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SYSTEMS CONTAINING ALKALI CARBONATES, ALKALINE EARTH CARBONATES, AND BOTH

By

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By George W. Morey

ABSTRACT

In this report is assembled the available information about the dissociation and melting of the alkali and the alkaline earth carbonates and the binary systems they form with each other. Information is also included about the oxides formed on dissociation of the carbonates, and when it exists pertinent information about the effect of water. Because the carbonates are compounds in binary systems that contain the volatile CO_2 component, the report contains a discussion of the complicated phase equilibrium relations in systems in which a compound is formed between volatile and nonvolatile components, including a discussion both of systems in which the solubility curve does not and does intersect the critical curve.

INTRODUCTION

The underground nuclear detonation of September 19, 1957 took place in a typical tuff formation, the Oak Spring tuff. Other types of formation are possible locations for future experiments, and one possible type of useful formation is composed wholly or in part of alkaline earth carbonates, calcite ($CaCO_3$), dolomite ($MgCO_3 \cdot CaCO_3$), or magnesite ($MgCO_3$). In that connection, it is useful to have assembled the physico-chemical information relative to the melting point and dissociation pressures of the various carbonates and systems containing more than one carbonate.

It was considered desirable to include the alkali carbonates, and accordingly in the following pages are assembled the pertinent data for sodium carbonate, potassium carbonate, magnesium carbonate, calcium carbonate, strontium carbonate, barium carbonate, and systems containing more than one of these compounds. Some information about the oxides formed on dissociation of the carbonates, and where it exists pertinent information about the effect of water is included.

DISCUSSION OF THE THEORY OF PHASE EQUILIBRIUM RELATIONSHIPS IN BINARY SYSTEMS CONTAINING A VOLATILE AND A NONVOLATILE COMPONENT

Calcium carbonate is a binary compound in the system CO_2-CaO, in which the components are of greatly different volatility. In such systems critical phenomena are met with. The critical point of liquid CO_2 is at 31° C and 73.76 bars pressure, and a hypothetical critical curve connects the critical point of CO_2 with the critical point of CaO. The solubility curve of $CaCO_3$ in liquid CO_2 is short because of its limited solubility, and it will be terminated at the point where it intersects the critical curve at a critical end-point. The critical point is a point at which two phases become identical; a critical end-point is a point at which two phases become identical in the presence of a third phase. A critical end-point always results from the intersection of a critical curve with a 3-phase curve, in this case the curve gas + liquid + $CaCO_3$. At the first critical end-point in the system CO_2-CaO the gas and liquid phases become identical in the presence of solid $CaCO_3$. Since $CaCO_3$ melts at 1,339° C and 40 bars pressure, giving rise to a liquid containing CO_2, there must be an upper critical end-point, a point at which the 3-phase curve on cooling intersects the critical curve. The relationships in systems of this type will be made clearer by considering first the simpler system in which a binary compound is formed, but in which the critical curve is not intersected by the solubility curve and there are no critical end-points.

The complete representation of such a system requires a solid model in which the axes are pressure, P, temperature, T, and composition, X. Figure 1 shows the projections of such a model on the T-X, P-T, and P-X sides. This model is hypothetical and the scales of temperature and pressure are chosen for convenience in drawing. In general, the critical temperature of component B is proportionally greater than is indicated and the content of component B in the gas phase is exaggerated.

Figure 1a gives the T-X projection of the solid model. The curve G+L+AB is the liquid branch of the solubility curve, that is, the liquid branch of the 3-phase curve, and the tie-lines indicate the composition of the coexisting gas. In the case assumed in figure 1, the compound melts to a liquid of its own composition, that is, it has a congruent melting point, but it does not evaporate to a liquid of its own composition, that is, it does not have a maximum sublimation point. In figure 1a, the gas E_G is in equilibrium with the eutectic liquid E_L, and the gas curve in equilibrium with the liquid curve in the univariant equilibrium G+L+AB is indicated by the tie-line. Both the gas and the liquid branches of this equilibrium rise from the eutectic E, the quadruple point G+L+AB+B, to a maximum temperature, then falls to the lower temperature eutectic e. Also proceeding from the eutectic E is the 3-phase curve G+L+B, the melting point curve of B which ends at the melting point of B; the curve G+AB+B, the dissociation pressure

