten replications gave the value of 0.093 $\pm$ 0.002 cm^3 for the volume of the stem alone and 0.110 $\pm$ 0.004 cm^3 for the volume of the stem plus the bomb valve.

The stem corrections were applied as follows. First it was necessary to know the amount of either pure CO_2 or pure H_2O that could be contained in the stem for any given pressure and run temperature. This is not simple because the amount depends on both the pressure and the temperature distribution along the stem, which is in turn dependent on the temperature of the bomb and the furnace. At each isotherm, the temperature distribution along the stem was measured with thermocouples that were tied on with a complete wrapping of fine nichrome wire. For each gauge pressure the density of H_2O at many points along the stem was calculated from the data of Holser and Kennedy (1959), and the total amount of H_2O in the stem found by graphical integration. The same procedure was followed for CO_2, using the data of Kennedy and Holser (1966). The H_2O correction was 0.100 grams at the lowest temperatures used and 0.058 grams at 800°C and 500 bars; the CO_2 correction, 0.090 grams at the lowest temperatures and 0.010 grams at the highest temperatures and pressures. Application of the corrections has little effect on the calculated compressibility factor at pressures above 200 bars, but at pressures below 50 bars the effect is considerable. At 25 bars and 700°C the stem correction for H_2O is approximately 12 percent of the total amount of material in the bomb.

Summary of calibrations and error propagation.—The measurements used to calculate the compressibility factor are all uncertain to some degree. The contribution of these uncertainties to uncertainty in the compressibility factor may be estimated as follows. From the properties of perfect differentials and the definition of Z,

$$dZ = \frac{Z}{T}\,dT + \frac{Z}{P}\,dP + \frac{Z}{V}\,dV + \frac{Z}{n}\,dn.$$

For a small finite variation in volume, pressure, temperature, and number of moles in the bomb,

$$\frac{\delta Z}{Z} = \frac{\delta T}{T} + \frac{\delta P}{P} + \frac{\delta V}{V} + \frac{n\delta}{n}$$

indicating that the proportional variation in Z is equal to the sum of the proportional variations in temperature, pressure, volume, and total moles of gas in the bomb. If the uncertainties are taken equal to these finite variations, in the neighborhood of 1000°K,

$$\frac{\delta Z}{Z} = 0.001 + 0.002 + 0.0035 + \frac{0.0001}{n}$$

$$= 0.0065 + \frac{0.0001}{n}$$

The sensitivity of the compressibility factor to the total content of gas in the bomb should be noted. At pressures above about 200 bars the total content is in the neighborhood of 0.10 moles, hence the uncertainty in Z is about 0.70 percent. However at 25 bars the uncertainty in Z becomes 1.65 percent. As the amount of gas in the bomb tends to zero at zero pressure the uncertainty in Z approaches infinity. For this reason data points below 49.0 bars were not used in computing the final tables.

The foregoing estimate of uncertainty in the compressibility factor is supported by the internal consistency of the data, where the standard deviation of the new data from the final smoothed tables averages about 0.5 percent, although the 500°C isotherm has a standard deviation of 0.92 percent. The estimate of uncertainty is further supported by the agreement between the new data and those of Kennedy and Holser (1966), where the standard deviation is also about 0.5 percent.

CALCULATIONS

The raw data collected in steps 1 to 31 were used to compute the compressibility factor and composition of the gas at each data point, the steps in the calculation being indicated in the descriptions of the steps in the experimental procedure. These calculations were performed partly on the IBM 7094 computer at the Princeton University Computer Center and partly on the IBM 7044 at the University of British Columbia Computer Center. The results of these calculations are referred to below as reduced data.

