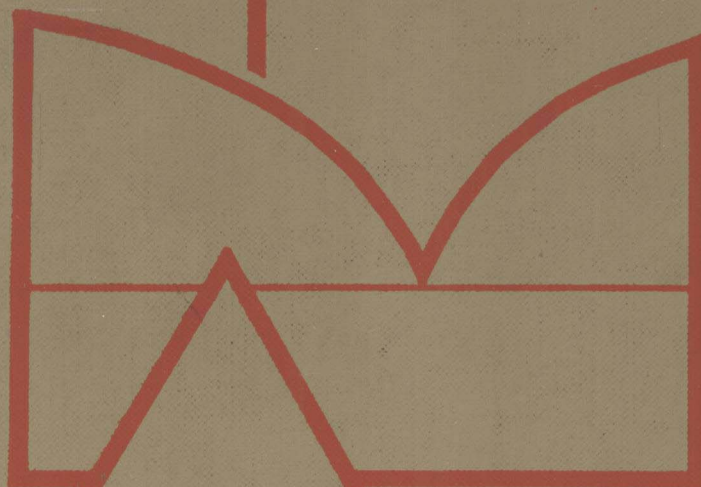


Bergeron and Risbud

Introduction to **Phase Equilibria**
in Ceramics



Introduction to Phase Equilibria in Ceramics

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It is the intent of the authors to provide a textbook which will serve the needs of an introductory course in phase equilibria designed for students in ceramic engineering and associated disciplines. A quantitative approach is taken throughout the book and the emphasis is placed on the interpretation and prediction of reactions. It has been the experience of the authors that the detailed sample problems are a necessary and important part of teaching the subject at the introductory level. Practice problems are of special benefit and consequently are included at the close of most chapters. The book is also designed to permit self-study for persons who are approaching phase equilibrium calculations for the first time, or are seeking a review.

The growing interest in computer calculations of phase diagrams and the increased awareness of the potential of nonoxide ceramics has prompted us to include brief sections on these topics. We hope that by touching on these areas we will motivate the reader to pursue the extensive and rapidly developing literature in this field, only some of which is listed in the Bibliography for this book.

A number of our colleagues at the University of Illinois contributed to this book over many years. A. I. Andrews first introduced the senior author to the subject, and A. L. Friedberg provided many fruitful discussions, shared his experiences, and made constructive comments. The manuscript in its initial form was used over a period of 10 years as the syllabus for a course in phase equilibria taught to junior-level ceramic engineering students at the University of Illinois. The experience thus gained and the helpful comments of those students guided the authors in putting together the present version.

Urbana, Illinois
February 1984

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An understanding of phase equilibria in ceramic systems is central to the utilization and development of materials in refractories, glass, and other high-temperature technologies. Phase equilibria address significant questions related to the flexibility and constraints, dictated by forces of nature, on the evolution of phase assemblages in ceramics. Phase boundaries also assist in the evaluation of the service stability of a ceramic material, both in the long and short time frames. Thus, knowledge of the stability of a ceramic or glass component in high-temperature or high-pressure environments can often be obtained from an appropriate stable or metastable phase diagram.

In the processing and manufacture of ceramic products, the reactions which occur are understood more clearly if the phase relations under equilibrium conditions are known. The chemical and physical properties of ceramic products are related to the number, composition, and distribution of the phases present. Temperature, pressure, and concentration are the principal variables which determine the kinds and amounts of the phases present under equilibrium conditions. To ceramists, who must understand the effects of these variables on both the processing and the properties of the finished product, the phase equilibrium relations (usually presented in the form of phase diagrams) provide the necessary fundamental information.

The study of phase relations is based on the assumption that the system under consideration is at equilibrium. In the development of reliable information on phase relations, this condition must be satisfied. In a practical sense, however, as in the manufacture or service of a ceramic product, circumstances may not permit a condition of equilibrium to be established. In many cases, it is known that the system is driving toward or approaching equilibrium, and knowledge of the direction in which the reaction is progressing or the direction by which it deviates from equilibrium can be of great value. In some instances involving ceramic processing, the approach to equilibrium actually may be quite close. The progress of a ceramic system toward its stable equilibrium state can often be halted for kinetic reasons, resulting in a phase assembly which can persist metastably for an extended period. The arrest of the equilibrium phases, either inadvertently or by deliberate processing, has given rise to some useful new materials in recent years. Thus, a study of stable and metastable phase equilibrium relations is particularly relevant to ceramic and glass compositions.

