The Generation of N₂-CO₂-H₂O Fluids for Use in Hydrothermal Experimentation

I. Experimental Method and Equilibrium Calculations in the C-O-H-N System

JOHN R. HOLLOWAY

Division of Geochemistry, Department of Chemistry, Arizona State University, Tempe, Arizona 85281

ROBERT L. REESE

Department of Geology, Arizona State University, Tempe, Arizona 85281

Abstract

The activities of H₂O and CO₂ can be varied independently in hydrothermal experiments by using certain C-O-H-N compounds to generate an essentially ternary H₂O-CO₂-N₂ fluid. For an initial bulk composition, the species composition of the fluid is a function of pressure, temperature, and hydrogen fugacity. The results of equilibrium calculations in the system C-O-H-N illustrate these relationships for typical experimental hydrogen fugacities in the range 10 kbar and 800 to 1200°C. Unless the hydrogen fugacity is externally controlled at low levels, the actual mole fraction of H₂O in the fluid may differ considerably from the nominal mole fraction in the ternary system, particularly when the mole fraction of H₂O is low. The formation of graphite, nitrides, and oxynitrides, and changes in fluid composition due to reaction with condensed species, are experimental problems which can be avoided or minimized.

Introduction

In nature the fluid phases involved in many geo-
logically important equilibria are usually impure with H₂O and CO₂ as major species. Early experimental studies usually duplicated only the limiting situation in which the fluid phase consisted of just one volatile species, and the equilibrium pressure of that species was equal to total pressure. Several investigators have therefore devised methods of controlling P₈₉,0 and P₂₉, at values less than P₉ by use of (1) mixtures of H₂O and H₂ (Shaw, 1967), (2) complex C-H-O fluids (Eugster and Skippen, 1967), (3) mixtures of H₂O and CO₂ in which the fluid controls the H₂O/CO₂ ratio (Holloway, Burnham, and Millhollen, 1968), and (4) mixtures of H₂O and CO₂ in which the fluid is analyzed at the end of the run (Greenwood, 1967; Metz, 1967). However, each of the above methods has disadvantages which limit its usefulness. For instance, the use of methods (1) and (2) results in fixed values of oxygen fugacity (f₉,ₙ) which may not be in the desired range; if relatively low values of P₈₉,0 are achieved using method (3), there is the possibility of crystallizing unwanted carbonates; and method (4) requires analysis of the fluid at the termination of each run.

This paper describes a method for generating H₂O-CO₂-N₂ fluids during experiments, thus allowing the independent variation of P₈₉,0, P₂₉, and f₉, at geologically significant temperatures and pressures. Important practical aspects of this method, namely the effects of P, T, and f₉, on fluid compositions, are evaluated by means of equilibrium calculations. An experimental application of the method is presented in part II of this study (Kesson and Holloway, 1974).

Experimental Method

A fluid phase containing the desired proportions of H₂O, CO₂, and N₂ is produced by the thermal decomposition of one or more C-O-H or C-O-H-N solid compounds sealed inside an inert metal capsule along with the sample. This is an extension of the method described by Holloway et al. (1968) and Holloway (1973) for generating H₂O-CO₂ fluids from mixtures of oxalic acid dihydrate + H₂O or from oxalic acid dihydrate + anhydrous oxalic acid. Several compounds which can be used either
I. R. HOLLOWAY AND R. L. REESE

TABLE 1. Symbols and Abbreviations Used

- \( P_i \): Equilibrium partial pressure of species \( i \)
- \( P_t \): Total pressure
- \( f_i \): Fugacity of species \( i \)
- \( X_i \): Actual mole fraction of species \( i \)
- \( X_{(\text{nom})} \): Mole fraction of \( \text{CO}_2, \text{N}_2 \) or \( \text{H}_2\text{O} \) in a fluid assuming complete loss of 'excess' \( \text{H}_2 \).
- \( \delta_{\text{H}_2\text{O}} \): Mole fraction of \( H_2O \) in a fluid.