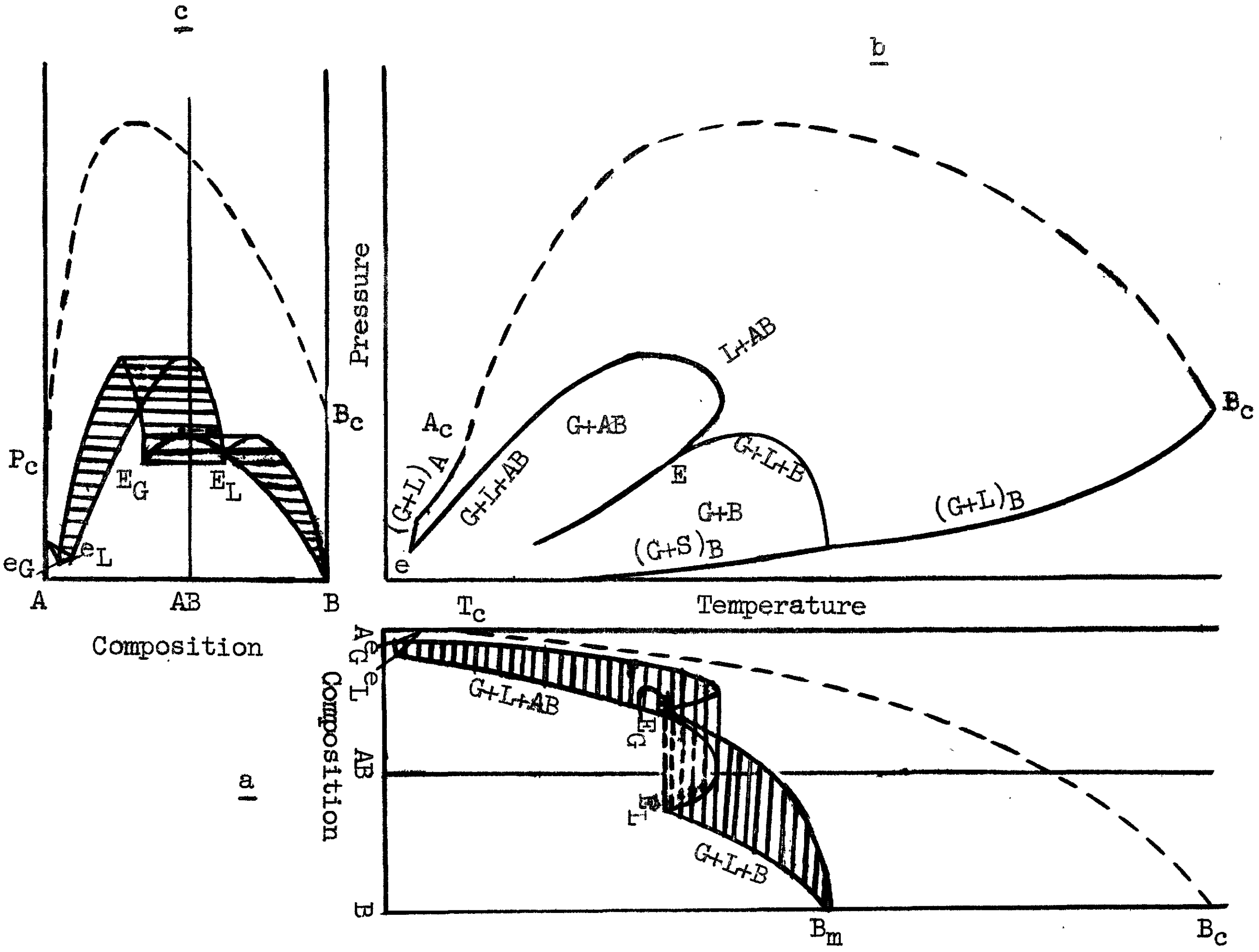


Figure 1.--Projections of a solid P-T-X model representing a system in which a compound with a congruent melting point is formed, there is no liquid immiscibility, and the solubility curve does not intersect the critical curve. Figure 1a is the projection on the T-X base; figure 1b the projection on the side P-T; figure 1c the projection on the end P-X.

curve of AB, and the curve L+AB+B, not shown in figure 1b, which gives the change in the eutectic temperature with pressure.

The pressure required to keep the volatile component in the liquid is represented by some of the curves of the P-T projection (fig. 1b). The curve $(G+L)_A$ is the vapor pressure curve of liquid A, terminating in critical point of A, A_c. The pressure of the 3-phase curve G+L+AB rises to a maximum point then falls to the quadruple point G+L+AB+B, point E. From this quadruple point proceed four univariant equilibria. Each of these univariant curves is represented by an equation of the form

$$\frac{dp}{dt} = \frac{\begin{vmatrix} s' & 1 & x' \\ s'' & 1 & x'' \\ s''' & 1 & x''' \end{vmatrix}}{\begin{vmatrix} v' & 1 & x' \\ v'' & 1 & x'' \\ v''' & 1 & x''' \end{vmatrix}} = \frac{(s' - s'') - \frac{x' - x''}{x''' - x''}(s''' - s'')}{(v' - v'') - \frac{x' - x''}{x''' - x''}(v''' - v'')}$$

in which s and v refer to the specific entropy and volume of the phases indicated by the superscripts. If the single, double, and triple primes represent gas, liquid, and solid, respectively, and $x'' = x'''$, as is the case at the congruent melting point of AB, this reduces to

$$\frac{dp}{dt} = \frac{s''' - s''}{v''' - v''} = \frac{s^S - s^L}{v^S - v^L}$$

and the slope of the curve G+L+AB at the congruent melting point becomes identical with that of the curve L+AB which gives the change of melting point of the compound AB with pressure. This point is known as the minimum melting point of the compound. In the usual case in which $(v^S - v^L)$ is negative the slope of L+AB is positive, since $(s^S - s^L)$ is always negative. Hence, the congruent melting point of a compound is not a point of maximum temperature in a system containing a volatile component, as it is in a condensed system, but the point of maximum temperature is displaced toward the more volatile component. The congruent melting point of $CaCO_3$ is near 1,339° C, and the pressure of CO_2 is 1,039 bars.

In addition to the 3-phase curve G+L+AB, three other P-T curves of univariant equilibria proceed from the quadruple point E. One of these represents the change of the temperature and composition of the equilibrium L+AB+B with pressure. It is not shown in figure 1. Another is G+L+B which goes from the eutectic E to the melting point of B. The fourth curve is the dissociation pressure curve of AB, G+AB+B, that goes from E to lower temperatures and pressures. For $CaCO_3$, the temperature of E is 1,240° C, the pressure 40.2 bars.

It is usually helpful in considering the phase equilibrium relationship as exhibited in a solid P-T-X model to consider sections at constant temperature, known as $(P-X)_T$ sections, and sections at constant pressure, $(T-X)_P$ sections. It is to be emphasized that these curves represent a hypothetical case. Some $(P-X)_T$ sections will be considered next.

Consider a section (fig. 2a) through the solid model at a temperature above the melting point of B, but below the critical point of B. At this temperature the only possible phases are gas and liquid, as shown in figure 1a. Point B is the vapor pressure of molten B at this temperature, and the loop BcB gives the composition of coexisting gas and liquid phases. The gas and liquid branches of the loop coincide at the critical point c, with a horizontal tangent. Any composition outside of this loop is a gas at this temperature. If a mixture of the composition given by the line aa' is compressed, liquid will be formed at a; on further compression the amount of liquid will just increase, then decrease, until it all evaporates at a'. This is an example of retrograde evaporation.