The reduced data for each isotherm consisted of triplets of numbers representing pressure, composition, and compressibility factor. The

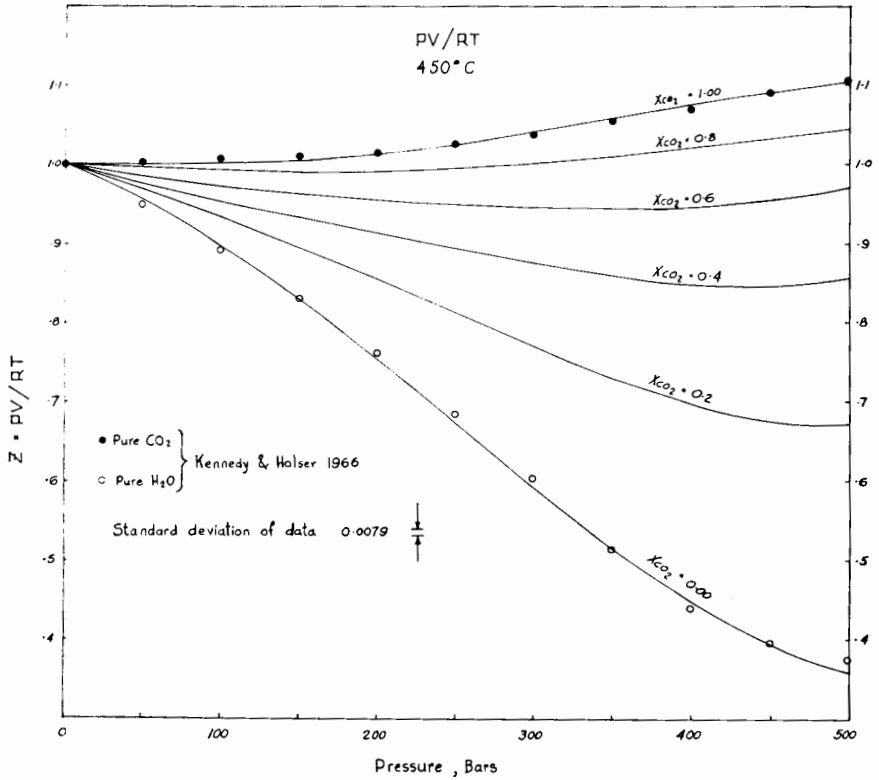

Fig. 3. Pressure-compressibility factor plot of the 450°C isotherm, showing the variation of compressibility factor with pressure at constant composition. Solid circles represent points calculated from the tables of Kennedy and Holser (1966) for pure CO_2, and open circles represent points calculated from the tables of Kennedy and Holser (1966) for pure H_2O. Standard deviation of the new data from the table and the figure is shown as 0.0079.

functional relationship between pressure, composition, and compressibility factor for each isotherm was then found by trend surface analysis. The program used for this analysis solves the normal equations for a least squares fit by inverting the matrix of detached coefficients by Gaussian reduction, pivoting on the largest row element at each step. Each isotherm was fitted by four polynomials in pressure and mole fraction of CO_2. These polynomials have the form shown below, where x = mole fraction of CO_2 and P = pressure in bars.

$$\begin{aligned} Z = A &+ Bx &+ CP \\ &+ Dx^2 &+ ExP &+ FP^2 \\ &+ Gx^3 &+ Hx^2P &+ IxP^2 &+ JP^3 \\ &+ Kx^4 &+ Lx^3P &+ Mx^2P^2 &+ NxP^3 &+ OP^4 \end{aligned}$$

The first order fit approximated the data with a function of the above form, truncated after the first three terms. The second order fit used a function consisting of the first six terms. The third order fit used a function consisting of the first ten terms, and the fourth order fit used a

