

The Generation of N_2 - CO_2 - H_2O Fluids For Use In Hydrothermal Experimentation II. Melting of Albite in a Multispecies Fluid

S. E. KESSON¹

Departments of Chemistry and Geology

J. R. HOLLOWAY

Division of Geochemistry, Department of Chemistry

Arizona State University, Tempe, Arizona 85281

Abstract

Three fluid compositions in the C-O-H-N system, each with nominal mole fraction of $H_2O = 0.25$, were used for comparative determinations of the solidus of synthetic albite at 4.4 kbar. The fluids were generated by the decomposition of guanidine nitrate $CH_5N_3 \cdot HNO_3$, ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$, and from a 1:2 molar mixture of oxalic acid dihydrate and anhydrous oxalic acid. Hydrogen fugacity during the experiments was not buffered and was found to lie between Ni-NiO- H_2O and MnO-Mn₂O₄- H_2O buffers. Excess H_2 produced by the decomposition of the C-O-H-N solid compounds diffuses out of the sample capsule, resulting in fluids consisting essentially of the species H_2O , CO_2 and N_2 . The ternary nature of these fluids, which was predicted by thermodynamic equilibrium calculations, is confirmed by quantitative gas chromatographic analysis of the quenched fluids. Reversals confine the albite solidus between 954°C and 958°C ($\pm 2^\circ C$) and within experimental limits there is no significant difference between solidus temperatures for each of the three fluid compositions. This suggests that activity coefficients for H_2O are similar in each case and are independent of the CO_2/N_2 ratio in the fluid. These data place an upper bound on the activity coefficient for H_2O at 960° and 4.4 kbar of approximately 1.8 in H_2O - CO_2 - N_2 fluids with the mole fraction of $H_2O = 0.25$.

Introduction

Holloway and Reese (1974) describe a method which allows the independent variation of P_{H_2O} ,² P_{CO_2} , and f_{O_2} during experiments at geologically significant pressures and temperatures. In this method, fluids produced by the decomposition of C-O-H-N solid compounds reach equilibrium at P and T consisting essentially of the species H_2O , CO_2 , and N_2 . Holloway and Reese evaluated the effects of P , T and f_{H_2} on fluid composition by means of equilibrium calculations, but in the absence of any data for

activity coefficients, had to assume that all fluid species mixed ideally.

This paper describes the results of an experimental application of the method outlined above. The results yield an estimate of the value of γ_{H_2O} at 4.4 kbar and 960°C, and also establish the relationship between γ_{H_2O} and the CO_2/N_2 ratio in the fluid at this P and T . Quantitative analysis gives the equilibrium species composition of quenched C-O-H-N fluids for comparison with theoretical calculations.

Experimental

The fluid-saturated solidus temperatures for synthetic crystalline albite at 4.4 kbar were determined using three different C-O-H-N fluids. The fluids were generated using the method of Holloway and Reese (1974). Table 1 lists the organic compounds used to generate these fluids and gives the nominal species composition in each case assuming that all excess H_2 is lost by diffusion through the capsule walls so

¹ Present address: Department of Earth and Space Sciences, State University of New York at Stony Brook, Stony Brook, N. Y. 11790.

² The symbols used throughout the paper are identical to those given in Table 1 of Holloway and Reese (1974) with the addition of: n_i , the number of moles of species i in a fluid; γ_i , the activity coefficient for species i in a fluid mixture at a given P and T ; and a_i , the activity of species i in a fluid mixture at a given P and T .

TABLE 1. Observed and Calculated Compositions of C-O-H-N Fluids

Formula	Guanidine nitrate $CH_3N_3 \cdot HNO_3$	Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$	Oxalic acid mix*** $H_2C_2O_4 + H_2C_2O_4 \cdot 2H_2O$
Nominal fluid composition*			
N_2	0.500	0.250	0
CO_2	0.250	0.500	0.750
H_2O	0.250	0.250	0.250
Calculated fluid composition**			
$f_{H_2} = MH, OH$			
N_2	0.500	0.250	0
CO_2	0.250	0.500	0.750
H_2O	0.250	0.250	0.250
Calculated fluid composition**			
$f_{H_2} = NNO, OH$			
N_2	0.495	0.246	0
CO_2	0.241	0.480	0.710
H_2O	0.254	0.259	0.264
Chromatographic analysis†			
N_2	0.495	0.247	n.d.††
CO_2	0.249	0.499	0.745
H_2O	0.256	0.254	0.255

* mole fraction, $X_1 = n_1 / (n_{N_2} + n_{CO_2} + n_{H_2O})$, calculated assuming no 'excess' H_2 .