| \( \text{Hematite + Magnetite + O-H fluid.} \) |
| \( \text{Manganosite (Mn}_{1-x}\text{O}) + \text{Hausmannite (Mn}_{x}\text{O}_4) + O-H fluid.} \) |
| \( \text{NiO + Ni + O-H fluid} \) |
| \( \text{Quartz + fayalite (Fe}_x\text{Si}_{1-x}\text{O}_4) + \text{Magnetite + O-H fluid} \) |
| \( \text{Wustite (Fe}_{1-x}\text{O}) + \text{Magnetite + O-H Fluid.} \) |

singly or in combination to generate ternary fluids in the system \( \text{C-O-H-N} \) are listed in Table 2 with their melting or decomposition points at 1 bar and their nominal species composition at \( P \) and \( T \) (mole fractions of \( \text{H}_2\text{O}, \text{CO}_2, \text{N}_2\) and \( \text{O}_2 \)). The nominal species compositions are shown in Figure 1A. The decomposition of compounds 1 to 7 produces excess \( \text{H}_2 \); the nominal mole fractions listed in Table 2 assume complete loss of this excess \( \text{H}_2 \). The excess \( \text{H}_2 \)-producing compounds are designated as such because the initial fluid produced by their decomposition contains free \( \text{H}_2 \) when oxygen is allocated to \( \text{C} \) as \( \text{CO}_2 \) and to \( \text{H} \) as \( \text{H}_2\text{O} \). Prior to the loss of excess \( \text{H}_2 \), the fluids lie in the \( \text{H}_2\text{O}-\text{CO}_2-\text{N}-\text{H} \) volume of the \( \text{C-O-H-N} \) tetrahedron illustrated in Figure 1B, and the mole fractions of \( \text{H}_2\text{O}, \text{CO}_2, \text{N}_2\) and \( \text{H}_2 \) in the initial fluids are also given in Table 2. Compounds 9 to 15 decompose to produce excess oxygen, and can be conveniently used in combination with excess \( \text{H}_2 \)-producing compounds to limit the amount of \( \text{H}_2 \) produced, and thus avoid certain experimental problems noted later in this paper. Silver, palladium, and platinum compounds decompose during experiments to precipitate the metal.

Most of the compounds are subject to large variations in water content if exposed to the atmosphere for a period of time. However, their stoichiometric compositions can be maintained if they are stored

TABLE 2. Fluid Generating Compounds

<table>
<thead>
<tr>
<th>Key to Fig. 1</th>
<th>Compound name</th>
<th>Empirical Formula</th>
<th>( \text{One atm. Melting or decom-} )</th>
<th>( \text{point (°C)} )</th>
<th>( \text{Initial mole fraction of:} )</th>
<th>( \text{Nominal mole fraction of:} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ammonium oxalate</td>
<td>( \text{C}_2\text{H}_4\text{O}_4\text{N}_2\text{H}_2\text{O} )</td>
<td>100</td>
<td>.125</td>
<td>.25</td>
<td>.125</td>
</tr>
<tr>
<td>2</td>
<td>Ammonium oxalate, acid</td>
<td>( \text{C}_2\text{H}_4\text{O}_4\text{H}_2\text{O} )</td>
<td>170</td>
<td>.083</td>
<td>.333</td>
<td>.167</td>
</tr>
<tr>
<td>3</td>
<td>Guanidine nitrate</td>
<td>( \text{CH}_3\text{N}_2\text{H}_2\text{N} )</td>
<td>214</td>
<td>.333</td>
<td>.167</td>
<td>.167</td>
</tr>
<tr>
<td>4</td>
<td>Guanidine carbonate**</td>
<td>( \text{C}_2\text{H}_4\text{N}_2\text{N}_2\text{CO}_2 )</td>
<td>197</td>
<td>.20</td>
<td>.20</td>
<td>.20</td>
</tr>
<tr>
<td>5</td>
<td>Nitro-guanidine</td>
<td>( \text{CH}_2\text{O}_2\text{N}_2 )</td>
<td>232</td>
<td>.40</td>
<td>.20</td>
<td>.20</td>
</tr>
<tr>
<td>6</td>
<td>Oxalic acid, dihydrate</td>
<td>( \text{H}_2\text{C}_4\text{O}_4\text{2H}_2\text{O} )</td>
<td>101</td>
<td>.40</td>
<td>.40</td>
<td>.20</td>
</tr>
<tr>
<td>7</td>
<td>Oxalic acid, anhydrous</td>
<td>( \text{H}_2\text{C}_4\text{O}_4 )</td>
<td>190</td>
<td>.667</td>
<td>.333</td>
<td>.100</td>
</tr>
<tr>
<td>8</td>
<td>Silver oxide</td>
<td>( \text{Ag}_2\text{O} )</td>
<td>140</td>
<td>1.00</td>
<td>.100</td>
<td>.100</td>
</tr>
<tr>
<td>9</td>
<td>Ammonium nitrate</td>
<td>( \text{NH}_4\text{NO}_3 )</td>
<td>170</td>
<td>.286</td>
<td>.571</td>
<td>.143</td>
</tr>
<tr>
<td>10</td>
<td>Silver nitrate</td>
<td>( \text{AgNO}_3 )</td>
<td>212</td>
<td>.25</td>
<td>.75</td>
<td>.75</td>
</tr>
<tr>
<td>11</td>
<td>Silver nitrate</td>
<td>( \text{AgNO}_3 )</td>
<td>140</td>
<td>.333</td>
<td>.667</td>
<td>.33</td>
</tr>
<tr>
<td>12</td>
<td>Silver carbonate</td>
<td>( \text{Ag}_2\text{CO}_3 )</td>
<td>218</td>
<td>.667</td>
<td>.333</td>
<td>.33</td>
</tr>
<tr>
<td>13</td>
<td>Silver oxide</td>
<td>( \text{Ag}_2\text{O} )</td>
<td>300</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>14</td>
<td>Platinum dioxide</td>
<td>( \text{PtO}_2 )</td>
<td>450</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>15</td>
<td>Palladium monoxide</td>
<td>( \text{PdO} )</td>
<td>870</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*\( \text{Mole fractions calculated assuming oxygen combines with carbon to form CO}_2 \), with hydrogen to form \( \text{H}_2\text{O} \) and remaining \( \text{H}_2 \) is removed from the system.