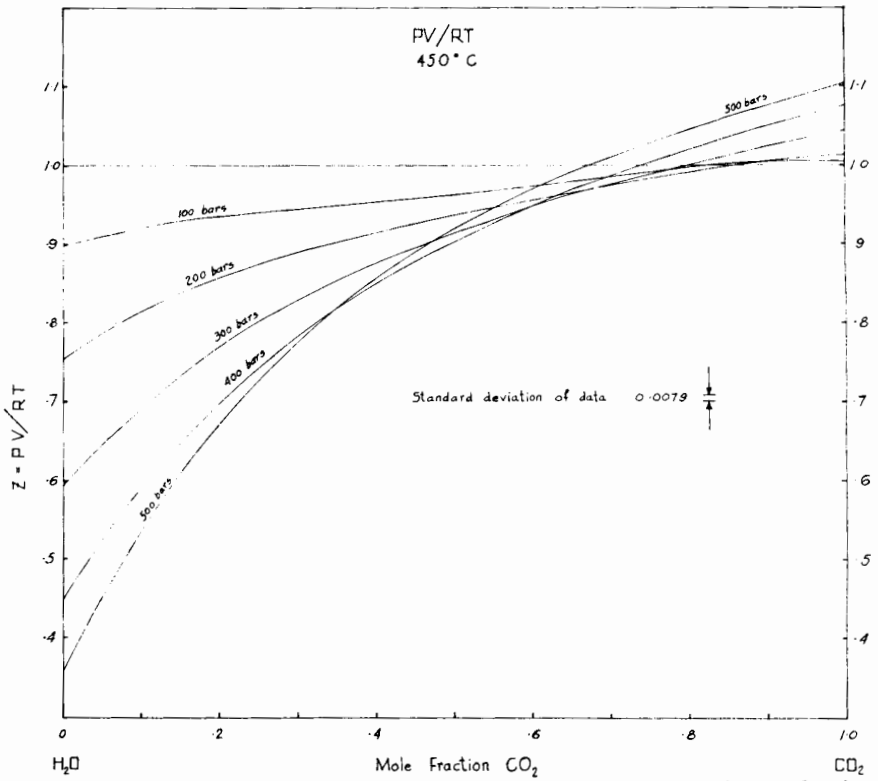

Fig. 4. Composition-compressibility factor plot of the 450°C isotherm, showing the variation in compressibility factor with composition at constant pressure. Note the increasing curvature with increasing pressure.

function consisting of all fifteen terms. It was found that for all except the 450°C isotherm the third order polynomial gave standard deviations as small as the fourth order polynomial. These were consistent with the uncertainty expected from the data on the basis of the calibrations. Most of the data have nearly insignificant cubic terms in pressure and significant cubic terms in composition. The fourth order polynomial was then used to compute the entries in table 1, and the third order polynomials to compute the entries in tables 2 to 8.

THE TABLES AND COMPARISON WITH OTHER DATA

The values of Z obtained by computer reduction are given in tables 1 to 8, and portions are illustrated in figures 3 through 6. Table 1, the isotherm for 450°C, will serve as an example of the use of the tables. The entries are arranged in rows at constant pressure, and columns at constant mole fraction of CO_2. The second column from the left, headed "K & H," contains entries calculated from data on H_2O presented by Kennedy and Holser (1966). These are to be compared with data from this study in the adjacent column. The standard deviation between these two columns is shown at the bottom of the table as the figure 0.0083. The last two columns permit a similar comparison between the new data and