** mole fraction, $X_1 = n_1 / (\text{total moles of all gaseous species found in the thermodynamic equilibrium calculations})$. In addition to those shown above, minor species were CH_4 , CO , H_2 , NH_3 , CH_2O , C_2H_4 , HCN , $HNCO$, and O_2 . The calculations were made using the same program and data described by Holloway and Reese (1974) but for 960°C and 4.4 kbar.

*** $H_2C_2O_4$ and $H_2C_2O_4 \cdot 2H_2O$ in 2:1 molar proportions.

† Normalized to 1.000. ††n.d. = not determined.

that only CO_2 , H_2O , and N_2 species are present. Each fluid contains $X(\text{nom})_{H_2O} = 0.25$ whereas $X(\text{nom})_{N_2} = 0.50$, 0.25 , and zero respectively.³

The aim of the experiments is to bracket the albite solidus at 4.4 kbar with each of the three fluids. If the solidus temperatures are significantly different, it would mean that γ_{H_2O} is dependent on the CO_2/N_2 ratio in the fluid. But if the solidus temperatures are the same within experimental precision, then either γ_{H_2O} is essentially independent of the CO_2/N_2 ratio or γ_{H_2O} is dependent on fluid composition, but the effect of increasing X_{N_2} is balanced by the effect of decreasing X_{CO_2} .

Starting Materials

The synthetic crystalline albite used as starting material in the experiments was prepared as a gel following the methods of Hamilton and Henderson (1968), and crystallized hydrothermally. The chemical analysis obtained by X-ray fluorescence analysis (Norrish and Hutton, 1969) and by flame photometric

methods (Cooper, 1963) gives $SiO_2 = 69.10$, $Al_2O_3 = 18.68$, and $Na_2O = 11.82$.

Experimental Techniques

Experimental runs were carried out in an argon gas media, internally heated, high pressure vessel of 5 cm internal diameter similar to that described by Holloway (1971). Temperature was controlled by a stepless proportional controller and measured with a precision of $\pm 2^\circ C$ by means of three sheathed chromel-alumel thermocouples in contact with the sample capsule. The accuracy of temperature measurement is believed to lie within $\pm 5^\circ C$. Pressures were measured with a Bourdon tube gauge.

The fluid-generating compounds followed by crystalline albite were loaded into Ag-Pd alloy capsules which were sealed by welding. At P and T , H_2O and albite are present in approximately 2:1 molar proportions.

In most cases the unreversed runs were held at P and T for approximately 6 hours. Runs were reversed by holding the charge for 6-7 hours above the solidus at $1050^\circ C$, then dropping the temperature to $954^\circ C$. A few of the larger albite crystals persisted as relics above the solidus, and acted as nuclei for extensive crystallization at subsolidus temperatures.

Problems associated with solution of albite in H_2O , and vice versa, are believed to be minimal. The activity of H_2O in each of the fluids is considerably less than unity and so the solubility of albite in the fluid phase is reduced considerably (Shettel, 1973). Calculations using the data of Burnham and Jahns (1962) plus the initial fluid/albite ratio show that during the melting experiments there is negligible change in the fluid composition due to solution of H_2O in albite melt.

After removal from the pressure vessel, the sample capsules were weighed to check for leakage. Capsules which did not leak during experiments were usually puffed and escaping gases were audible during opening. When analysis of the quenched fluid was required, the capsule was punctured under vacuum in the analytical system.