**\( \text{Mole fractions calculated assuming the addition of 3 moles of H}_2\text{O} \) for each mole of guanidine carbonate.
in well-sealed containers. It must be noted that most of the compounds can react explosively if exposed to air at moderate temperatures, and consequently great care is needed during capsule welding. The sample capsule can be kept sufficiently cool during welding by immersing its lower portion in ice + water, dry ice + alcohol, or liquid nitrogen. Excellent technical advice on the preparation of sample capsules is given by Huebener (1971).

**Equilibrium Calculations**

**Introduction**

The equilibrium calculations discussed in this section have allowed us to predict the variations in fluid compositions as \( \text{H}_2 \) diffuses through the sample capsule walls during the initial stages of an experiment, and also to specify the equilibrium species compositions when \( f_{\text{H}_2} \) is externally controlled.

Equilibrium species compositions have been calculated for selected bulk compositions throughout the C–H–O system with closely spaced composition points chosen near the \( \text{H}_2\text{O}–\text{CO}_2 \) join. Similar calculations have been made in the C–O–H–N system at selected ratios of \( N/(C + H + O) \) for several of the fluids produced by compounds listed in Table 2. The calculations were made at 1, 5, and 10 kbar and 800, 1000, and 1200°C plus 500°C at 1 kbar.

Equilibria involving graphite + fluid in the C–H–O system have been calculated for a wide range of \( P-T \) conditions by French and Eugster (1965) and French (1966). Calculations in the C–O–H–N system have been made by Dayhoff et al (1967) and have provided useful guidelines for our studies. However, most of the equilibria presented in this paper cover \( P, T, \) and bulk composition conditions which have not been covered in those investigations.

**Method**

The equilibrium calculations involve minimizing the Gibbs free energy of the system under consideration, using a technique known as the "NASA method" (Huff, Gordon, and Morrell, 1951) as described by van Zeggern and Storey, (1970). The computation utilizes a modified version of a program written by Gordon and McBride (1971); the modifications are discussed in detail by Reese (1973). Important modifications include the consideration of the fugacity coefficients of fluid species, and the consideration of molar volumes for solid phases. Thermodynamic data were taken from Robie and Waldbaum (1968) and Stull and Prophet (1971). The following species were considered in the calculations: graphite, CH, CH\(_2\)O, CO, CO\(_2\), C\(_2\)H, C\(_2\)H\(_4\), C, C\(_2\), C\(_3\), C\(_4\), H, HO\(_2\), H\(_2\)O, O, O\(_2\), CH\(_2\), CH\(_3\), CH\(_4\), C\(_2\)H\(_2\), C\(_2\)O, C\(_3\)O\(_2\), HCO, H\(_2\), H\(_2\)O\(_2\), OH, C\(_2\)N, C\(_2\)N\(_2\), HCN, HNCO, N, NH, NH\(_2\), NH\(_3\), NO, N\(_2\)H\(_4\), N\(_2\)O\(_4\), CN, CN\(_2\), C\(_2\)N\(_2\), HNO, NCO, NO, N\(_2\)O, N\(_2\), and N\(_3\).