While most phase equilibrium diagrams have been and continue to be determined by experimental laboratory techniques, there is a growing trend toward calculation of multicomponent equilibria from thermodynamic data. The validity of many classic ceramic phase equilibrium diagrams, while not basically in doubt, continues to be questioned and revised because the experimental techniques and interpretation of data can vary from one study to another. Nevertheless, the student needs to be aware of both experimental and theoretical methods of determining phase diagrams. The principles of thermodynamics are at the core of much important phase equilibria information. It is thus appropriate for us to begin with a brief review of the definitions and principles of thermodynamics that pertain to phase relations.

The phase rule developed by J. Willard Gibbs was derived from the first and second laws of thermodynamics. If sufficient thermodynamic data were available, equilibrium relations of the phases could be calculated. Usually, such data have not been generated, but nevertheless, the understanding of the thermodynamic basis for the phase rule and the manner by which phase relations can be represented in temperature-composition-pressure diagrams is extremely helpful to ceramists.

1.1. Systems, Phases, and Components

Before proceeding with development of the concept of equilibrium between phases and a derivation of the phase rule, it will be useful to define certain terms commonly used in a treatment of phase equilibria.

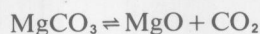
System: Any portion of the material universe which can be isolated completely and arbitrarily from the rest for consideration of the changes which may occur within it under varying conditions. Often a system may be considered as composed of smaller systems, which together make up the larger system. For example, consider the reactions between SiO_2 and Al_2O_3 . These two materials constitute a system which is called the system $\text{Al}_2\text{O}_3\text{-SiO}_2$. We could deal with smaller systems within this system, such as the system SiO_2 or the system Al_2O_3 , or even a small compositional range, and analyze its behavior with respect to variations in temperature, pressure, and composition.

Phase: Any portion including the whole of a system which is physically homogeneous within itself and bounded by a surface so that it is mechanically separable from any other portions. A separable portion need not form a continuous body as, for example, one liquid dispersed in another. A system may contain one phase or many phases. Phases are distinguished by their different physical characters. The physical character in the physical states of matter—gases, liquids, and crystals—is different. These states of matter, then, are physically distinct and represent different phases. Although gases are completely soluble (miscible) in one another and thus represent only one phase, liquids or crystals may be found to exist in several phases, each phase physically distinct from the others. Water and mercury, for example, are both liquids, each representing a different phase. Crystalline silica, SiO_2 , may exist in several crystalline configurations, each consisting of a different phase. As exemplified by solutions, either liquid or crystalline, the homogeneous character of the phase is not confined to a rigid chemical composition, since the existence of a variation in chemical composition of liquid or crystalline phases often does not alter the homogeneous character nor cause any abrupt or distinctive change in the physical structure of the phase. As phases are considered to be distinguished mainly by their physical character, such physical characteristics as density, X-ray diffraction behavior, or optical properties are used to aid in the identification and distinction of phases in a system.

A system composed of only one phase is described as a homogeneous system. A system composed of two or more phases is termed a heterogeneous system.

Components: The components of a system are the smallest number of independently variable chemical constituents necessary and sufficient to express the composition of each phase present in any state of equilibrium. In the alumina-silica system, Al_2O_3 and SiO_2 are the components of the system, since all phases and reactions can be described by using only these two materials. Al, Si, and O would not be the components for they are not the *least*

number of chemical substances by which the system can be quantitatively expressed. Consider the reaction:



At equilibrium, all three chemical constituents are present, but they are not all components because they are not all independently variable. Choosing any two of the three phases fixes the composition of the remaining phase.

In selecting the components of this system, it is helpful to arrange the information in tabular form (as shown in Table 1.1) where the composition of each phase is expressed in terms of positive, negative, or zero quantities of the chemical constituents chosen as components.

Table 1.1. Chemical Composition of System $\text{MgCO}_3 \rightleftharpoons \text{MgO} + \text{CO}_2$

Phase	Composition of phase in terms of chemical constituents		
	MgCO_3 and MgO	MgO and CO_2	MgCO_3 and CO_2
MgCO_3	$\text{MgCO}_3 + 0 \text{ MgO}$	$\text{MgO} + \text{CO}_2$	$\text{MgCO}_3 + 0 \text{ CO}_2$
MgO	$0 \text{ MgCO}_3 + \text{MgO}$	$\text{MgO} + 0 \text{ CO}_2$	$\text{MgCO}_3 - \text{CO}_2$
CO_2	$\text{MgCO}_3 - \text{MgO}$	$0 \text{ MgO} + \text{CO}_2$	$0 \text{ MgCO}_3 + \text{CO}_2$

Table 1.1 shows that any two of the chemical constituents could be selected as the components of the system because each selection resulted in a suitable expression for the composition of each phase present at equilibrium. Note, however, that only one of the selections MgO and CO_2 resulted in an expression involving positive quantities only. In selecting the components of a system, it is preferable to use only positive quantities.