All species except H_2O in the quenched fluids were determined by quantitative gas chromatographic analysis. The 2-column gas chromatograph was constructed from parts contained in a Laboratory Equipment Corporation (LECO) carbon analyzer. The chromatograph uses a thermal conductivity bridge for a detector and has the capacity to determine CO_2 , propane, butane, and more complex C-O-H gas

³ Note that the defining relation for mole fraction will change depending on the fluid considered. For example, in a simple ternary fluid $X_{H_2O} = n_{H_2O} / (n_{H_2O} + n_{CO_2} + n_{N_2})$ while for a multispecies COHN fluid at P and T , $X_{H_2O} = n_{H_2O} / (n_{H_2O} + n_{CO_2} + n_{N_2} + n_{CH_4} + n_{CO} + n_{NH_3} + n_{H_2} + \dots + n_{O_2})$.

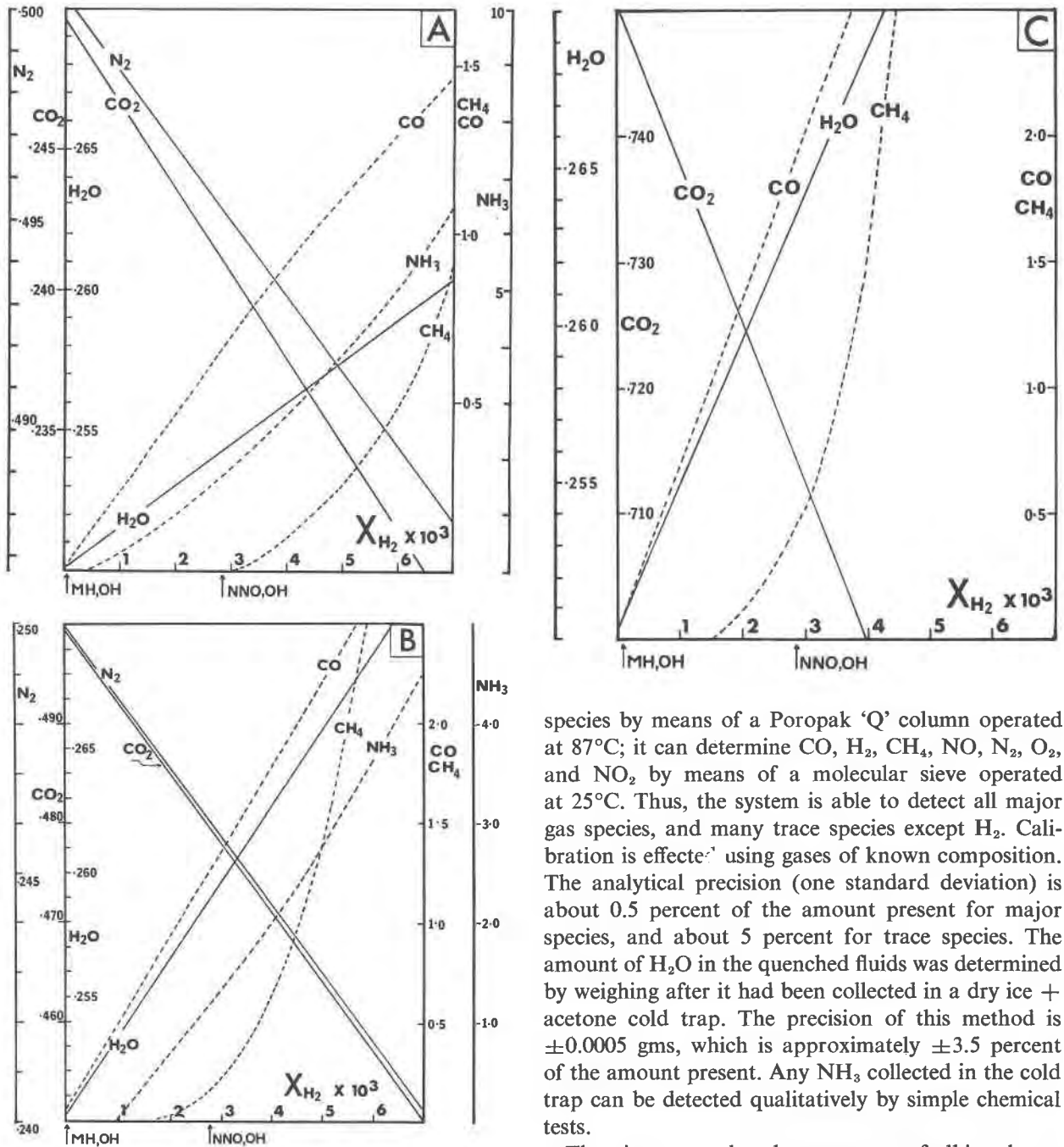


FIG. 1. Calculated species compositions of fluids generated by the decomposition of (A) guanidine nitrate, (B) ammonium oxalate, (C) a 1:2 molar mixture of oxalic acid dihydrate and anhydrous oxalic acid, are shown as a function of X_{H_2} at 960°C and 4.4 kbar. Left-hand ordinates refer to mole fractions of major species; right-hand ordinates to mole fractions $\times 10^4$ of minor species (dashed curves). The X_{H_2} produced by the MH, OH and NNO, OH buffers is indicated at the base of each diagram. Note that the position of the initial fluids (before loss of H_2) would lie far off the diagrams to the right.

species by means of a Poropak 'Q' column operated at 87°C; it can determine CO , H_2 , CH_4 , NO , N_2 , O_2 , and NO_2 by means of a molecular sieve operated at 25°C. Thus, the system is able to detect all major gas species, and many trace species except H_2 . Calibration is effected using gases of known composition. The analytical precision (one standard deviation) is about 0.5 percent of the amount present for major species, and about 5 percent for trace species. The amount of H_2O in the quenched fluids was determined by weighing after it had been collected in a dry ice + acetone cold trap. The precision of this method is ± 0.0005 gms, which is approximately ± 3.5 percent of the amount present. Any NH_3 collected in the cold trap can be detected qualitatively by simple chemical tests.

The nitrogen and carbon contents of albite glasses were determined by quantitative methods (Moore *et al*, 1970).