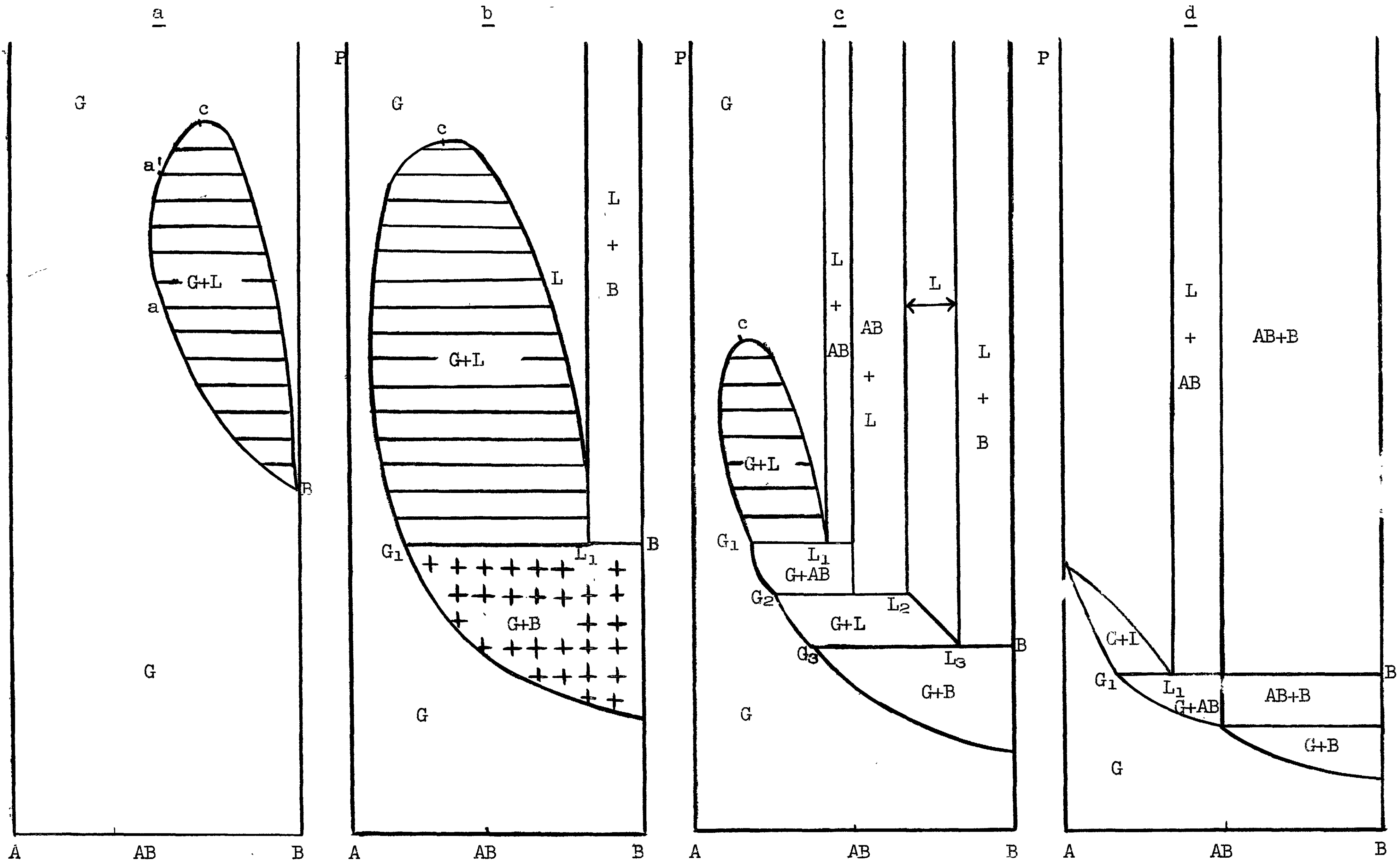


Figure 2.--Sections at constant temperature through the solid P-T-X model, $(P\text{-}X)_T$ sections. Figure 2a is at a temperature below the critical point of B, but above its melting point. Figure 2b is below the melting point of B, but above the minimum melting point of AB. Figure 2c is above the quadruple point G+L+AB+B, but below the minimum melting point of AB. Figure 2d is below the quadruple point and below the critical

Next consider a section (fig. 2b) through this solid model at a temperature above the maximum on the 3-phase curve G+L+AB, but below the melting point of B. At low pressures the material is entirely gaseous. As pressure is increased crystals of B will begin to condense from any mixture richer in B than G_1, that is, the region G+B is entered. On further compression, at the pressure of the line G_1L_1B, liquid will be formed of composition L_1, in equilibrium with gas of composition G_1 and solid B. This is an invariant point at constant temperature. The three phases can coexist at this temperature only at this pressure, and if the pressure is increased one phase will disappear. If the original mixture is richer in B than L_1, the gas will be condensed and the mixture will enter the region L+B. The slope of the boundary of this region will depend on the relative specific volumes of the saturated solution and solid B, and may be either positive or negative. In any case this curve is very steep, and is drawn as vertical. Ultimately as the pressure is increased indefinitely the liquid will solidify. If the mixture is between G_1 and L_1, on compression the solid disappears and the region entered is G+L, which is terminated by the two phases becoming identical when the critical curve is reached at point c where the loop G_1cL_1 has a horizontal tangent. If the composition of the original mixture is between G_1 and the vertical tangent to the gas curve, retrograde evaporation will take place.

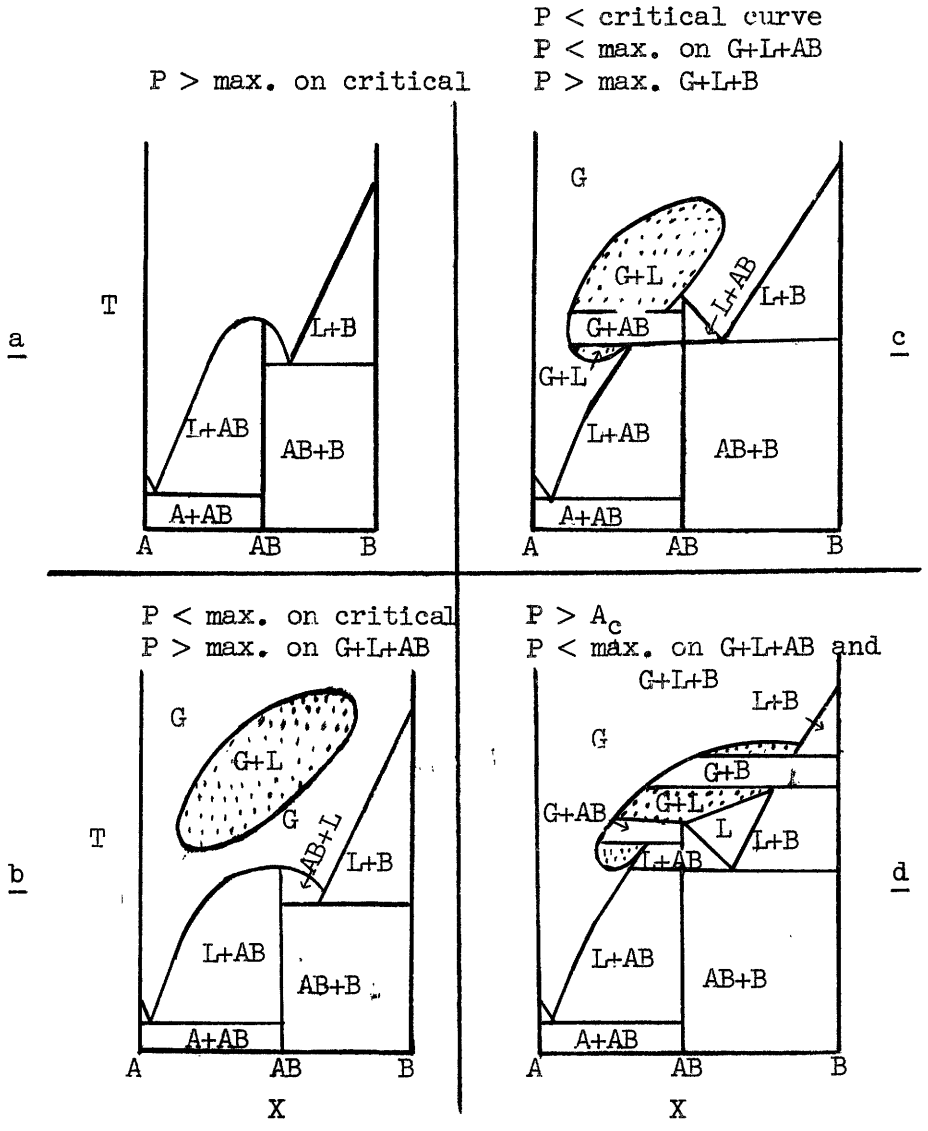
Now consider a P-X reaction (fig. 2c) at a temperature above the eutectic E of figure 1b, but below the minimum melting point of AB. From figure 1b it is evident that a section at this temperature passes from a region of G+B into a region of unsaturated solution, then meets the branch of the 3-phase curve G+L+AB, between the eutectic E and the minimum melting point of AB, then enters the region G+AB, then again meets the curve G+L+AB, this time in the part at a temperature below both the minimum melting point of AB and the maximum temperature on the 3-phase curve.