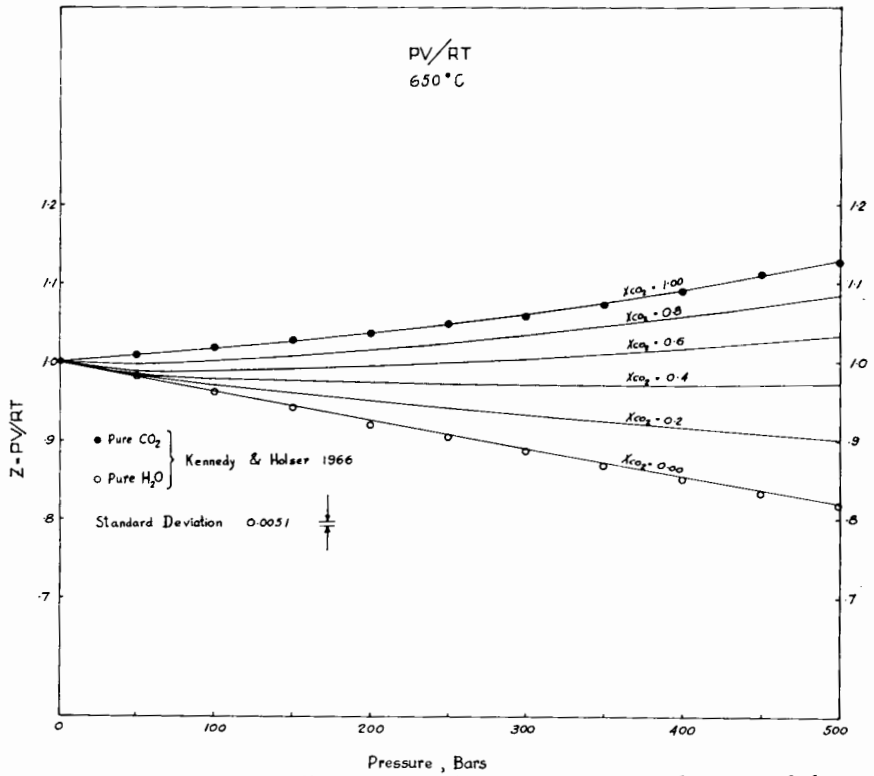

Fig. 5. Pressure-compressibility factor plot for the 650°C isotherm. Symbols are as in figure 3. Note the nearly linear P-Z relationship at this temperature, in contrast with 450°C, figure 3.

the data for CO_2 from Kennedy and Holser (1966). The standard deviation between the last two columns is also presented at the bottom of the table as the figure 0.0044. Agreement with Kennedy and Holser (1966) is consistent with the precision of the new data.

Figure 3 is a plot of data at 450°C from table 1 showing the form of Z-P curves and their comparison with data of Kennedy and Holser (1966). Although the 450°C isotherm is not the best of the isotherms the agreement may be seen to be satisfactory. Figure 4 shows the same information plotted from another viewpoint, showing the variation of the compressibility factor with composition at constant temperature and pressure. The upward convexity of the curves indicates that there is positive deviation from the assumption of ideal mixing as well as deviation from the ideal gas law. It will be seen that in figure 6 the variation of compressibility factor with pressure is less curvilinear than at 450°C, and that the curves of constant pressure in figure 6 are also straighter. This is to be expected at higher temperature where the mean free path of the molecules is greater.

Comparison of the tables with data presented by Greenwood and Barnes (1966) shows that the new data agree well with those of Liley,

TABLE 1

450°

PV/RT

H_2O-CO_2

Mole fraction of carbon dioxide

Pressure, bars	K & H 0.000	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000	K & H 1.000
100	0.8919	0.8982	0.9210	0.9353	0.9454	0.9542	0.9636	0.9743	0.9859	0.9968	1.0044	1.0047	1.0082
150	0.8311	0.8303	0.8703	0.8982	0.9185	0.9349	0.9497	0.9641	0.9784	0.9914	1.0011	1.0041	1.0110
200	0.7620	0.7545	0.8136	0.8567	0.8890	0.9147	0.9365	0.9564	0.9749	0.9916	1.0049	1.0121	1.0159
250	0.6848	0.6741	0.7535	0.8130	0.8585	0.8944	0.9244	0.9506	0.9743	0.9957	1.0135	1.0256	1.0246
300	0.6037	0.5933	0.6934	0.7698	0.8288	0.8755	0.9139	0.9468	0.9761	1.0022	1.0247	1.0419	1.0373
350	0.5146	0.5163	0.6371	0.7302	0.8026	0.8597	0.9063	0.9456	0.9800	1.0106	1.0373	1.0591	1.0539
400	0.4389	0.4480	0.5887	0.6978	0.7826	0.8493	0.9031	0.9478	0.9863	1.0203	1.0502	1.0755	1.0694
450	0.3947	0.3938	0.5529	0.6765	0.7723	0.8471	0.9065	0.9550	0.9960	1.0316	1.0629	1.0899	1.0911
500	0.3746	0.3594	0.5350	0.6709	0.7755	0.8561	0.9190	0.9690	0.0101	1.0450	1.0754	1.1017	1.1054

		Standard deviation
Internal consistency of data		0.0079
Comparison with Kennedy and Holser (1966)	H_2O	0.0083
	CO_2	0.0044