Effect of f_{H_2} on Fluid Composition

Holloway and Reese (1974) used the results of thermodynamic equilibrium calculations to investigate the relationship between the species composition of C-O-H-N fluids and externally controlled f_{H_2} . They

showed that the species composition of an equilibrium fluid at P and T did not lie exactly on the H_2O - CO_2 - N_2 plane of the C-O-H-N tetrahedron. When X_{H_2O} is low (<0.25), this deviation becomes increasingly significant as the external f_{H_2} increases above that of the MH, OH buffer. Thus, the species compositions of the equilibrium fluids produced by the compounds listed in Table 1 differ slightly from the nominal fluid compositions (also given in Table 1). Of particular importance to the albite melting experiments is the difference (δ_{H_2O}) between the actual mole fraction of H_2O in each of the three fluids and the nominal mole fraction of H_2O (0.250) in the capsule. This is evaluated by means of thermodynamic equilibrium calculations, the results of which are shown graphically in Figure 1.⁴ During experiments the ambient f_{H_2} in the pressure apparatus has been found to lie between NNO, OH and MH, OH. The calculated curves (Fig. 1) reveal that the actual value of X_{H_2O} should be somewhere between 0.250 and 0.254, 0.250 and 0.259, 0.250 and 0.264 for fluids for which the nominal values of X_{N_2} in the fluid are 0.500, 0.250, and zero, respectively.

Experimental Results and Interpretations

Fluid Analysis

The species composition of the fluid is very sensitive to X_{H_2} ; thus reaction during the quench would occur if there was diffusion of H_2 into the sample capsule. But X_{H_2} is believed to remain essentially constant during quenching because the diffusion rate of H_2 is relatively slow compared to the quenching time (Makrides and Jewett, 1966), and f_{H_2} in the pressure vessel is very similar to that in the capsule during the quench. The fluid analyses were complicated by the formation of a water-soluble C-O-H compound during quenching. Heating the quenched fluid to $\sim 350^\circ C$ in a large volume container caused the compound to break down to H_2O and CO_2 , and it did not reappear as the gases cooled to room temperature.

