Phase relations in model fluid systems

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ABSTRACT. — Phase relations in geologic fluids are described by a general P-T-X model in which the relationships among solids, liquids, vapours and supercritical fluids are developed in a manner consistent with the phase rule and the principles of phase theory. The general P-T-X model is described for a binary system with a single critical endpoint and involving two solid phases that show no mutual solubility as well as a liquid and vapour that are completely miscible in the two components. A binary system of this type describes the behaviour of the geologically important system, NaCl-H2O. Isothermal, isobaric and iso-compositional sections through the P-T-X model are used to illustrate the behaviour of fluids as, for example, under a heating-cooling stage on the petrographic microscope.

Key words: binary, phase relations, P-T-X, fluid inclusions, NaCl-H2O.

Introduction

The study of geologic fluids within the Crust has been greatly advanced by a knowledge of the phase relations in simple systems. These systems are used to model the behaviour of more complex natural fluids. Important model system are the unaries, CO2, H2O, the binaries, CO2-H2O (TAKENOUCI and KENNEDY, 1964) and H2O-NaCl (SOURIRAJAN and KENNEDY, 1962), as well as the ternary, CO2-H2O-NaCl (TAKENOUCI and KENNEDY, 1965; GEHRIG, 1980). In this paper, we examine certain aspects of the phase relations in these systems and their application to geologic problems such as the interpretation of fluid inclusions.

Unary Phase Relations

The phase rule indicates the number of phase elements that must exist on a phase diagram. Each element can be stable or metastable although it is not unusual to show only the stable elements. All of the possible elements must exist somewhere on a phase diagram.

The phase rule is written as,

$$f = c + 2 - \phi$$

where f is the variance, (the number of variable parameters such as pressure, temperature, or the chemical potential of each

Fig. 1. — Pressure-Temperature diagram for a typical unary system such as H2O. Inclusions of H2O trapped initially within the stippled area will exhibit two phases at 25 C., S, solid; L, liquid; V, vapour. T indicates the triple point and C indicates the critical point.
compotent); $c$ is the number of components; 
$\phi$ is the number of phases present. Unary 
phase relations are illustrated on Figure 1. The 
maximum of three phases exists at the triple 
point, $T$, where the variance is zero. Along 
a univariant curve such as liquid + vapour 
($L + V$), two phases coexist in stable 
equilibrium. Within the divariant fields of a 
single fluid phase, either liquid or vapour, it 
is possible to draw lines of constant volume 
(isochors) or constant density as shown by the 
dashed curves on Figure 1. Fluid inclusions 
that initially trapped pure $H_2O$ at a pressure 
and temperature within the stippled area will 
consist of a liquid and vapour under 0.03 bars 
of pressure at $25^\circ C$. Other conditions of 
entrapment result, after cooling to $25^\circ C$, in 
a single liquid phase at a pressure greater than 
0.03 bars or a single vapour phase at a pressure 
less than 0.03 bars. All fluid inclusions are, 
of course, constrained to room temperature 
under the normal petrographic microscope. 
The pressure of such inclusions can have a 
range of values up to a limit determined by 
the strength of the crystal; beyond this limit, 
the fluid inclusion decrepitates.

The $L + V$ curve ends at the critical point. 
Above the critical point, the liquid and vapour 
phases become indistinguishable and a single 
phase, the supercritical fluid, is involved in 
phase relations.

**Binary Phase Relations**

The application of the phase rule to binary 
systems is summarised in Table 1. For a binary 
system consisting of a relatively volatile 
component such as $H_2O$ (component A) and 
a relatively involatile component such as $NaCl$ 
(component B) the maximum number of 
phases that can coexist at stable or metastable 
equilibrium is four as for the element, ice (A)- 
halite (B)-liquid (L)-vapour (V). If the phase 
relations among these four phases plus one 
additional phase such as hydrohalite 
($NaCl.2H_2O$) were under consideration, 
then five invariant elements would exist 
on the phase diagram to depict stable 
and metastable phase relations. Further 
consideration is only given here to phase 
relations among two immiscible solid phases, 
with compositions of the pure components, 
A and B, as well as L and V that are miscible 
in the two components. These four phases 
result in the single invariant point on Table 1. 