This sequence of phase changes is shown in the P-X section of figure 2c. On compression, a mixture which passes through the region G+B reaches the 3-phase line G_3L_3B, at which pressure some gas condenses and a liquid of composition L_3 is formed. If the original mixture contains more B than corresponds to L_3, on further compression the gas is all condensed and the mixture enters the region L+B. Here again the slope of the boundary curve is either positive or negative, but very steep. If the original mixture was between G_3 and L_3 a region of unsaturated solution, indicated by $G_3 + L_3$, is reached on further compression. If the composition of the mixture is between G_3 and L_3 the unsaturated liquids from L_3 to L_2 are in equilibrium with gases from G_3 to L_3. If the original mixture is of composition between L_2 and L_3, on crossing this line it passes into a region of unsaturated liquids without a coexisting gas phase. If the composition is between L_2 and AB, at pressures above that of the line G_2L_2 it passes into the region AB+L, but if it is between G_2 and AB it passes into a region G+AB. On further compression the pressure G_1L_1 is reached at the second intersection of the 3-phase curve G+L+AB and a liquid of composition L_1 is formed. If the pressure is further increased and the composition is between L_1 and AB, the region L+AB will be entered, but if the composition is between G_1 and L_1 the region entered will be that of unsaturated liquid in equilibrium with gas, the region G+L. The loop G_1cL_1 has a horizontal tangent at point c, the critical point at this temperature. If the mixture is richer in A than indicated by point G_1 there is again the possibility of retrograde evaporation.

Figure 2d is at a temperature below the eutectic E. On compression from the gas the mixture first passes into the region G+B or G+AB, until the pressure of the 3-phase equilibrium G+L+AB is reached. If the original mixture was richer in B than AB the sequence of phase areas in G+B → AB+B; if between L and AB, it is G+AB → G+L+AB → L+AB; if between G_1 and L_1, G+AB → G+L+AB → G+L → L; if richer in A than G_1, G → G+L → L.

The preceding sections through the solid model were made at a series of temperatures and show the phase changes which result from a change in pressure at constant temperature. It is also instructive to consider a series of temperature-concentration sections at constant pressure, $(T\text{-}X)_p$ sections (fig. 3). Figure 3a is a section at a pressure above the maximum on the critical curve. No gas can form, and the system is a condensed one with a T-X section like that of two nonvolatile salts. The section figure 3b is below the maximum on the critical curve, but above the 3-phase pressure G+L+AB; and, hence, shows an isolated gas-liquid region with two critical points. If a composition near AB is cooled from a very high temperature its cooling path crosses this region of G+L, and the amount of liquid first increases, then decreases until when the lower boundary of the G+L region is crossed it then all changes to gas. In the next section, figure 3c, the pressure is below the maximum on the 3-phase curve G+L+AB, but above the maximum on the 3-phase curve G+L+B. The last section is above the critical temperature of A, so that the G+L region cannot extend to the A axis, but below the maximum on both the curves G+L+AB. On cooling a mixture between the eutectic AB+B and the side B, first the 3-phase curve G+L+B is met, then the gas condenses and the region L+B is entered. Then the "second boiling point" is met, the liquid evaporates and the mixture enters the region G+B. Comparison with figure 1 shows the curve G+L+B cut in two places by a line of constant temperature, giving the first and second boiling points; the first is reached on heating, the second on cooling. On further cooling the mixture passes into the region AB+B.

Section $(T\text{-}X)_P$



P > max. on critical

P < critical curve
P < max. on G+L+AB
P > max. G+L+B

P < max. on critical
P > max. on G+L+AB

$P > A_c$
P < max. on G+L+AB and G+L+B

Figure 3.--Sections at constant pressure through the solid P-T-X model, $(T\text{-}X)_P$ sections. Figure 3a is the pressure above the maximum on the critical curve. Figure 3b is the pressure above the maximum on the 3-phase curve G+L+AB, but below the maximum on the critical curve. Figure 3c is the pressure greater than the maximum on the 3-phase curve G+L+B, but less than the maximum on the curve G+L+AB. Figure 3d is the pressure greater than the critical pressure of A, but less than the maxima on the 3-phase curves G+L+AB and G+L+B.

One mixture containing a little more A than the eutectic AB+B after condensing on the 3-phase curve enters the region G+L, then the region G+B, and then a region of unsaturated liquid, shown by a triangle in figure 3d. This region is that in figure 1 between the curves G+L+B and G+L+AB below the minimum melting point of AB. If the mixture contained a little more A than the compound AB the phase sequence on cooling at this pressure would be G → G+B → G+L → G+AB → L+AB → A+AB.