Analyses of the quenched fluids are presented in Table 1. Fluids produced by the decomposition of the C-O-H-N compounds consist essentially of the species H_2O , CO_2 , and N_2 , and fluids derived from C-O-H compounds consist essentially of H_2O and

CO_2 . No NH_3 , N-O, C-H or complex C-O-H gases were detected. Within the limits of analytical uncertainty, the species compositions of the fluids compare very favorably with compositions predicted from the thermodynamic calculations for f_{H_2} between MH, OH and NNO, OH. Those calculations were made using the program and data described by Holloway and Reese (1974) for $T = 960^\circ C$ and $P = 4.4$ kbar. Table 3 and Appendix II in Holloway and Reese should be consulted for representative minor and trace species.

Solubility of CO_2 and N_2 in Albite Melt

Quantitative analysis has shown that at $P_t = 4.4$ kbar the solubility of CO_2 in albite glass is roughly 0.1 wt percent/kbar P_{CO_2} . Thus the mole percent CO_2 in the liquid (assuming a molecular weight of 262 for anhydrous liquid albite) ranges from 0.5 to 2.2, depending on X_{CO_2} in the fluid. Rough comparison with the freezing point depression of albite due to dissolved H_2O suggests that the depressant effect of CO_2 on the albite solidus will not exceed $-10^\circ C$. Figure 2 illustrates the relationship between the N_2 content of albite glass and the partial pressure of N_2 , and shows that the solubility of N_2 in albite glass at 4.4 kbar is negligible.

Melting of Albite

No graphite, nitrides, oxynitrides, or carbonates were observed in the run products. Albite glass can be identified without difficulty in the charge and in grain mounts. In all runs above the solidus, crystals

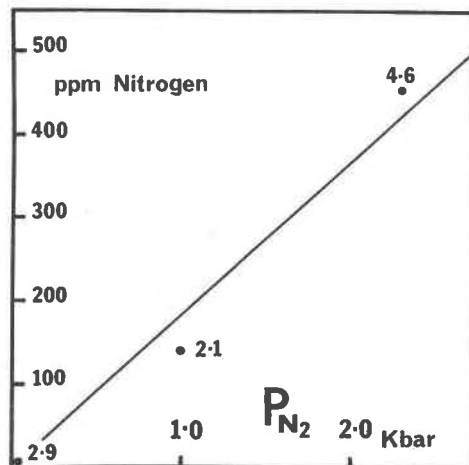


FIG. 2. Solubility of nitrogen in albite glass is illustrated as a function of P_{N_2} . Numbers beside each point refer to load pressure (kbar).

⁴ Note that the initial fluid composition in each case plots off the figure at a much higher value of X_{H_2} . The appearance of the diagrams at higher values of X_{H_2} may be obtained by referring to Figure 7 in Holloway and Reese (1974).

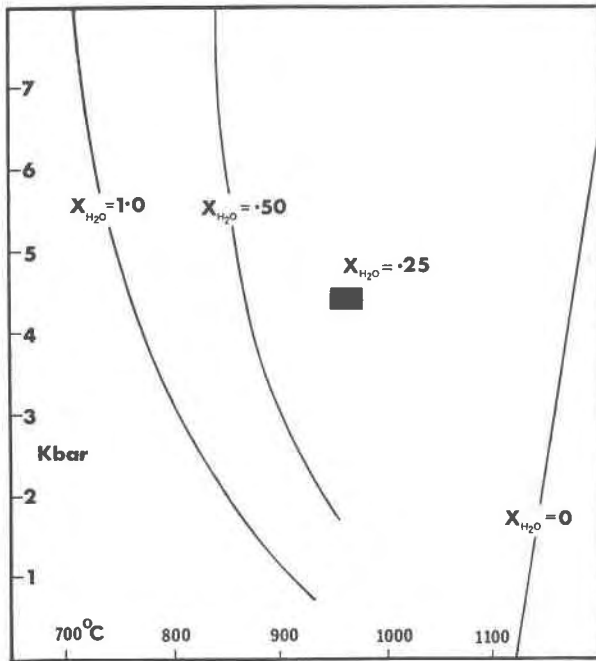


FIG. 3. Projections of contours on the albite solidus surface. Solidus contour for $X_{\text{H}_2\text{O}} = 1.0$ for Boettcher and Wyllie (1969); for $X_{\text{H}_2\text{O}} = 0.5$ from Millhollen, Wyllie, and Burnham (1971); for $X_{\text{H}_2\text{O}} = 0.0$ from Bell and Roseboom (1969).