Variance (or degrees of freedom): The number of intensive variables, such as temperature, pressure, and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined. A system is described as invariant, monovariant, bivariant, etc. according to whether it possesses, respectively, zero, one, two, etc. degrees of freedom.

1.2. Equilibrium

Equilibrium in a system represents a condition in which: (1) the properties of a system do not change with the passage of time, and (2) the same state can be obtained by approaching this condition in more than one manner with respect to the variables of the system.

From a practical point of view, this is an adequate definition. It is somewhat lacking in precision, however, because we have set no limits to the term "time." A small change in properties which is discernible only after many years would indicate that the system is still approaching equilibrium. The approach may be so slow as to be beyond our capability to readily detect a change in some property of the system and, thus, we are led to assume that the system is at equilibrium.

A more precise definition is the thermodynamic definition which states that a system at equilibrium has a minimum free energy. The free energy of a system is the energy available for doing work and is defined by the following relationship:

$$G = E + PV - TS \quad (1.1)$$

where G = Gibbs free energy, E = the internal energy, P = the pressure on the system, V = the volume of the system, T = the absolute temperature, and S = the entropy of the system.

The internal energy, E , of a system represents the total energy of the system, that is, the total of the kinetic and potential energies of all the atoms or molecules in the system. It is not a quantity which can be measured; we

can, however, measure differences in internal energy when a system undergoes a change:

$$\Delta E = E_2 - E_1 = q - w \quad (1.2)$$

where E_2 and E_1 represent the final and initial states of the system, respectively, q is the heat added to the system, and w is the work done on the system.

If a reaction is carried out in a constant-volume calorimeter so that no pressure-volume work is done by the system, then the amount of heat liberated or absorbed by the reaction is a measure of the change in internal energy, ΔE .

If, however, the same reaction is carried out in a constant-pressure calorimeter, the pressure-volume work must be considered:

$$\Delta E = E_2 - E_1 = q - W = q - P(V_2 - V_1)$$

Rearranging terms,

$$E_2 - E_1 = q - PV_2 + PV_1$$

$$q = (E_2 + PV_2) - (E_1 + PV_1)$$

The term $(E + PV)$ is defined as the heat content or enthalpy, H , and is equal to the heat absorbed at constant pressure. H and E are useful terms because they have characteristic and definite values for any system at any definite state of pressure, temperature, and aggregation.

Absolute values of H and E are not known, and consequently, it is necessary to select some arbitrary zero point for these quantities. By convention, the heat contents of elements in their standard states (liquid, solid, gas) at 25°C and 1 atm of pressure are set equal to zero.

In practice, we deal with changes in heat content, ΔH , or changes in internal energy, ΔE . For any change, such as a chemical reaction, the change in heat content is called the heat of reaction and is determined by the difference in heat contents between the products and the reactants.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \quad (1.3)$$

If ΔH is positive, heat is absorbed during the reaction and the reaction is called endothermic. If ΔH is negative, heat is evolved during the reaction and the reaction is called exothermic.

To raise the temperature of a material, a certain amount of heat must be added. By definition, the heat required to raise the temperature of a given amount of material 1°C is the heat capacity. The units chosen are usually calories per mole per degree. If the heat capacity has been determined at constant volume, the term c_v is used. The heat capacity increases with temperature; the relationship can be expressed by an equation of the form

$$c_p = a + bT + cT^2 + dT^3 \quad (1.4)$$

where a , b , c , and d are constants.

If the temperature dependency of the heat capacity is known, the change in heat content which occurs during the heating of a given material can be calculated from the following expression:

$$\Delta H = H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} c_p dT \quad (1.5)$$

Most ceramic reactions are carried out at atmospheric pressure; consequently, the enthalpy changes are more conveniently used in calculations than are changes in internal energy.