The preceding discussion has dealt with the P-T-X relations in a binary system in which the critical temperature of one component is below both the congruent melting point of a binary compound and the melting point of the second component, and the solubility curve does not intersect the critical curve. In systems such as CO_2-CaO, however, the critical curve is intersected by the solubility curve. Alkali and alkaline earth carbonates all form systems with CO_2 on which the critical curve is intersected by the solubility curve. Büchner (1906) found that both $CaCO_3$ and Na_2CO_3 have so little solubility in liquid CO_2 that no increase of the critical temperature of liquid CO_2 could be detected. There are many possibilities in systems of this type, including the formation of second layer high pressures. Figure 4 shows the projections of the solid P-T-X model for one case where liquid immiscibility does not take place.

The melting point and the critical point of the volatile component, A_m and A_c, are shown at low temperature in the T-X projection (fig. 4a). The short curve A_cp is a part of the critical curve, A_cB_c, which at p is intersected by the solubility curve of AB in liquid A. This solubility curve is the curve G+L+AB, shown in figure 4a as the curve e_Lp, which at p merges with a horizontal tangent with the coexisting gas curve, e_Gp. At p liquid

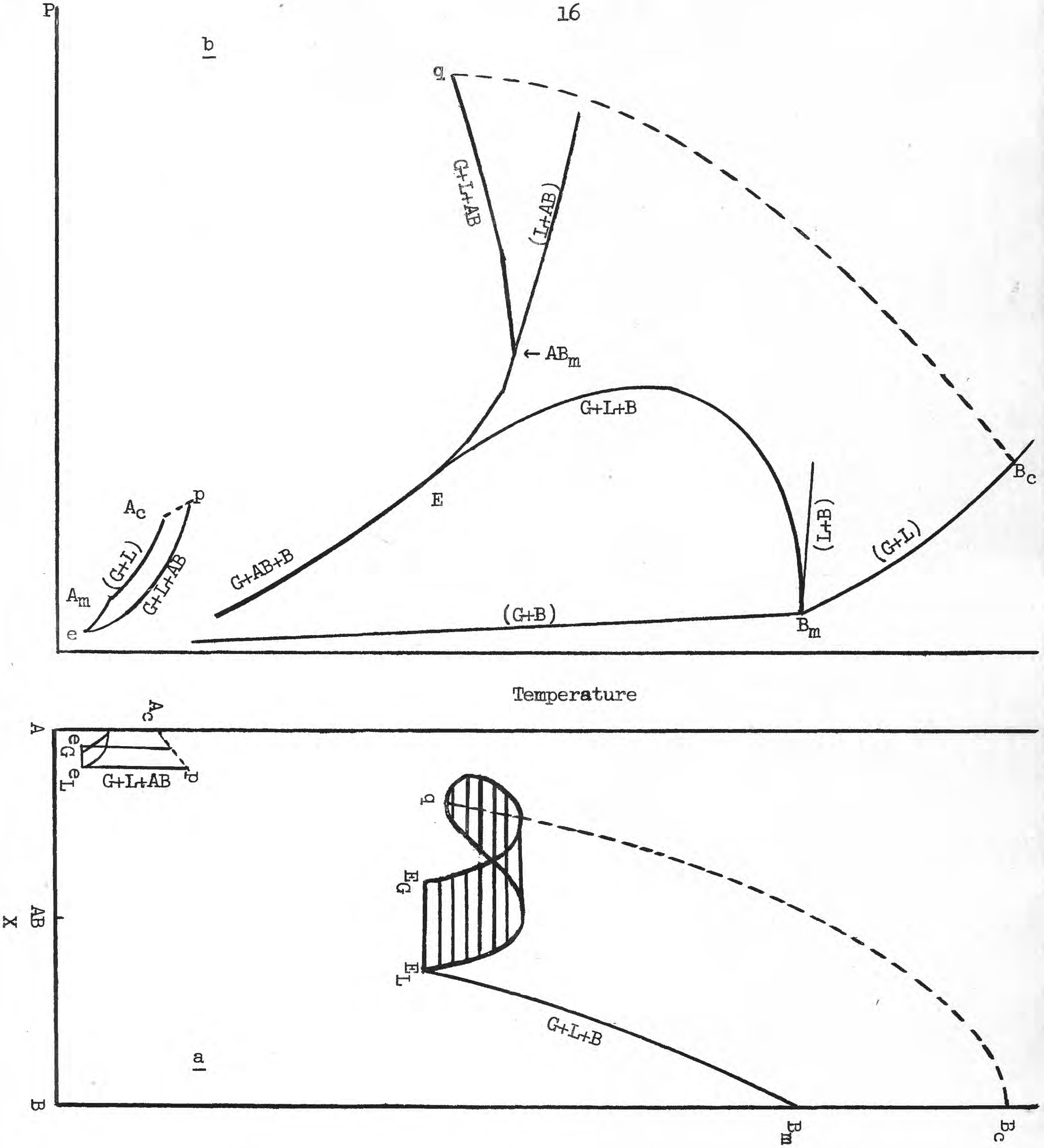


Figure 4.--Projections of a solid P-T-X model representing the relations in which a compound is formed with a congruent melting point, there is no liquid immiscibility, and the critical curve is intersected by the solubility curve, giving rise to two critical end-points. The upper critical end-point q is at a temperature above the eutectic between the compound AB and the component B, but below the minimum melting point of AB. Figure 4a is the projection on the T-X base; figure 4b on the side P-T. The curve E_Lq gives the composition of the liquids of the 3-phase curve G+L+AB; curve E_Gq the coexisting gases.

and gas become identical, giving rise to a critical end-point of the type [G=L]+S. In systems formed by CO_2 and basic oxides this curve is diagrammatic because the solubility of carbonates in liquid CO_2 is very small.

The classic study of systems of this type is ether-anthraquinone, and the T-X projection of this system is shown in figure 5. At the first critical end-point p both gas and liquid contain 0.15 percent anthraquinone. The second critical end-point is at q, and both gas and liquid contain 13 percent anthraquinone. The curve qb is part of the critical curve that ends at the critical point of anthraquinone, and the curve qd is the 3-phase curve G+L+B that ends at the melting point of anthraquinone. This 3-phase curve shows how the melting point of anthraquinone is lowered by an increasing pressure of gaseous ether until at the critical end-point q a liquid phase can no longer be obtained, no matter what the pressure of ether.

The system ether-anthraquinone is an excellent example of systems in which critical end-points are formed, and there are experimental data for the existence of both of the critical end-points p and q, and for the region between p and q in which the formation of a liquid is not possible. In figure 4b the 3-phase curve which ends at the critical end-point p is the curve G+L+AB. The curve (G+L) is the vapor-pressure curve of pure A, which ends at the critical point of A, A_c, and the curve A_cp is the section of the critical curve which is terminated by an intersection with the 3-phase curve at p.