**Accuracy**

The numerical programming technique used is essentially error-free for problems of this type. Consequently the accuracy of the calculations depends on (1) the Gibbs free energy data at one atmosphere, (2) the fugacity coefficients at \( P \) and \( T \), (3) the molar volume of graphite (the only crystalline phase), and (4) the absence of any species not explicitly considered. Inclusion of 47 species in the calculations, including all species detected by qualitative gas chromatographic analyses of C–O–H–N fluids produced in experimental runs, makes an error of type (4) unlikely. The one atmosphere free energy data are accurately known for gaseous species. The molar volume of graphite is accurately known and is assumed to be independent of \( P \) and \( T \) in the calculations. Because thermal expansion and compressibility are small and tend to cancel, this assumption should not introduce significant error. The largest source of uncertainty is undoubtedly the species fugacity coefficients, first in the values for the pure species, and second in the effects of fluid composition.

The fugacity coefficients of the pure species are known with varying degrees of uncertainty. The coefficients for H\(_2\)O are computed (Holloway, Eggler, and Davis, 1971) from precise and accurate \( P-V-T \) data (Burnham, Holloway, and Davis, 1969), and the error in these coefficients has a negligible effect on the final results of the equilibrium calculations. Fugacity coefficients for \( \text{H}_2 \) are calculated using equations given by Shaw and Wones (1964) and agree within 2 percent with coefficients derived from experimental \( P-V-T \) data (Presnall, 1969). The fugacity coefficients for CO, CO\(_2\), CH\(_4\), HCN, N\(_2\), NH\(_3\), N\(_2\)H\(_4\), N\(_2\)O, NO, N\(_2\)O\(_4\), and \( \text{O}_2 \) were computed from the Redlich-Kwong corresponding state equation (Redlich and Kwong, 1949) using a numerical technique proposed by Edmister (1968).\(^1\) Values for

\(^1\) A brief description of the calculations and a FORTRAN IV subroutine are contained in Appendix I. Appendices I and II can be obtained by ordering NAPS Document 02344 from ASIS c/o Microfiche Publications, 305 East 46th Street, New York, N. Y. 10017. Please remit in advance $1.50 for microfiche or $25.25 for photocopy. Please check the most recent issue of this journal for the current address and prices.
the critical temperatures and pressures required by
the Redlich-Kwong equation were taken from
Matthews (1972). The fugacity coefficients for all
other species were set equal to unity.

For lack of other data, all fluid species are here
assumed to mix ideally following the Lewis and
Randall rule (Lewis and Randall, 1961). French
(1966) has discussed the probable error involved in
that assumption and concludes that calculated
(1966) has discussed the probable error involved in
assumed to mix ideally following the Lewis and
within 5 percent with values derived from the free
coefficients derived from experimental data. The
coefficients can be evaluated by comparison with
Randall (Lewis and Randall, 1961). French
computed from P-V-T data for the entire P-T range
coefficients for H, lie within 20 percent of the coefficients
(kennedy, 1954). The redlich-kwong fugacity coefficients for CO$	extsubscript{2}$ agree
in the redlich-kwong fugacity coefficients.

For example, variations of +10 percent in the
maximum relative error of ±10 percent
considered (Lewis and Randall, 1961), it is reasonable
to assume a maximum relative error of ±0.002 in the mole fractions of
H$	extsubscript{2}$O, CO$	extsubscript{2}$, N$	extsubscript{2}$, and H$	extsubscript{2}$, and errors of ±0.1 in log$	extsubscript{10}$ f$	extsubscript{o}$.
Errors of that magnitude should have no effect on
the conclusions reached in this paper.

Results of Equilibrium Calculations

The results of equilibrium calculations for the
system C-H-O and the system C-O-H-N are presented primarily in graphical form, together with one
representative table (Table 3). More extensive tables
are contained in Appendix II (see footnote 1).