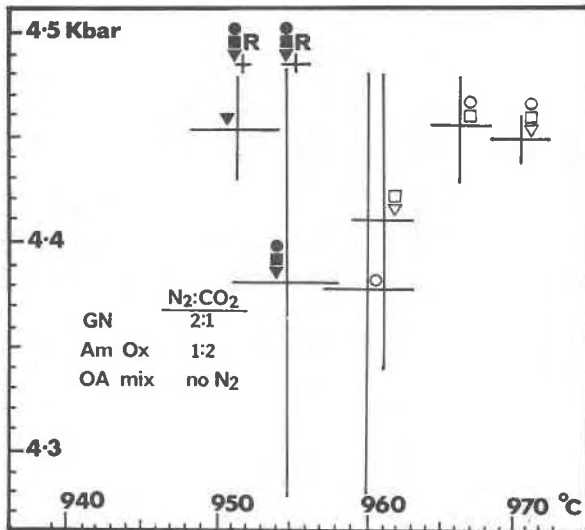


FIG. 4. Critical runs bracketing albite solidus for $X_{\text{H}_2\text{O}} = 0.25$. The range in P and T for each run is indicated by the intersecting vertical and horizontal lines. Subsolidus runs are indicated by solid symbols; hypersolidus runs by open symbols. R designates reversed runs.

and glass were both present, and melting typically occurred on the outer portions of the charge, with the amount of melt produced depending on the duration of the run. Low refractive index isotropic spheres which are occasionally found on the capsule walls in runs both below and above the solidus are believed to be fluid phase precipitates. The results of Shettel (1973) suggest that the solubility of $\text{NaAlSi}_3\text{O}_8$ in these H_2O -poor fluids is considerably less than its solubility in pure H_2O fluids.

Figure 3 shows published solidus curves for albite with $X(\text{nom})_{\text{H}_2\text{O}} = 1.0, 0.5,$ and zero. Critical runs bracketing the solidus with $X(\text{nom})_{\text{H}_2\text{O}} = 0.25$ at 4.4 kbar lie within the black rectangle which also corresponds to the P - T field of Figure 4. The results of the critical runs for each of the three fluids are illustrated in Figure 4, and a complete listing of experimental results is contained in Table 2. The solidus temperatures of 957°C, 958°C, and 958°C for fluids with $X(\text{nom})_{\text{N}_2} = 0.5, 0.25,$ and zero respectively are the same within experimental precision ($\pm 2^\circ\text{C}$).

Estimate of $\gamma_{\text{H}_2\text{O}}$

Because the solidus temperatures for the three fluids are identical within experimental precision, one can reasonably conclude that $\gamma_{\text{H}_2\text{O}}$ is essentially independent of the CO_2/N_2 ratio in the fluid.