The triple point of B is at B_m, and the curve E_LB_m gives the lowering of melting point of B with addition of AB, and the curve E_GB_m gives the composition of the coexisting gas of the univariant equilibrium G+L+B. The corresponding curve in the P-T projection is E B_m. In the P-T projection

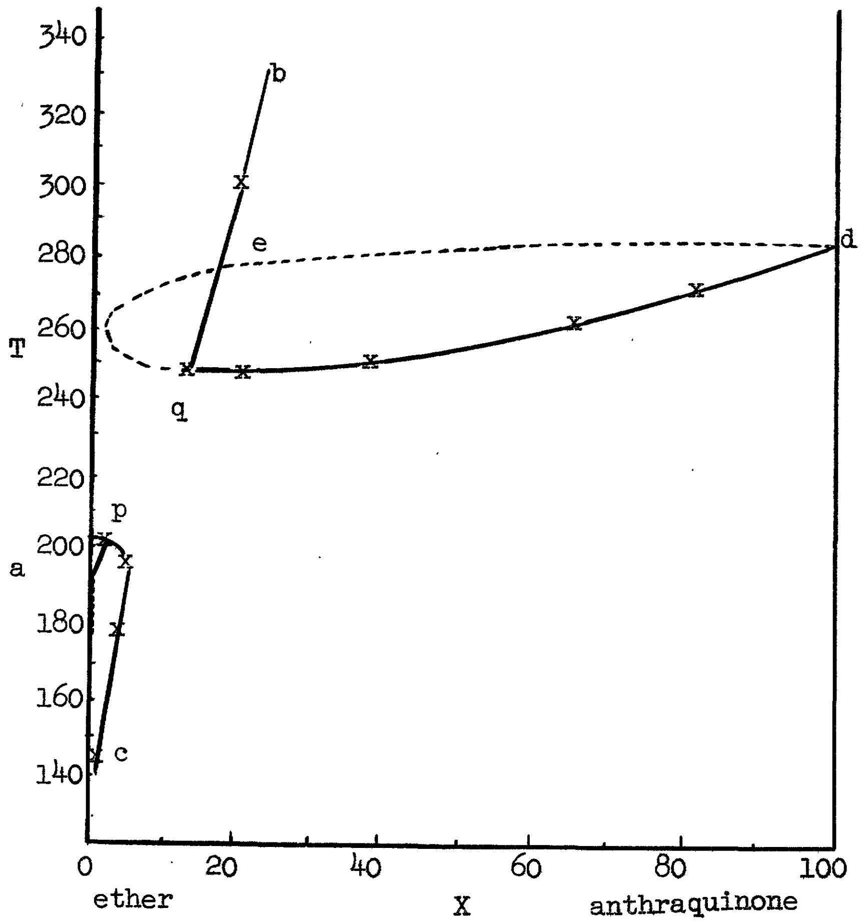


Figure 5.--The binary system ether-anthraquinone, in T-X projection. The critical end-points are p and q, qb is part of the critical curve, and qd is the 3-phase curve G+L+S. (After Smits, 1905.)

proceeding from E to lower temperatures is the dissociation pressure curve of AB, along which the reaction AB = G+B takes place.

The minimum melting point of AB is at AB_m which is not the point of maximum temperature on the 3-phase curve G+L+AB. Figure 4b also shows the curve (L+AB) which gives the change of melting point of AB with pressure. It is assumed that there is no gas phase of the composition of AB in equilibrium with AB, that is, that there is no maximum sublimation point.

It is assumed that the second critical end-point q is at a temperature below the minimum melting point of AB, but above the eutectic E. That will probably be the case with calcium carbonates. In the T-X projection are shown the coexisting gas and liquid compositions of the equilibrium G+L+AB, forming a closed curve with a horizontal tangent at q, where there is a second critical end-point of the type [G=L]+S. In the P-T projection the slope of this curve is very steep, as would be the case with the alkaline earth carbonates.

(P-X) sections through this solid model at temperatures above the second critical end-point q are adequately represented by figure 2a, b. Figure 6a, which closely resembles figure 2a, represents a section at a temperature between the critical end-point q and the minimum melting point of AB. The line 3-3 is at a pressure of the 3-phase curve G+L+B; lines 2-2 and 1-1 the two intersections of the 3-phase curves G+L+AB. At a slightly lower temperature, that of the second critical end-point, liquid becomes unstable and the (P-X) section becomes as shown in figure 6b. The assumption was made that the temperature of q was above that of the eutectic E, so that the eutectic is still stable and the part of the section richer in B than compound AB resembles figure 6a, up to the first intersection of the 3-phase curve G+L+AB at the line 2-2. But, as can be seen from figure 4, a liquid phase is