### Table 3. Calculated Compositions of Guanidine Nitrate
Fluids as a Function of X$	extsubscript{f}$ at 800° and One Kbar

<table>
<thead>
<tr>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
<th>(7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$	extsubscript{2}$O</td>
<td>0.333</td>
<td>0.367</td>
<td>0.400</td>
<td>0.434</td>
<td>0.467</td>
<td>0.500</td>
</tr>
<tr>
<td>H$	extsubscript{2}$O$	extsubscript{2}$</td>
<td>0.167</td>
<td>0.181</td>
<td>0.200</td>
<td>0.222</td>
<td>0.239</td>
<td>0.250</td>
</tr>
<tr>
<td>H$	extsubscript{2}$</td>
<td>0.333</td>
<td>0.366</td>
<td>0.400</td>
<td>0.434</td>
<td>0.467</td>
<td>0.500</td>
</tr>
<tr>
<td>CO$	extsubscript{2}$</td>
<td>0.167</td>
<td>0.181</td>
<td>0.200</td>
<td>0.222</td>
<td>0.239</td>
<td>0.250</td>
</tr>
</tbody>
</table>

**Bulk Composition**

**Major Species**

| CH$	extsubscript{4}$ | 0.652 | 0.444 | 0.362 | 0.263 | 0.157 | 0.087 |
| H$	extsubscript{2}$O | 0.365 | 0.340 | 0.314 | 0.283 | 0.216 | 0.152 |
| N$	extsubscript{2}$ | 0.365 | 0.340 | 0.314 | 0.283 | 0.216 | 0.152 |
| CO$	extsubscript{2}$ | 0.365 | 0.340 | 0.314 | 0.283 | 0.216 | 0.152 |

**Minor Species**

| CH | 0.862 | 0.001 | 0.002 | 0.003 | 0.004 | 0.005 |
| H$	extsubscript{2}$ | 0.862 | 0.001 | 0.002 | 0.003 | 0.004 | 0.005 |
| N$	extsubscript{2}$ | 0.862 | 0.001 | 0.002 | 0.003 | 0.004 | 0.005 |
| CO$	extsubscript{2}$ | 0.862 | 0.001 | 0.002 | 0.003 | 0.004 | 0.005 |

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*The corresponding f$	extsubscript{o}$ values for buffers are: H$	extsubscript{2}$O, 0.1169,
O$	extsubscript{2}$, 0.0122, and CO$	extsubscript{2}$, 0.0047.

**Blanks indicate the value was less than 10^{-9}**.
GENERATION OF N₂-CO₂-H₂O FLUIDS, I.

Fig. 2. Contours in the C-H-O system. The C apex (not shown) lies at the top apex of the equilateral triangle. Numbers on contours represent \( X_{H_2} \). The curved line falling close to the CO₂ and CH₄ compositions is the graphite boundary, graphite being stable in the region above the line. Hydrogen buffer contours are shown by the dashed line for NNO, OH; the dot-dashed line for QFM, OH; and the dotted line for WM, OH. The point indicated by ‘X’ indicates the initial composition of a fluid generated from oxalic acid dihydrate.

C₂H₄, (3) H₂O-CO₂-CH₄; this is the region of prime interest in the present study. Most of the graphite boundary is contained within this triangle. (4) The graphite stability field; the species composition of the fluid at a fixed \( P \) and \( T \) is fixed by the O/H ratio of the bulk composition. Equilibria in this region have been extensively discussed by French and Eugster (1965) and French (1966).

Qualitative differences between the four regions are illustrated by \( X_{H_2} \) contours in Figure 2. In this paper we are concerned with compositions near the CO₂-H₂O join in which \( f_{H_2} \) is either controlled externally or is floating at the ambient level of the pressure vessel. In either case the \( X_{H_2} \) values are usually between MH, OH, and QFM, OH (see Whitney, 1972). It can be seen in Figure 2 that the region of interest is thus restricted to a narrow strip parallel to and including the H₂O-CO₂ join. In order to illustrate compositional variations in this region, diagrams have been constructed by expanding the narrow strip in the direction perpendicular to the H₂O-CO₂ join. One such diagram is shown in Figure 3, where the vertical axis represents C + H in excess of H₂O + CO₂. Note particularly the directions of the C and H apices of the C-H-O equilateral triangle on the rectangular diagram. Directional lines (“to H” and “to C”) show the path that bulk compositions would follow due to addition or subtraction of H at a constant C/O ratio, or of C at a constant H/O ratio. They are hydrogen reaction lines and carbon reaction lines respectively and are exactly analogous to the oxygen reaction lines discussed by Muan and Osborn (1965). Note that because of the nature of the scale expansion, the angle between the reaction lines and the coordinate axes changes across the diagram. \( X_{H_2O} \) contours are shown and plot as straight lines on this diagram. Also shown are the contours which correspond to the \( X_{H_2} \) produced by the MH, NNO, and QFM oxygen buffers plus an O-H fluid. These contours are henceforth referred to as hydrogen buffer lines.