TABLE 2

500°

PV/RT

H_2O-CO_2

Mole fraction of carbon dioxide

Pressure, bars	K & H 0.000	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000	K & H 1.000
50	0.9610	0.9643	0.9718	0.9757	0.9771	0.9771	0.9767	0.9771	0.9792	0.9841	0.9928	1.0066	1.0068
100	0.9196	0.9214	0.9387	0.9513	0.9603	0.9669	0.9719	0.9766	0.9820	0.9891	0.9990	1.0128	1.0113
150	0.8749	0.8761	0.9034	0.9250	0.9419	0.9552	0.9660	0.9754	0.9843	0.9938	1.0051	1.0192	1.0178
200	0.8285	0.8290	0.8666	0.8974	0.9225	0.9429	0.9597	0.9739	0.9866	0.9989	1.0119	1.0265	1.0226
250	0.7826	0.7809	0.8291	0.8694	0.9029	0.9306	0.9536	0.9730	0.9898	1.0051	1.0200	1.0354	1.0323
300	0.7323	0.7325	0.7915	0.8416	0.8838	0.9191	0.9486	0.9734	0.9946	1.0131	1.0302	1.0467	1.0469
350	0.6821	0.6846	0.7547	0.8148	0.8659	0.9091	0.9454	0.9759	1.0016	1.0237	1.0432	1.0611	1.0636
400	0.6323	0.6378	0.7193	0.7896	0.8500	0.9013	0.9446	0.9811	1.0117	1.0376	1.0597	1.0792	1.0799
450	0.5858	0.5928	0.6860	0.7669	0.8367	0.8964	0.9471	0.9897	1.0255	1.0554	1.0806	1.1020	1.0995
500	0.5467	0.5506	0.6556	0.7474	0.8269	0.8952	0.9534	1.0026	1.0438	1.0780	1.1064	1.1299	1.1157

		Standard deviation
Internal consistency of data		0.0092
Comparison with Kennedy and Holser (1966)	H_2O	0.0034
	CO_2	0.0049

TABLE 3

550°

PV/RT

H_2O-CO_2

Mole fraction of carbon dioxide

Pressure, bars	K & H 0.000	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000	K & H 1.000
50	0.968	0.9684	0.9758	0.9806	0.9835	0.9852	0.9865	0.9880	0.9905	0.9947	1.0014	1.0113	1.0079
100	0.935	0.9340	0.9487	0.9600	0.9687	0.9755	0.9812	0.9863	0.9918	0.9983	1.0065	1.0171	1.0127
150	0.901	0.8997	0.9218	0.9398	0.9545	0.9665	0.9766	0.9856	0.9941	1.0029	1.0127	1.0243	1.0207
200	0.869	0.8658	0.8954	0.9202	0.9409	0.9582	0.9729	0.9858	0.9975	1.0087	1.0203	1.0328	1.0289
250	0.836	0.8323	0.8695	0.9011	0.9279	0.9507	0.9702	0.9870	1.0019	1.0157	1.0291	1.0428	1.0399
300	0.801	0.7992	0.8441	0.8827	0.9158	0.9441	0.9684	0.9893	1.0076	1.0241	1.0394	1.0543	1.0525
350	0.767	0.7666	0.8193	0.8650	0.9045	0.9384	0.9676	0.9927	1.0145	1.0338	1.0511	1.0673	1.0697
400	0.733	0.7347	0.7952	0.8481	0.8940	0.9338	0.9680	0.9974	1.0228	1.0449	1.0644	1.0820	1.0853
450	0.701	0.7033	0.7719	0.8321	0.8846	0.9302	0.9695	1.0034	1.0325	1.0576	1.0793	1.0985	1.1070
500	0.672	0.6728	0.7495	0.8171	0.8762	0.9278	0.9724	1.0107	1.0436	1.0718	1.0959	1.1167	1.1219

		Standard deviation
Internal consistency of data		0.0047
Comparison with Kennedy and Holser (1966)	H_2O	0.0019
	CO_2	0.0043