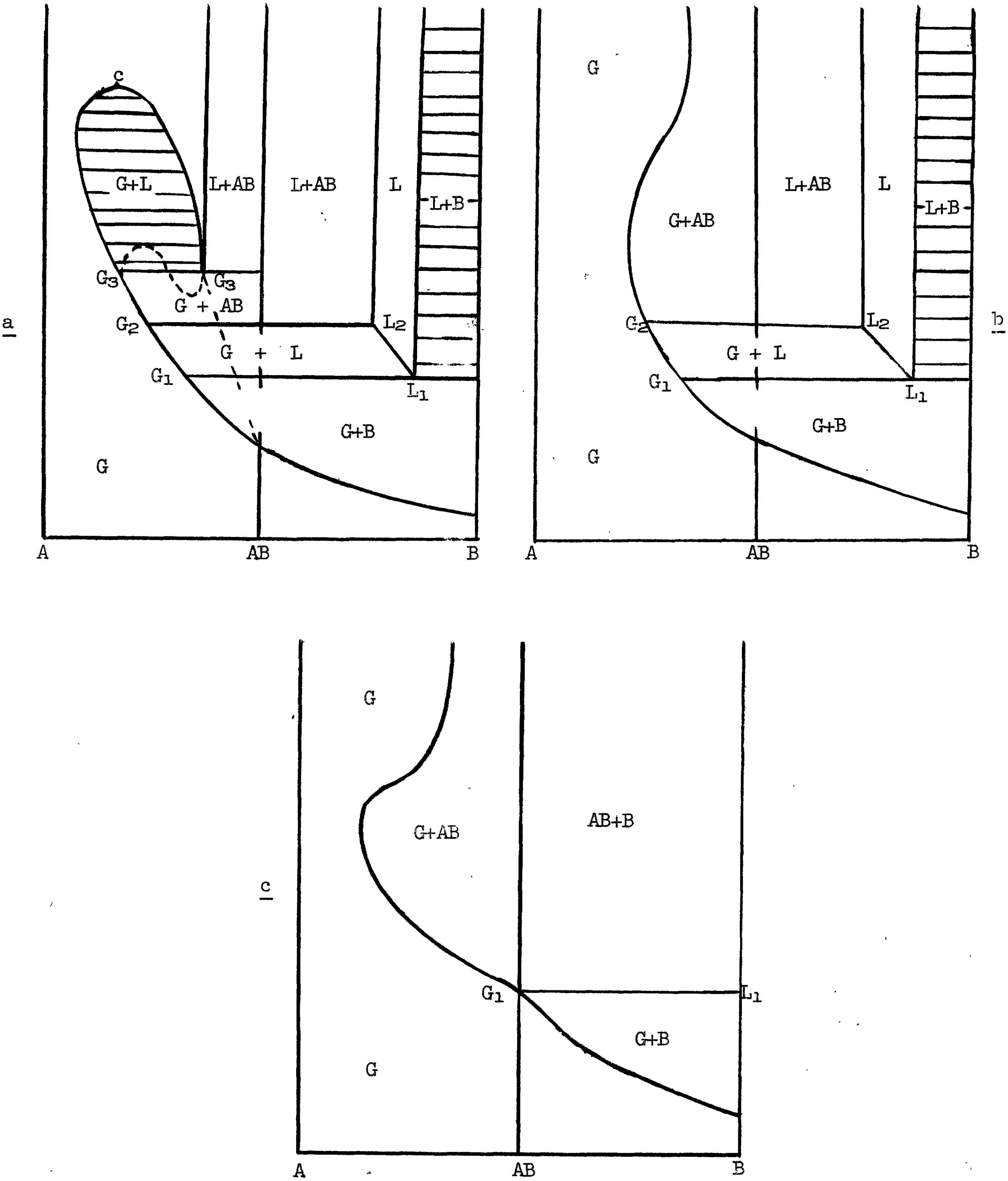


Figure 6.--Sections at constant temperature through the solid P-T-X model of figure 4. Figure 6a is at a temperature between the critical end-point q and the minimum melting point of AB. Figure 6b corresponds to the temperature of the critical end-point q, and figure 6c at a temperature below q.

not stable in the temperature region between p and q (fig. 6c), so that any mixture richer in A than AB at 2-2 passes into a region of G+AB. In this temperature region a liquid cannot be formed at any pressure.

The preceding discussion has dealt with two specific cases of systems in which a binary compound with a congruent melting point is formed, but many more possibilities exist which give rise to variations in the forms of the curves. The basic relationships remain unchanged, however, and in the lack of more information as to the specific relationships it is not possible to present any other than a highly generalized discussion.

PROPERTIES OF OXIDES

Magnesium oxide, MgO.--The melting point of MgO, the mineral periclase, is 2,800° C (Kanolt, 1914). The cubic crystals react with water to form $Mg(OH)_2$. The rate of reaction depends on the history of the sample. MgO prepared at low temperatures reacts rapidly with water, although less rapidly than CaO similarly prepared, but when prepared at high temperatures the reaction is slow, especially with large crystals. The hydration takes place more rapidly with steam under pressure. Roy, Roy, and Osborn (1953) found the dissociation pressure of $Mg(OH)_2$, the 3-phase pressure of the reaction $Mg(OH)_2 = MgO + H_2O$ to be 500 psi at 475° C, 20,000 psi at 670° C. Kelley and Anderson (1935) give for the specific heat

$$MgO{:}C_p = 10.86 + 1.197 \times 10^{-3}\ T - 2.087 \times 10^{5}\ T^{-2}.$$

Calcium oxide, CaO.--The melting point of CaO is 2,572° C (Kanolt, 1914), and it has an inversion temperature at 420° C (Sosman, Hostetter, and Merwin, 1915). Both forms are cubic. Kelley and Anderson (1935) give for the specific heat $CaO{:}C_p = 10.00 + 4.84 \times 10^{-3}\ T - 1.080 \times 10^{5}\ T^{-2}$, and CaO

reacts rapidly with water with formation of $Ca(OH)_2$. The rate of reaction is smaller with coarse crystals formed at high temperatures, and is greatly diminished by the presence of MgO resulting from the presence of dolomite.

Majumdar and Roy (1956) found the dissociation pressure of the reaction $Ca(OH)_2 = CaO + H_2O$ to increase from 150 psi (10 bars) at 536° C to 44,100 psi (2,940 bars) at 779° C. Halstead and Moore (1957) found this dissociation pressure reaches 760 mm at 512° C and the average heat of reaction over the range 300° to 510° C is 24.9 kcal/mol.

PROPERTIES OF CARBONATES

Single carbonates

Sodium carbonate, Na_2CO_3.--The melting point of Na_2CO_3 is 851° C (Kracek, 1942), and the melt dissociates on heating. Howarth and Turner (1930) found the pressure of the reaction $Na_2CO_3 = Na_2O + CO_2$ to be essentially zero at 950° C; 1.5 mm, 1,000° C; 66 mm, 1,400° C; and extrapolation gave 760 mm at 1,750° C. The dissociation is complicated by the dissociation of the Na_2O into sodium and oxygen.

In the binary system H_2O-Na_2CO_3, the solubility curve cuts the critical curve giving rise to a critical end-point (Morey and Chen, 1956). Schroeder, Berk, and Gabriel (1936) found that the solubility of Na_2CO_3 in water diminished from 27.3 percent at 150° C to 1.96 percent at 350° C. Sodium bicarbonate, $NaHCO_3$, is a compound in the ternary system CO_2-H_2O-Na_2O, and its dissociation pressure according to the reaction $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$ was found by Caven and Sand (1911) to be represented by $\log p = 11.8185 - 3340/T$. Measurements were made up to 110° C where the pressure was 1,252.6 mm.

Potassium carbonate, K_2CO_3.--The melting point of K_2CO_3 is 895° C (Kracek, 1942). Howarth and Turner (1931) found that the dissociation pressure of the reaction $K_2CO_3 = K_2O + CO_2$ first became appreciable at 950° C where it was 1.2 mm, and increased to 35.6 mm at 1,400° C. The reaction is complicated by the dissociation of the K_2O into potassium and oxygen.

Morey and Chen (1956) found that the solubility curve of K_2CO_3 in H_2O is continuous and the maximum pressure of about 210 bars is reached at about 625° C. The solubility in water is 53.8 weight percent at 25° C; 60.9 percent at 100° C; and 67.2 percent at 135° C, the highest temperature measured. Potassium bicarbonate, $KHCO_3$, dissociates according to the reaction $2KHCO_3 = K_2CO_3 + CO_2 + H_2O$, and Caven and Sand (1914) found the pressure to be represented by $\log p = 10.832 - 3420/T$. At 63.7° C the pressure was 4.7 mm; at 155.4° C, 706 mm.