The Effect of \( f_{H_2} \) on Fluid Composition

The relationships between fluid compositions and externally controlled \( f_{H_2} \) have been investigated at a representative \( P \) and \( T \) (1 kbar, 800°C) and are contained in Figure 3. These relationships are relevant to several experimental methods commonly used to generate CO₂ + H₂O fluids. For example, decomposition of oxalic acid dihydrate produces a fluid whose bulk composition lies at X in Figure 3. The intermediate products of the decomposition process are unknown, but qualitative gas chromatographic analyses indicate that after only a few minutes at temperatures above 500°C the major species are CO₂, H₂O, and H₂. If the initial fluid at X is contained in a capsule permeable to H₂ and if \( X_{H_2} \) is externally controlled by QFM, OH, then H₂ will diffuse out of

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The quantity \( X_{H_2} \) is used in preference to \( f_{H_2} \) because it is relatively insensitive to \( P \) and \( T \) whereas the value of \( f_{H_2} \) varies over a wide range. \( X_{H_2} \) is thus a more convenient numeric quantity.
the capsule, and the fluid composition will follow a hydrogen reaction line passing through X toward the H₂O-CO₂ join. The fluid reaches its equilibrium composition at X’ (the intersection of the hydrogen reaction line with the QFM, OH hydrogen buffer line). The value of XH₂O in the fluid at X’ is 0.504, which can be estimated by interpolation between the 0.5 and 0.6 XH₂O contours. XH₂O in the equilibrium fluid is thus slightly greater than the nominal value of 0.500 calculated assuming loss of all H₂ in excess of H₂O-CO₂. If XH₂O in the system were controlled by NNO, OH, the equilibrium fluid composition would be given by X” and the actual XH₂O would be 0.502.

The same sort of behavior would be shown by a fluid generated by the decomposition of a mixture of oxalic acid dihydrate and anhydrous oxalic acid in 1:2 molar proportions. The initial fluid composition lies at Y in Figure 3, and changes along a hydrogen reaction line to reach equilibrium at Y’ or Y” when the XH₂O is externally controlled by QFM, OH or NNO, OH respectively.

The decomposition of silver oxalate results in somewhat different behavior. The initial fluid composition corresponds to pure CO₂ (point Z in Figure 3) but if the external H₂, corresponds to e.g., NNO, OH, then H₂ diffuses into the capsule, reacts with CO₂ to produce H₂O and CO, and the fluid composition follows a hydrogen reaction line to Z’. XH₂O in the supposedly pure CO₂ fluid is in fact = 0.06.

**The Graphite Stability Field**

Let us consider the decomposition of silver oxalate when XH₂O is controlled by QFM, OH. The initially pure CO₂ fluid would become progressively diluted with H₂ as the fluid composition follows the hydrogen reaction line from Z through Z’, to Z”, to intersect the graphite boundary. Graphite begins to precipitate at Z”, so that although the **bulk** composition continues to follow the hydrogen reaction line to Z”, the **fluid** composition now follows a path from Z” to W along the graphite boundary, while its C/O ratio changes due to the subtraction of C as graphite. Thus a fluid which was initially pure CO₂ reaches equilibrium at W with XH₂O = 0.17! Graphite however, nucleates

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**Fig. 3.** Expanded scale diagram of a portion of the C-H-O system at 800°C and 1 kbar. The area pictured in the rectangular diagram is shown as the stippled area in the inset. Heavy solid lines are XH₂O contours. Stippled area is in the graphite stability field. The symbols for hydrogen buffer contours are the same as for Figure 2 except that the dotted curve represents the XH₂O = 0.03 contour. The solid triangle represents the initial composition of oxalic acid dihydrate. See text for further explanation.
very reluctantly, and it is quite possible that it might never precipitate during an experimental run. In these circumstances the fluid composition would continue to follow the hydrogen reaction line from Z'' towards Z''' but would intersect the metastable QFM, OH hydrogen buffer line at the point M. The initially pure CO₂ fluid thus reaches metastable equilibrium at M with X_{H₂O} = 0.15.