TABLE 4

600°

PV/RT

H_2O-CO_2

Mole fraction of carbon dioxide

Pressure, bars	K & H 0.000	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000	K & H 1.000
50	0.9752	0.9804	0.9781	0.9762	0.9750	0.9748	0.9756	0.9779	0.9819	0.9876	0.9955	1.0057	1.0070
100	0.9501	0.9571	0.9613	0.9653	0.9694	0.9737	0.9786	0.9842	0.9907	0.9985	1.0077	1.0186	1.0155
150	0.9248	0.9321	0.9429	0.9529	0.9622	0.9712	0.9801	0.9890	0.9982	1.0080	1.0187	1.0303	1.0252
200	0.9009	0.9060	0.9235	0.9394	0.9541	0.9678	0.9807	0.9930	1.0050	1.0169	1.0289	1.0414	1.0328
250	0.8761	0.8793	0.9035	0.9255	0.9456	0.9640	0.9810	0.9967	1.0115	1.0256	1.0391	1.0524	1.0452
300	0.8511	0.8526	0.8835	0.9116	0.9372	0.9604	0.9815	1.0008	1.0184	1.0347	1.0498	1.0639	1.0561
350	0.8259	0.8265	0.8642	0.8985	0.9295	0.9576	0.9829	1.0057	1.0263	1.0448	1.0615	1.0766	1.0722
400	0.8019	0.8015	0.8461	0.8866	0.9232	0.9561	0.9857	1.0121	1.0356	1.0564	1.0748	1.0909	1.0888
450	0.7786	0.7783	0.8297	0.8764	0.9187	0.9566	0.9905	1.0205	1.0470	1.0702	1.0902	1.1074	1.1103
500	0.7564	0.7573	0.8157	0.8687	0.9166	0.9595	0.9978	1.0315	1.0611	1.0866	1.1084	1.1266	1.1256

		Standard deviation
Internal consistency of data		0.0027
Comparison with Kennedy and Holser (1966)	H_2O	0.0041
	CO_2	0.0051

TABLE 5

650°

PV/RT

H_2O-CO_2

Mole fraction of carbon dioxide

Pressure, bars	K & H 0.000	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000	K & H 1.000
50	0.9806	0.9815	0.9812	0.9814	0.9821	0.9835	0.9856	0.9884	0.9922	0.9968	1.0025	1.0094	1.0095
100	0.9621	0.9630	0.9669	0.9709	0.9750	0.9795	0.9843	0.9895	0.9953	1.0016	1.0087	1.0165	1.0184
150	0.9418	0.9449	0.9530	0.9608	0.9686	0.9762	0.9839	0.9917	0.9996	1.0078	1.0163	1.0252	1.0276
200	0.9248	0.9269	0.9394	0.9513	0.9627	0.9737	0.9844	0.9948	1.0051	1.0152	1.0253	1.0356	1.0359
250	0.9054	0.9090	0.9260	0.9422	0.9574	0.9719	0.9857	0.9990	1.0117	1.0239	1.0358	1.0474	1.0479
300	0.8872	0.8913	0.9130	0.9334	0.9527	0.9708	0.9879	1.0041	1.0193	1.0338	1.0476	1.0608	1.0579
350	0.8675	0.8736	0.9001	0.9250	0.9484	0.9703	0.9908	1.0100	1.0281	1.0449	1.0608	1.0756	1.0720
400	0.8504	0.8560	0.8874	0.9169	0.9446	0.9704	0.9945	1.0169	1.0378	1.0572	1.0752	1.0919	1.0911
450	0.8332	0.8383	0.8749	0.9091	0.9411	0.9710	0.9988	1.0246	1.0485	1.0705	1.0909	1.1095	1.1117
500	0.8168	0.8206	0.8624	0.9016	0.9381	0.9722	1.0038	1.0331	1.0601	1.0850	1.1077	1.1285	1.1261

		Standard deviation
Internal consistency of data		0.0051
Comparison with Kennedy and Holser (1966)	H_2O	0.0040
	CO_2	0.0021