The entropy, S , of a system is most easily defined as a measure of the randomness or disorder of a system. A perfect crystal, free of impurities and defects, would have zero entropy at 0 K. As the temperature of the crystal is increased, its atoms absorb energy by thermal motion, some disordering oc-

Table 1.2. Phase-Composition Possibilities

Components	Phases				
	α	β	γ	δ	θ
C_1	X_1^α	X_1^β	X_1^γ	X_1^δ	X_1^θ
C_2	X_2^α	X_2^β	X_2^γ	X_2^δ	X_2^θ
C_3	X_3^α	X_3^β	X_3^γ	X_3^δ	X_3^θ
C_j	X_j^α	X_j^β	X_j^γ	X_j^δ	X_j^θ

curs, and as a consequence, the entropy of the crystal increases to a value characteristic of that temperature and degree of randomness. The entropy of the crystal at some temperature T is given by

$$dS = \frac{dq_r}{T} \quad (1.6)$$

where dq_r = the heat absorbed reversibly.

Because the energy involved in the entropy change is tied up in the random arrangement and thermal motion of the atoms, it is often referred to as unavailable energy.

All spontaneous processes occur with an increase in the entropy of the system and its surroundings; that is, the system goes to a more probable state.

The Gibbs free energy, $G = H - TS$, is a measure of the available energy. It represents the driving force for a reaction. For a reaction to occur spontaneously, the free energy change must be negative (the free energy of the system decreases). When the free energy change is zero ($\Delta G = \Delta H - T\Delta S = 0$), the system is in a state of equilibrium and no further change will occur.

1.3. The Phase Rule

Originally deduced by Gibbs and brought to general use by Roozeboom, the phase rule serves to define the conditions of equilibrium in terms of a relationship between the number of phases and the components of a system.

$$F = C - P + 2 \quad (1.7)$$

where F = the variance or degrees of freedom, C = the number of components, and P = the number of phases.

Every system possesses a certain number of independent variables to which values must be assigned in order to describe the system. Temperature, pressure, composition of phases, magnetic forces, gravitational fields, etc. are variables which may pertain to a given system. In deriving the phase rule, Gibbs considered the following variables: (1) temperature, (2) pressure, and (3) composition (of phases in terms of the components of the system).

To calculate the number of independent variables which a system at equilibrium possesses, we can make a general statement, as follows:

$$\text{Variance} = \left[\begin{array}{l} \text{Total No. of intensive} \\ \text{variables which a system} \\ \text{possesses} \end{array} \right] - \left[\begin{array}{l} \text{No. of intensive variables} \\ \text{which are fixed if the} \\ \text{system is in equilibrium} \end{array} \right] \quad (1.8)$$

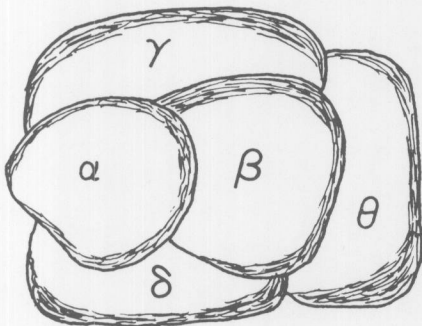


Fig. 1.1. Schematic diagram of system of five phases.

Consider a system of C components existing in P phases, as shown schematically in Fig. 1.1: To describe the composition of each phase, the amount of each component in each phase must be specified. As shown in Table 1.2, the result is represented by PC composition variables. The temperature and pressure must also be specified; thus, the total number of variables is $PC + 2$.

A convenient way to describe the composition of a phase is to use mole fractions. If a given phase contains n_1 moles of component 1, n_2 moles of component 2, and n_3 moles of component 3, the mole fraction of component

1 in the phase is

$$X_1 = \frac{n_1}{n_1 + n_2 + n_3} \quad (1.9)$$

For each phase the sum of the mole fractions equals unity:

$$X_1 + X_2 + X_3 = 1$$

If all but one mole fraction is specified, the remaining one can be determined by difference. If there are P phases, there are P equations of this type and, therefore, P mole fractions that need not be specified. The total number of variables thus becomes $PC + 2 - P$, which is the first term on the right side of the equation.

To calculate the second term, Gibbs introduced the concept of the thermodynamic or chemical potential which each component possesses. The chemical potential is an intensity term rather than a capacity term. For example, if two phases at different temperatures are brought into contact, heat will flow from the hotter phase to the cooler phase until both are at the same temperature. Each phase may have a different *amount* of heat energy, but thermal equilibrium depends only on the intensity factor, i.e., the temperature.

Similarly, mechanical equilibrium requires that the pressure of all phases be the same; otherwise, one phase will increase in volume at the expense of another until the pressures are equal.