Figures 4A–4F show that the graphite field expands with increasing P at constant T, and contracts with increasing T at constant P. The initial fluid composition resulting from the decomposition of oxalic acid dihydrate, plus the appropriate hydrogen reaction line, are shown in the Figure to demonstrate that the initial fluid composition of an excess H₂-generating compound may lie within the stability field of graphite during the initial stages of an experiment, when the system is under high pressure at low temperatures.

Fig. 4. Expanded scale diagrams similar to Figure 3. Symbols as in Figure 3. A. 1 kbar, 1000°C; B. 1 kbar, 1200°C; C. 5 kbar, 800°C; D. 10 kbar, 800°C; E. 10 kbar, 1000°C; F. 10 kbar, 1200°C.
There is the real danger that graphite may precipitate and persist metastably, as evidenced by the sporadic appearance of graphite in experimental run products. $X_{H,0}$ and $X_{H}$ contours for other $P$, $T$ conditions are shown in Figure 4. Both the position of the hydrogen buffer lines and the slope of the $X_{H,0}$ contours change with $P$ and $T$. Thus for a particular hydrogen buffer $\delta_{H,0} (= X_{\text{real}}_{H,0} - X_{\text{nom}}_{H,0})$ increases with $P$ and decreases with increasing $T$, except in regions where the graphite boundary overlaps the hydrogen buffer line. The magnitude of $\delta_{H,0}$ is small ($< \pm 0.015$) in the range $1.0 > X_{\text{nom}}_{H,0} > 0.4$ and increases rapidly between $0.4 > X_{\text{nom}}_{H,0} > 0.0$.

$X_{CO,0}$ contours at 800°C, 1 kbar are shown in Figure 5. The overall position and slope of the contours remains much the same at other $P$, $T$ conditions, but at any given $P$ and hydrogen fugacity buffer the minor species CO becomes increasingly important as temperatures increase.

Variation of $f_{o}$, with $X_{H,0}$

In either the C–H–O or C–O–H–N systems at a given $P$ and $T$, if $X_{H,0}$ in the fluid has a fixed value, then $f_{o}$, is dependent on $X_{H,0}$ in the fluid. This relationship is discussed by Whitney (1972) who shows that, if $X_{H,0}$ remains constant, then decreasing $X_{H,0}$ from 1.0 to 0.25 lowers $f_{o}$, by slightly more than one order of magnitude.

II. The System C–O–H–N

Introduction

The system C–H–O constitutes the base of the C–H–O–N tetrahedron shown in Figure 1B. Equilibrium calculations for the quaternary system show that N is almost invariably represented by the species $N_{2}$ under the usual range of experimental conditions. Consequently, fluid composition paths for which the ratio $N/(C + H + O)$ is constant can be projected without distortion from the N apex onto the base of the tetrahedron.

The horizontal plane $N/(C + H + O) = 2/3$ (see Fig. 1B) was selected to illustrate various features of the quaternary system, and equilibrium calculations were carried out for compositions in this plane. The plane can be subdivided into four regions similar to those described for the C–H–O system (Figure 2), except that $N_{2}$ is now a major species throughout the plane. Assuming complete loss of excess $H_{2}$, a fluid generated by the decomposition of guanidine nitrate (Table 2) lies exactly in this plane, on its intersection with the vertical $H_{2}O$–CO$_2$–N plane (stippled in Figure 1B).

Figure 6A shows the $N/(C + H + O) = 2/3$ plane contoured for $X_{H,0}$. In Figure 6B the MH, NNO, and QFM (OH fluid) hydrogen buffers and graphite boundary (dashed lines) are projected from the $N/(C + H + O) = 2/3$ plane onto the base of the tetrahedron. The buffers and boundary curve for the quaternary system are displaced relative to those of the C–H–O system because the presence of $N_{2}$, essentially an inert dilutant, changes the mole fraction of the other fluid species.

The Effect of $f_{o}$, on Fluid Compositions

A C–O–H–N fluid generated by the decomposition of a compound producing excess $H_{2}$ (Table 2) follows a path through the tetrahedron along a hydrogen reaction line. The variation in species composition along such a path is illustrated in Figure 7 in which, for a fluid produced by guanidine nitrate, the mole fractions of various species at constant $P$ and $T$ are plotted against $X_{H,0}$. Table 3 contains the results of the equilibrium calculations for this particular example. Appendix II (see footnote 1) contains the results of equilibrium calculations for oxalic acid dihydrate, guanidine nitrate, anhydrous oxalic acid (or silver oxalate), ammonium oxalate, and a 2:1 mixture of anhydrous oxalic acid with oxalic acid dihydrate.