TABLE 6

700°

PV/RT

H_2O-CO_2

Mole fraction of carbon dioxide

Pressure, bars	K & H 0.000	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000	K & H 1.000
50	0.9841	0.9838	0.9864	0.9885	0.9902	0.9915	0.9923	0.9927	0.9927	0.9922	0.9913	0.9900	1.0110
100	0.9699	0.9686	0.9741	0.9792	0.9838	0.9880	0.9917	0.9951	0.9980	1.0004	1.0025	1.0041	1.0186
150	0.9549	0.9539	0.9624	0.9703	0.9779	0.9850	0.9917	0.9980	1.0038	1.0092	1.0142	1.0187	1.0276
200	0.9414	0.9398	0.9512	0.9621	0.9726	0.9827	0.9923	1.0015	1.0102	1.0186	1.0264	1.0339	1.0380
250	0.9263	0.9263	0.9406	0.9545	0.9679	0.9809	0.9934	1.0055	1.0172	1.0285	1.0393	1.0497	1.0493
300	0.9125	0.9134	0.9306	0.9474	0.9638	0.9797	0.9952	1.0102	1.0248	1.0390	1.0527	1.0661	1.0610
350	0.8986	0.9011	0.9212	0.9409	0.9602	0.9790	0.9975	1.0154	1.0330	1.0501	1.0668	1.0830	1.0774
400	0.8860	0.8893	0.9124	0.9350	0.9572	0.9790	1.0003	1.0212	1.0417	1.0618	1.0814	1.1005	1.0922
450	0.8734	0.8781	0.9041	0.9297	0.9548	0.9795	1.0038	1.0276	1.0510	1.0740	1.0966	1.1187	1.1101
500	0.8612	0.8675	0.8965	0.9250	0.9530	0.9807	1.0079	1.0346	1.0610	1.0869	1.1123	1.1373	1.1238

		Standard deviation
Internal consistency of data		0.0065
Comparison with Kennedy and Holser (1966)	H_2O	0.0029
	CO_2	0.0106

TABLE 7

750°

PV/RT

H_2O-CO_2

Mole fraction of carbon dioxide

Pressure, bars	K & H 0.000	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000	K & H 1.000
50	0.9870	0.9899	0.9865	0.9838	0.9819	0.9809	0.9810	0.9823	0.9849	0.9890	0.9947	1.0022	1.0104
100	0.9755	0.9794	0.9800	0.9810	0.9824	0.9843	0.9869	0.9904	0.9948	1.0004	0.0071	1.0152	1.0184
150	0.9642	0.9685	0.9731	0.9777	0.9823	0.9872	0.9923	0.9980	1.0042	1.0111	0.0189	1.0277	1.0292
200	0.9526	0.9572	0.9659	0.9741	0.9820	0.9897	0.9973	1.0051	1.0131	1.0214	0.0302	1.0396	1.0399
250	0.9414	0.9459	0.9585	0.9703	0.9814	0.9920	1.0021	1.0120	1.0217	1.0314	1.0412	1.0513	1.0489
300	0.9314	0.9345	0.9511	0.9665	0.9809	0.9943	1.0069	1.0189	1.0303	1.0414	1.0522	1.0629	1.0630
350	0.9214	0.9235	0.9440	0.9630	0.9805	0.9968	1.0118	1.0259	1.0391	1.0515	1.0632	1.0745	1.0765
400	0.9115	0.9128	0.9372	0.9598	0.9805	0.9996	1.0171	1.0332	1.0481	1.0618	1.0745	1.0864	1.0920
450	0.9020	0.9027	0.9311	0.9571	0.9810	1.0029	1.0228	1.0410	1.0576	1.0726	1.0862	1.0987	1.1081
500	0.8937	0.8933	0.9256	0.9552	0.9823	1.0069	1.0293	1.0495	1.0677	1.0840	1.0986	1.1116	1.1232

		Standard deviation
Internal consistency of data		0.0036
Comparison with Kennedy and Holser (1966)	H_2O	0.0031
	CO_2	0.0059