The chemical potential of a component must be the same in all of the phases in which it appears or matter will flow from one phase to another until the chemical potentials are equal. The chemical potential of component i is given by the following expression:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_j} \quad (1.10)$$

where μ = chemical potential, n_i = number of moles of component i , n_j = number of moles of all the other components, G = Gibbs free energy, P = pressure, and T = absolute temperature.

The chemical potential is equivalent to the partial molar free energy of a component in a given phase. In Eq. (1.10) is represented the change in free energy which accompanies the addition or removal of a small increment of component i from a given phase while the temperature, pressure, and the number of moles of all the other components in the phase remain constant. Consider the two-phase system shown in Fig. 1.2. If dn_i moles of component i are transferred from phase β to phase γ while all other variables are held constant, the change in free energy of the β phase during this transfer is given by

$$dG^\beta = \mu_i^\beta dn_i \quad (1.11)$$

The change in free energy of the γ phase is given by

$$dG^\gamma = -\mu_i^\gamma dn_i \quad (1.12)$$

The total change in the free energy of this two-phase system is given by the following expression:

$$dG = dG^\beta + dG^\gamma = (\mu_i^\beta - \mu_i^\gamma) dn_i \quad (1.13)$$

If the system is at equilibrium, this transfer results in a net free energy change of zero; thus

$$dG = (\mu_i^\beta - \mu_i^\gamma) dn_i = 0$$

Therefore

$$\mu_i^\beta = \mu_i^\gamma$$

and the chemical potential of component i is the same in both phases.

At equilibrium the temperatures of all the phases are equal, their pressures are equal, and the chemical potentials of the respective components are the same between phases. If the concentration of component one in any

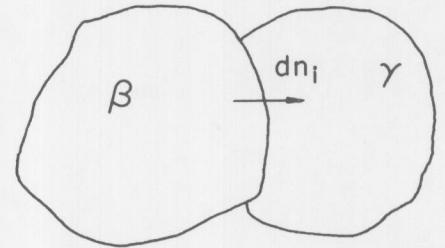


Fig. 1.2. Two-phase system showing dn_i moles of component i transforming from β to γ phase.

phase is specified, the concentration of component one in all of the other phases in which it appears becomes fixed because the chemical potential of the component is the same in each phase. (The concentration of component one is not necessarily the same in each phase, however.) Thus, for each component ($P - 1$), variables are fixed, and since there is a total of C components, the total number of variables which are fixed is $(P - 1)C$. Substituting into Eq. (1.8), we derive Eq. (1.14), which is a statement of the phase rule:

$$F = (PC + 2 - P) - (P - 1)C$$

$$F = PC + 2 - P - PC + C$$

$$F = C - P + 2 \quad (1.14)$$

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Phase equilibrium relations have been studied for many one-, two-, three-, and multicomponent systems of ceramic materials. For a one-component system, $C=1$, the statement of the phase rule is as follows:

$$F = 1 - P + 2$$

$$F = 3 - P$$

In a one-component system, a phase experiences two degrees of freedom: $F = 3 - 1 = 2$. The two variables which must be specified to define the system are temperature and pressure. Chemical composition is not a variable, since only one component is being considered. Where two phases ($P=2$) coexist in a one-component system, there is one degree of freedom, $F = 3 - 2 = 1$. Where three phases ($P=3$) coexist in a one-component system, the degrees of freedom equal zero, $F = 3 - 3 = 0$, as is the case for point *I* in Fig. 2.1, which shows a hypothetical one-component system. At point *I*, three phases (vapor, liquid, and crystals) coexist under equilibrium conditions. Point *I* is called an invariant point, for there are no degrees of freedom at this point. Point *I* is also called a triple point, since three phases coexist at this point.

On the boundary lines, *IA*, *IB*, and *IC*, two phases are in equilibrium, and any point on these lines has one degree of freedom. The one degree of freedom on the boundary line indicates that pressure and temperature are dependent on each other and the specification of one of these variables will automatically fix the other variable. Where only one phase exists (an area), pressure and temperature may be varied independently of each other. Thus, in one-component systems, the degree of freedom may be zero, one, or two.

To summarize: three phases coexisting, $F = 3 - 3 = 0$, an invariant point; two phases coexisting, $F = 3 - 2 = 1$, univariant equilibrium (boundary lines); one phase, $F = 3 - 1 = 2$, bivariant equilibrium (areas).