Magnesium carbonate, $MgCO_3$.--Harker and Tuttle (1955) measured the pressure of the reaction $MgCO_3 = MgO + CO_2$, and the following values were taken from their curve: 743° C, 10,000 psi; 777° C, 15,000 psi; 808° C, 20,000 psi; 843° C, 30,000 psi; and 890° C, 40,000 psi. Kelley and Anderson, (1935) give for the specific heat of $MgCO_3$:

$$MgCO_3 : C_p = 10.25 + 27.54 \times 10^{-3}\ T - 0.32 \times 10^{5}\ T^{-2}.$$

The melting point has not been determined, and it is not known whether or not it melts congruently, like $CaCO_3$, or incongruently. If the melting is incongruent, the reaction $MgCO_3 = MgO + CO_2$ takes place at a composition richer in CO_2 than dolomite, there is no eutectic, and the dissociation pressure curve ends at this incongruent melting point. It is a quadruple point, and the sequence of P-T curves around the invariant point will be (L) (B) (G) (AB), instead of (L) (G) (B) (AB) as in figures 1 and 4.

Calcium carbonate, $CaCO_3$.--The congruent melting point is at about 1,339° C and 1,039 bars CO_2 pressure (this $CaCO_3$ contained 0.38 percent CaO). The eutectic between $CaCO_3$ and CaO is at 1,240° C and 40.2 bars (Smyth and Adams, 1923). The dissociation pressure curve, which ends at this eutectic, $CaCO_3 = CaO + CO_2$, is represented by $\log p = -11355/T - 5.388 \log T + 29.119$, in which p is given in millimeters of mercury (1 bar = 7.5×10^2 mm). Harker and Tuttle (1955) got values for the dissociation pressure lower than those of Smyth and Adams, but they did not follow the curve up to the melting point of $CaCO_3$. Paterson (1958) found that calcite will melt around 900° to 1,000° C at a total pressure of water and carbon dioxide of 50 bars; the proportion of the two gases was not known.

Strontium carbonate, $SrCO_3$.--Boeke (1913) found the melting point of $SrCO_3$ to be 1,497° C and 66 atmospheres CO_2 pressure. Kelley and Anderson (1935) state that no high-temperature specific-heat data are available for SrO or $SrCO_3$, but a value of $C_p = -6$ does not seem unreasonable. They give for the reaction $SrCO_3 = SrO + CO_2$, $\Delta F^o = 56,590 + 13.8\ T \log T - 81.05\ T$ which gives $\log p = -1.237\ T^{-1} - 3.02 \log T + 17.2$.

Barium carbonate, $BaCO_3$.--This occurs as the mineral witherite. Boeke (1913) found that the rhombic witherite ($\gamma BaCO_3$) at 811° C inverts to a cubic form at 982° C. He found no trace of melting at 1,600° C under 60 atmospheres CO_2 pressure and extrapolated the melting point to about 1,740° C at 90 atmospheres CO_2 pressure from the binary system $CaCO_3$-$BaCO_3$.

Binary carbonate systems

Sodium carbonate-magnesium carbonate, Na_2CO_3-$MgCO_3$.--Eitel and Skaliks (1929) studied this system and found the binary compound $Na_2CO_3 \cdot MgCO_3$ which melts congruently at 677° C, and a 3-phase pressure $G+L+Na_2CO_3 \cdot MgCO_3$ 1,240 kg/cm^2 or 1,215 bars.

Potassium carbonate-magnesium carbonate, K_2CO_3-$MgCO_3$.--Eitel and Skaliks (1929) studied this system and found the binary compound $K_2CO_3 \cdot MgCO_3$. This compound which was melted under 1,200 atmospheres CO_2 pressure, normally cools to a glass but it can be crystallized by heat treatment.

Sodium carbonate-calcium carbonate, Na_2CO_3-$CaCO_3$.--Eitel and Skaliks (1929) studied the binary system Na_2CO_3-$CaCO_3$ and found the compound $Na_2CO_3 \cdot CaCO_3$ which melts at 813° C.

Magnesium carbonate-calcium carbonate, $MgCO_3$-$CaCO_3$.--This is the mineral dolomite. Harker and Tuttle (1955) found the pressure of the reaction $MgCa(CO_3)_2 = CaCO_3 + MgO + CO_2$ to be 800° C, 10,000 psi; 828° C, 15,000 psi; 852° C, 20,000 psi; 903° C, 30,000 psi; 943° C, 40,000 psi. Graf and Goldsmith (1955) studied this decomposition up to a CO_2 pressure of 20,000 psi, at which pressure they found dolomite to decompose at 857° C in excellent agreement with Harker and Tuttle. The actual decomposition reaction is not that given above because calcites in equilibrium with either MgO or dolomite contain Mg in solid solution. Dolomite has not been melted, and it is not known if it melts congruently in the binary system $MgCO_3$-$CaCO_3$, or if in the ternary system CO_2-MgO-CaO the field of MgO (periclase) spreads over the composition of dolomite.

Calcium carbonate-barium carbonate, $CaCO_3$-$BaCO_3$.--Boeke (1913) found mixed crystal formation between these two carbonates, with a minimum melting point at 1,139° C and 52.5 mol percent of $CaCO_3$, at a CO_2 pressure of 148 atmospheres.

Calcite-nepheline, $CaCO_3$-$NaAlSiO_4$.--Eitel (1922) working at a CO_2 pressure of 108 bars found that the compound $CaCO_3 \cdot 3NaAlSiO_4$, probably corresponding to pure cancrinite, was formed. It has a eutectic with $CaCO_3$ at 1,190° C and melts congruently at 1,252° C.

Calcium carbonate-calcium orthosilicate, $CaCO_3$-Ca_2SiO_4.--This system was studied by Eitel (1923) at a CO_2 pressure greater than 120 atmospheres. The mineral spurrite, $CaCO_3 \cdot 2Ca_2SiO_4$, is formed. It melts congruently at 1,380° C, and has a eutectic with $CaCO_3$ at 1,180° C and 68 percent $CaCO_3$. The conditions for the formation of tilleyite, $CaCO_3 \cdot Ca_3Si_2O_7$, and of scawtite, $2CaCO_3 \cdot 2CaO \cdot 3SiO_2$, are not known.

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