Univariant phase relations in a binary 
system require that three phases coexist along 
a phase element with a variance of unity. The 
combination of four into groups of three 
produces four such univariant elements as 
indicated in Table 1. Each of these elements 
plots as a line in P-T space. In a similar 
manner, it is possible to define six divariant 
phase elements in Table 1; these elements 
occupy an area in P-T space. Four trivariant 
elements are possible. The two solid phases, 
A and B, exhibit no mutual solid solution and 
are therefore confined to the planes for the 
unary system in the P-T-X diagram. The 
elements, L and V, are binary solutions that 
require three dimensions to illustrate 
geometrically; these two elements therefore 
appear as projected volumes in P-T space.

**Projected Binary Phase Relations**

Figure 2 presents the phase relations of

<table>
<thead>
<tr>
<th>Variance</th>
<th>Number of Phases</th>
<th>Phase Elements</th>
<th>Geometry in P-T Space</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
<td>$A + B + V$</td>
<td>point</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>$A + B + L$, $A + B + V$, $A + L + V$, $B + L + V$</td>
<td>line</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>$A + B$, $A + L$, $A + V$, $B + L$, $B + V$, $L + V$</td>
<td>area</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$A$, $B$, $L$, $V$</td>
<td>projected volume</td>
</tr>
</tbody>
</table>
Table 1 on P-T, T-X and P-X projections. The two unary systems with compositions, A and B, are shown as described above for Figure 1. The points, T and C, are the triple point and critical point in the indicated unary. The triple point for A is at much lower temperature than which both solids are stable on the P-T diagram. The curves along which either solid coexists with two fluids (A + L + V or B + L + V) are bounded by the unary and binary invariant points. Two solids coexist with liquid (A + B + L) along a steep melting

B as for H2O (0°C, 0.006 bars) compared to NaCl (800.5°C, ≈ 1 bar). The critical points, C, in H2O (374°C, 220 bars) and NaCl (≈ 3600°C, ≈ 258 bars) are joined by a dashed curve representing the binary critical curve. This binary critical curve indicates the points at which each bulk composition in the binary reaches supercritical conditions. From a point below this binary supercritical curve, a vapour enriched in H2O relative to the bulk composition and a liquid enriched in NaCl approach one another in all properties and finally become identical at the critical curve.

The invariant element, E, requires two solid phases as well as a liquid and vapour to be stable at the indicated P and T; this element must therefore plot within the P-T range over

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Fig. 2. — Phase relations on pressure (P), temperature (T), composition (X), projections for a typical binary system such as H2O-NaCl with solid phases showing no mutual solid solution and a liquid and vapour phase with complete miscibility of the two components, A and B. T, triple point in the subscripted binary. C, critical point in the subscripted binary. E, binary invariant point along which the two solid phases as well as a liquid, L, and a vapour, V, coexist. CA, CB indicates the binary critical curve. The stippled area indicates the projected two-phase element, L + V. The composition of the liquid and vapour coexisting with solid B is fixed at a specified P and T as indicated by the points, V and L, along the same dashed tie-line on the three-phase element, B + L + V. The points, X1 and X2, indicate the compositions for which the sections on Figure 5 have been drawn. 2a: Pressure-composition projection. 2b: Temperature-pressure projection. 2c: Temperature-composition projection.
curve originating at point E in P-T space. Two solids and a vapour \((A + B + V)\) coexist along a shallow curve in P-T space that originates at the invariant point, E.

The \(A + L + V\) and \(B + L + V\) curves are further illustrated in Figures 2a and 2c as P-X and T-X projections. The elements \(A + B + L\) and \(A + B + V\) are omitted from Figures 2a and 2c for clarity. Dashed tie-lines parallel to the X axis have been included on 2a and 2c to emphasize that the composition of the vapour and liquid that coexist with solids are fixed at a particular temperature and pressure. For example, along the element \(B + L + V\), the temperature and pressure at which B coexists with saturated liquid, L, and saturated vapour, V, are indicated on the three diagrams of Figure 2.