The experiments also yield an estimate of the value of $\gamma_{\text{H}_2\text{O}}$ at 960°C and 4.4 kbar. Figure 5 illustrates the relationship between $a_{\text{H}_2\text{O}}$ and the temperature of the albite solidus at 4.4 kbar. The solid curve is a second degree polynomial fitted to points taken from published albite solidi with $X_{\text{H}_2\text{O}} = 1.0, 0.5,$ and zero (see Fig. 3 for sources). The activity values used in calculating the curve were obtained assuming activity coefficients of unity at $X_{\text{H}_2\text{O}} = 1.0$ and zero, and $\gamma_{\text{H}_2\text{O}} = 1.2$ at $X_{\text{H}_2\text{O}} = 0.5$ (the latter value from personal communication with C. Wayne Burnham, Pennsylvania State University, 1973). The dashed curve is similar, except that $\gamma_{\text{H}_2\text{O}}$ at $X_{\text{H}_2\text{O}} = 0.5$ is chosen as unity. In order for the experimentally-determined albite solidus to fall on the solid curve, the value of $\gamma_{\text{H}_2\text{O}}$ at $X_{\text{H}_2\text{O}} = 0.25$ must be about 1.8; this implies a significant positive deviation from ideality. However, because of the method of calculation, the estimated value of $\gamma_{\text{H}_2\text{O}}$ at $X_{\text{H}_2\text{O}} = 0.25$ is very dependent on the value chosen for $\gamma_{\text{H}_2\text{O}}$ at $X_{\text{H}_2\text{O}} = 0.5$. For example: if the experimentally-determined solidus were to lie on the dashed curve, $\gamma_{\text{H}_2\text{O}}$ at $X_{\text{H}_2\text{O}} = 0.25$ would be about 1.2. Due to this

TABLE 2. Experimental Results

Temperature °C	Pressure kbar	Duration of run (hrs.)	Guanidine nitrate	Ammonium oxalate	Oxalic acid mix
1011-1012	4.55-4.62	14.0	XG	XG	XG
1003-1008	4.14-4.21	8.0	XG	XG	XG
1005-1010	4.48-4.45	7.5	XG	XG	XG
919-922	4.36-4.46	7.3	X	X	X
1002-1005	4.44-4.45	6.4	XG	XG	XG
995-998	4.44-4.48	6.2		XG	XG
989-991	4.44-4.48	6.7		XG	XG
948-954	4.43-4.48	5.3			X
968-972	4.44-4.46	7.3	XG	XG	XG
964-968	4.43-4.48	6.5	XG	XG	
951-958	4.28-4.48	6.3	X	X	X
959-963	4.34-4.48	5.7		XG	XG
957-963	4.28-4.48	25.7	XG		
1027-993	4.28-4.48	6.8	XG		
1044-1058	4.48-4.48	6.0	XG		
1053-1054	4.85-4.48	6.4			
951-952	4.48-4.49	12.5	X	X	X
1054-1055	4.40-4.50	5.8			
954-956	4.48-4.49	10.0	X	X	X

XG = glass + fluid + minor albite crystals
 X = albite crystals + fluid

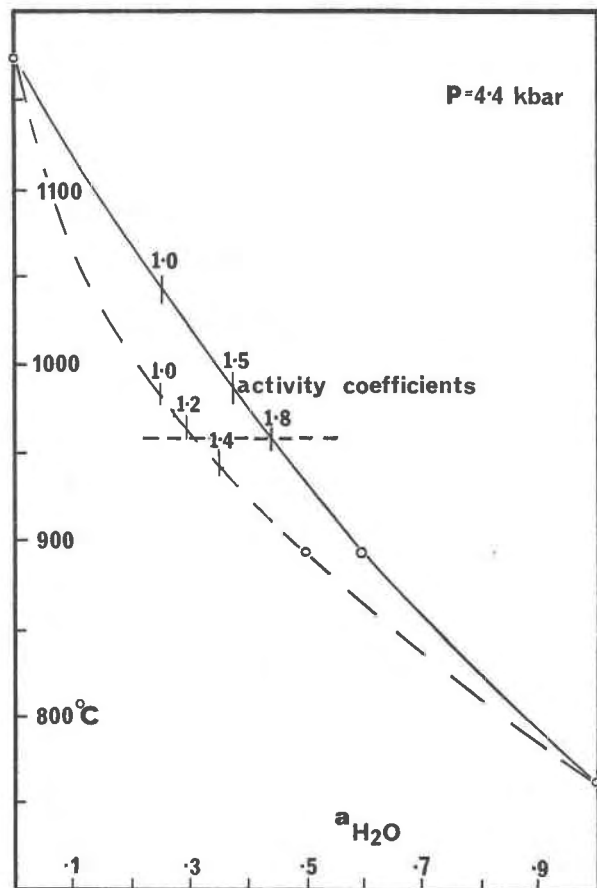


FIG. 5. Solidus temperature for albite at 4.4 kbar is shown as a function of a_{H_2O} . The dashed horizontal line indicates an experimentally-determined solidus temperature of 958°C with $X_{H_2O} = 0.25$. The solid curve was calculated assuming $\gamma_{H_2O} = 1.2$ at $X_{H_2O} = 0.5$; the dashed curve, assuming $\gamma_{H_2O} = 1.0$ at $X_{H_2O} = 0.5$.