The Graphite Stability Field

The stability field of graphite is of considerable importance in the generation of C–O–H–N fluids.
As in the system C–H–O, a fluid composition moving towards equilibrium along a hydrogen reaction line may intersect the graphite stability field, with consequences that have been discussed in an earlier section of this paper. There is likewise the problem of the early nucleation and metastable persistence of graphite during an experiment.

P and T affect the stability field of graphite in the quaternary system in a manner analogous to that described for the C–H–O system.

**Experimental Limitations and Techniques**

*Low \( X_{\text{H},o} \) Fluids*

The results of the equilibrium calculations show that in order to produce fluids with \( X_{\text{H},o} < 0.25 \) anP with \( X_{\text{H},o} \approx X(\text{nom})_{\text{H},o} \), the value of \( X_{\text{H}} \) must be considerably lower than that produced by NNO, OH. Also, to generate fluids consisting of pure CO₂ or N₂ in which \( X_{\text{H},o} \) is effectively zero the value of \( X_{\text{H}} \) must not be much greater than that produced by MnO–Mn₂O₄, OH. Such low \( X_{\text{H}} \) levels may be difficult to attain in some pressure vessels, especially solid-media apparatus with graphite furnaces and talc or pyrophyllite media. One possible remedy is to surround the sample capsule with an H₂ sink such as hematite (Millhollen, Wyllie, and Burnham, 1971). A second method which could be used in conjunction with the first would be to surround the sample with a phase which would decompose to CO₂. These large amounts of CO₂ would lower \( f_{\text{H},o} \) in the capsule surroundings, and in conjunction with hematite greatly lower \( f_{\text{H}} \) (cf Whitney, 1972).

**Suppression of Graphite**

The formation of graphite during the initial part of an experiment can be suppressed in some cases...
by using a combination of starting materials which together do not decompose to produce a large quantity of excess $H_2$. For example, a combination of $PtO_2 + anhydrous oxalic acid$ could replace oxalic acid dihydrate, and the decomposition of the mixture would be as follows:

$$\frac{1}{2}PtO_2 + H_2C_2O_4 = 2CO_2 + H_2O$$

with no excess $H_2$ produced. In situations where a fluid which nominally consists of pure $CO_2$ is required, silver oxalate would be a better starting material than the excess $H_2$-producing anhydrous oxalic acid.

Changes in Fluid Composition by Reaction with Condensed Phases

The fluid phase composition may differ from that predicted if reaction with the condensed phases occurs. The fluid composition after reaction with the volatile species can be calculated, and the change is usually small or negligible when the fluid/condensed phase ratio is high. At high values of $X_{H_2O}$, a high ratio of fluid to condensed phase results in solution of large quantities of condensed phases in the fluid, but Holloway (1971) and Shettel (1973) have shown that a reduction of $X_{H_2O}$ from 1.0 to 0.5 causes an exponential decrease in solute concentration. Holloway and Burnham (1972) found that a fluid/condensed phase ratio of 1:1 by weight was sufficient to maintain $X_{H_2O}$ in the fluid within ±2 percent during hyper-solidus runs in the system basalt-$H_2O-CO_2$.

Formation of Nitrides and Oxynitrides

The formation of nitrides and oxynitrides depends on the ratio $P_{N_2}/P_{O_2}$. Atmospheric pressure data indicate that the most stable simple metal nitrate $FeN$ is stable at $P_{N_2}/P_{O_2}$ ratios $> 10^{10}$ (Muan and Osborn, 1965). Few data exist for the more complex oxynitrides, but Ryall and Muan (1969) have shown that in the system $Si-O-N$, silicon oxynitride is stable at $P_{N_2}/P_{O_2}$ ratios $> 10^{10}$. The effect of total pressure on the ratios should be small. These data suggest that, at low $f_{O_2}$, oxynitrides could form in silicate systems at high nitrogen pressures.

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References


——, AND C. W. BURNHAM (1972) Melting relations of basalt with equilibrium water pressure less than total pressure. J. Petrol. 13, 1-29.


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