The two-phase element, \(L + V\), is of considerable interest in the geological study of fluids. This element plots as an area on a P-T diagram (the stippled area on Figure 2a) and expands into a volume when the compositional dimension, X, is considered in addition to P and T. The \(L + V\) volume is illustrated in a P-T-X block diagram in Figure 3. It is bounded by the three-phase surfaces (stippled) on which the two fluids, L and V, are simultaneously saturated in either solid A or solid B. It is also bounded by the unary \(L + V\) curves and the binary critical curve, \(C_A - C_B\). A series of isothermal sections through the \(L + V\) volume is sketched into Figure 3 with a series of isothermal, isobaric tie-lines joining coexisting liquid and vapour. The vapour is more A-rich and the liquid more B-rich than any bulk composition along a tie-line. The tie-lines become shorter as the binary critical curve is approached and finally decrease to a point at the critical curve. If \(B\) is added to a typical bulk composition within the \(L + V\) region, then the bulk composition will eventually shift into the \(L\) only field; as more \(B\) is added, the liquid will reach saturation and the bulk composition will enter the \(L + B\) volume. Addition of \(H_2O\) to a bulk composition within the \(L + V\) field eventually shifts the system into the \(V\) only field.

To gain familiarity with the phase elements listed in Table 1 and illustrated on Figures 1 to 3, it is helpful to draw isotherms, isobars

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**Fig. 3.** — The liquid (L)-vapour (V) volume for a binary system such as \(H_2O-NaCl\). T, triple point for the subscripted unary. C, critical point in the subscripted unary. \(C_A - C_B\) indicates the binary critical curve. Unary \(L + V\) curves are also indicated. The three-phase surfaces, \(A + L + V\) and \(B + L + V\), are shown in a stippled pattern. Typical isothermal sections through the volume are indicated with tie-lines parallel to composition plane. The tie-line becomes shorter as the binary critical curve is approached and eventually becomes a single point along the binary critical curve. Above the critical curve, only one fluid phase, the supercritical fluid, exists.
and iso-composition sections (isopleths) through the binary P-T-X space. Figure 4b is an isobar drawn for the pressure indicated on Figure 4a. The dashed lines between 4a and 4b emphasise that the temperature at which each phase element is intersected by the isobar, $P_1$, on 4a can be transferred to 4b. A similar method is used to construct the isotherm, $T_1$, drawn on 4c for the temperature indicated on 4a.

Isotherm and isobars such as shown in Figures 4b and 4c are helpful in understanding the phase relations in fluid systems. It should be emphasized, however, that fluids in natural systems are not generally constrained to an isobaric or isothermal plane. Isobars such as drawn on Figure 4 are, nevertheless, widely used in the study of fluids inclusions; the curve representing the composition of liquid saturated with halite, L ($H_1$), can be used to determine the salinity of the liquid from the temperature at which the halite crystal disappears by rehomogenisation. A similar diagram is given in many reference sources for microthermometry (see for example, Crawford, 1981, Figure 4.2; Roedder, 1984; Figures 8-11a, 8-14). The suggestion in these references that a vapour phase coexists with liquid and salt at 1 bar of pressure is not meant to imply that the pressure within the inclusion is, in fact, 1 bar; rather, the pressure within the inclusion is that indicated by the three-phase curve, $L + V + H$, for the temperature of interest. The composition of the homogenised liquid is normally a close approximation to the bulk composition of the fluid inclusion in $H_2O-NaCl$ since the vapour phase has much lower density than the liquid and solid phases. The influence of pressure on the position of the curve, liquid in equilibrium with halite, is sufficiently low that pressure variations within inclusions are assumed to have negligible effect on salinity determinations by the above method.
Isocomposition sections through the P-T-X model are also useful in the study of fluid inclusions that can be modeled by the system, NaCl-H₂O. Two representative sections are given in Figure 5 for the two compositions, X₁ and X₂, that are shown on Figure 2. The invariant element, E, and the univariant elements with three coexisting phases are constant in P-T space as well as for all isopleths. The three-phase curves for a solid coexisting with liquid and vapour terminate at the appropriate temperature and pressure for that composition, as can be seen on Figures 2a and 2c. The saturated liquid and vapour shown by the points on the three-phase elements on Figure 5 do not coexist; each of these fluids is in equilibrium with a coexisting fluid that plots outside of the plane of the section.