uncertainty, as well as the possibility of minor additional freezing-point depression due to dissolved N_2 and CO_2 , we suggest that the estimate of $\gamma_{H_2O} = 1.8$ at $X_{H_2O} = 0.25$ be considered an upper bound.

Acknowledgments

This research was supported by NSF Grant GA-32442. We are indebted to C. F. Lewis and F. Delles of the Center for Meteorite Studies, Arizona State University, for the carbon and nitrogen analyses. We thank D. R. Waldbaum for suggestions which improved the manuscript, and C. Wayne Burnham for sharing his unpublished information on the activity of H_2O in H_2O - CO_2 mixtures.

References

- BELL, P. M., AND E. H. ROSEBOOM (1969) Melting relationships of jadeite and albite to 45 kilobars with comments on melting diagrams of binary systems at high pressures. *Mineral. Soc. Am. Spec. Pap.* **2**, 151-161.
- BOETTCHER, A. L., AND P. J. WYLLIE (1969) Phase relations in the system $NaAlSi_3O_8$ - SiO_2 - H_2O to 35 kilobars pressure. *Am. J. Sci.* **267**, 875-909.
- BURNHAM, C. W., AND R. H. JAHNS (1962) A method for determining the solubility of water in silicate melts. *Am. J. Sci.* **260**, 721-745.
- COOPER, J. A. (1963) The flame photometric determination of potassium in geological materials used for K-Ar dating. *Geochim. Cosmochim. Acta*, **27**, 525-546.
- HAMILTON, D. L., AND C. M. B. HENDERSON (1968) The preparation of silicate compositions by a gelling method. *Mineral. Mag.*, **36**, 832-838.
- HOLLOWAY, J. R. (1971) Internally heated pressure vessels. In: G. C. Ulmer, Ed., *Research Techniques for High Pressure and High Temperature*. Springer Verlag, New York.
- _____, AND R. L. REESE (1974) The generation of H_2O - CO_2 - N_2 fluids for use in hydrothermal experimentation. Part 1. Experimental methods and equilibrium calculations in the C-O-H-N system. *Am. Mineral.* **59**, 587-597.
- MAKRIDES, A. C., AND D. M. JEWETT (1966) Diffusion of hydrogen through palladium. *Engelhard Industries Tech. Bull.* **7**, 51-54.
- MILLHOLLEN, G. L., P. J. WYLLIE, AND C. W. BURNHAM (1971) Melting relations of $NaAlSi_3O_8$ to 30 kbar in the presence of H_2O : $CO_2 = 50:50$ vapor. *Am. J. Sci.* **271**, 473-480.
- MOORE, C. B., E. K. GIBSON, J. W. LARIMER, C. F. LEWIS, AND W. NICHIPORUK (1970) Total carbon and nitrogen abundances in Apollo 11 lunar samples and selected achondrites and basalts. *Proc. Apollo 11 Lunar Sci. Conf. Geochim. Cosmochim. Acta Suppl.* **1**, **2**, 1375-1382.
- NORRISH, K., AND J. T. HUTTON (1969) An accurate X-ray spectrographic method for a wide range of geological samples. *Geochim. Cosmochim. Acta*, **33**, 431-453.
- SHETTEL, D. L. (1973) Solubility of quartz in H_2O - CO_2 fluids at 5 kb. and 500-900°C (abstr.). *Trans. Am. Geophys. Union*, **54**, 480.

Manuscript received, August 1, 1973; accepted for publication, February 15, 1974.