TABLE 8

800°

PV/RT

H_2O-CO_2

Mole fraction of carbon dioxide

Pressure, bars	K & H 0.000	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000	K & H 1.000
50	0.9900	0.9910	0.9767	0.9697	0.9676	0.9682	0.9703	0.9731	0.9764	0.9808	0.9872	0.9973	1.0107
100	0.9801	0.9821	0.9745	0.9731	0.9755	0.9798	0.9846	0.9893	0.9940	0.9989	1.0055	1.0152	1.0191
150	0.9710	0.9727	0.9709	0.9744	0.9806	0.9879	0.9951	1.0015	1.0072	1.0128	1.0194	1.0290	1.0305
200	0.9623	0.9633	0.9665	0.9741	0.9837	0.9936	1.0028	1.0107	1.0174	1.0236	1.0306	1.0404	1.0406
250	0.9535	0.9542	0.9617	0.9729	0.9854	0.9977	1.0087	1.0179	1.0257	1.0327	1.0404	1.0507	1.0512
300	0.9456	0.9456	0.9569	0.9712	0.9863	1.0007	1.0135	1.0242	1.0332	1.0414	1.0501	1.0615	1.0638
350	0.9385	0.9375	0.9522	0.9694	0.9869	1.0034	1.0180	1.0303	1.0409	1.0505	1.0609	1.0740	1.0770
400	0.9312	0.9301	0.9478	0.9676	0.9875	1.0061	1.0227	1.0370	1.0494	1.0612	1.0737	1.0894	1.0925
450	0.9250	0.9231	0.9437	0.9661	0.9883	1.0092	1.0280	1.0446	1.0596	1.0740	1.0896	1.1087	1.1048
500	0.9191	0.9162	0.9396	0.9646	0.9894	1.0129	1.0344	1.0538	1.0719	1.0898	1.1093	1.1328	1.1225

		Standard deviation
Internal consistency of data		0.0031
Comparison with Kennedy and Holser (1966)	H_2O	0.0015
	CO_2	0.0060

1956 (*in* Greenwood and Barnes, 1966) and poorly to fairly well with those of Franck and Todheide (1959). Little more can be said about the absolute accuracy and precision of the new data, except that they have good internal consistency and agree well with the data of Kennedy and Holser (1966) for the pure end members.

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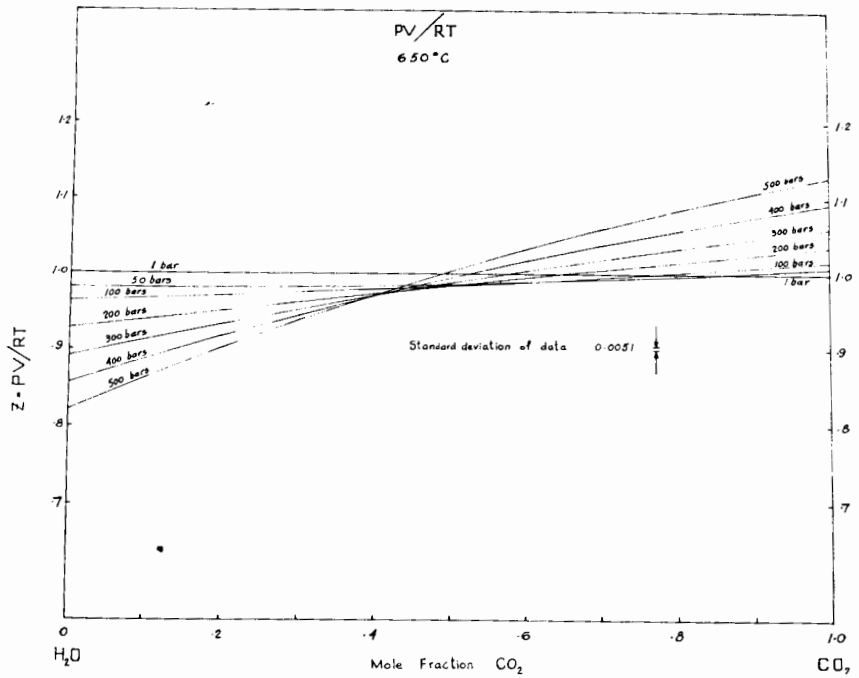

Fig. 6. Composition-compressibility factor plot of the 650°C isotherm. Note that the high pressure isobars at 650°C are much straighter than at 450°C.

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