The bulk composition of a fluid inclusion is taken, as a first approximation, to be constant over the history of an inclusion (excluding problems such as diffusion, chemical reaction with the crystal, necking down). The liquid or the vapour obviously have this composition when a single phase is present and can be plotted within the plane of a constant composition section such as 5a and 5b. In a two-phase region such as L + V, L + B or V + B, the compositions of the two phases lie outside of the plane of the constant composition section. The compositions of the liquid and vapour in multiphase inclusions must be read for a specific temperature and pressure from quantitative projections such as those determined by Sourirajan and Kennedy (1962, Figure 13 or 19 etc.).

A fluid inclusion trapped at a P and T above the two-fluid element, L + V, can eventually reach the two-fluid element on cooling; the P and T at which two phases appear are dependent on the bulk composition and density of the inclusion (see Figure 5). The inclusion will subsequently follow a P-T trajectory through the L + V volume with the composition of the L and V phases plotting outside of the plane of the isocomposition section. Many fluid inclusions that were initially trapped above the two-phase region are sufficiently dense that they become saturated in one of the two solid phases and...
subsequently follow a three-phase curve to lower temperatures.

Ternary Phase Relations

Few experimental data are available for important ternary fluid systems. One of the best studied is the system CO₂·H₂O·NaCl that is discussed elsewhere in this volume in more detail. Gehrig (1980) has measured P-V-T data for this ternary to pressures of 3000 bars and temperatures to 500°C. Bowers and Helgeson (1983a, 1983b) have fitted an equation of state to the measured data and provided a discussion of the phase relations in the ternary system. Bowers and Helgeson (1985) have also written a Fortran computer code, DENFIND, that uses the equation of state to calculate isochors in P-T space for ternary fluids of a specified composition.

The computer code, DENFIND, has been used to calculate a representative series of isochors as shown on Figure 6. All of these isochors pass through 500°C and 2000 bars and continue to the point at lower P and T where a single fluid enters the two-phase region; the lower limit for each curve on

Figure 6 corresponds to the point that would be measured as the homogenisation temperature in microthermometry.

The isochor for pure H₂O has a density of 0.69 and terminates at the L + V curve in the unary system as illustrated on Figure 1. The isochor for pure water has been calculated from an equation given by Haar and Coworkers (1979). The addition of 10 weight percent NaCl to the pure water results in a fluid with a density of 0.80; this isochor on Figure 6 is similar in slope to that for pure water. The isochor for pure CO₂ as calculated from the Bowers and Helgeson computer code has a density of 0.77 and is much flatter than that for water and brine; the isochor for CO₂ continues to the lowest temperatures shown on Figure 6 due to the low critical temperature and pressure for this gas.

The addition of 20 mole percent CO₂ to pure water results in a density of 0.70. The addition of 20 mole percent CO₂ to the 10 weight percent NaCl solution produces a solution with a density of 0.73 and a higher homogenisation temperature than pure water or the CO₂-free brine.

Concluding Statement

The isochors shown on Figure 6 provide a general illustration of the influence of salinity and volatile content on the slope of isochors and the homogenisation temperature to be expected under the microscope. The computer code, DENFIND, can be used on personal type computers and is a valuable tool for understanding the geologic behaviour of fluids in the ternary CO₂·H₂O·NaCl and its constituent binary and unary systems.

There is, of course, a continuing and important need to obtain more P-V-T data for fluids that model the relationships among liquids, vapours and supercritical fluids in geologic processes.

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REFERENCES