The line *AI* is called the sublimation curve. It represents the conditions of temperature and pressure under which solid and vapor can coexist. The upper end of the sublimation curve is at the triple point, where solid, liquid, and vapor coexist. The curve *IC* is called the vaporization curve and represents the temperature–pressure conditions under which liquid and vapor can coexist. In the absence of supercooling, its lower terminus is the triple point. Its upper terminus is the critical point (the temperature above which the gas cannot be liquefied, no matter how great the pressure).

The curve *IB* is the fusion curve or melting point curve. It represents the line at which solid and liquid are in equilibrium under varied conditions of temperature and pressure. Line *IB* may be considered as the change in melting point of the solid phase with change in pressure. Increased pressure causes an increase in this melting point. The slope of line *IB* also indicates the relative density between the crystals and the liquid. A solid is generally more dense than its liquid. This is so in Fig. 2.1, where the liquid–crystal boundary line, *IB*, slopes with increasing pressure toward the right. Increase in pressure increases density, and from Fig. 2.1 it may be noted that an increase in pressure alone (temperature constant) can cause the liquid to change to its more dense crystalline phase.

2.1. Le Chatelier's Principle

In a qualitative way, one can predict the effect of changes on the equilibrium of a system by means of the principle of Le Chatelier, as follows: “If an attempt is made to change the pressure, temperature, or concentration

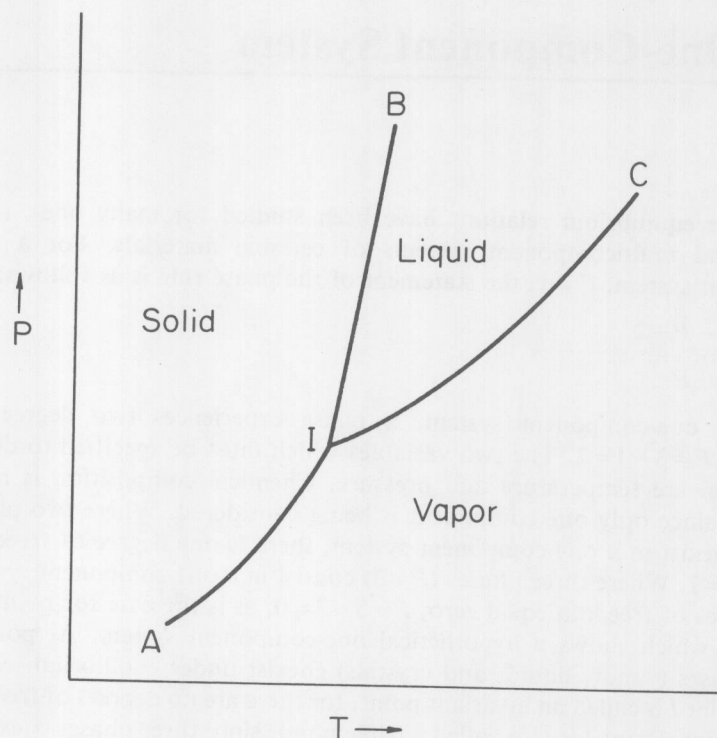


Fig. 2.1. Hypothetical one-component system.

of a system in equilibrium, then the equilibrium will shift in such a manner as to diminish the magnitude of the alteration in the factor which is varied."

In the example cited previously (solid and liquid in equilibrium), if the volume of the system were held constant and heat were added to the system, the expected result would be an increase in the temperature of the system. According to the Le Chatelier principle, that reaction will occur which tends to diminish the magnitude of the temperature rise. In this case, more of the solid would melt because melting absorbs heat (endothermic). The greater specific volume of the melt would cause an increase in the pressure of the system, and the equilibrium between solid and liquid would thus shift to a position of higher pressure and temperature (toward *B* on curve *IB* of Fig. 2.1).

If the heat content of the solid-liquid system were held constant and the pressure were decreased, a reaction would occur which would tend to diminish the effect of the pressure decrease; that is, the volume would increase. More of the solid would melt, because melting is accompanied by an increase in volume. The heat absorbed by melting causes the temperature of the system to decrease. Thus, the equilibrium between solid and liquid would shift to a position of lower temperature and pressure (toward point *I* on curve *IB* of Fig. 2.1).

Similar examples can be worked out for solid-vapor and for liquid-vapor systems at equilibrium.

A quantitative expression of the principle of Le Chatelier is given by the Clausius-Clapeyron equation which can be related to the slopes of the lines in the pressure-temperature diagram.

$$dP/dT = \Delta H / T \Delta V \quad (2.1)$$

where *P* = pressure on the system, *T* = the absolute temperature, ΔH = the enthalpy change accompanying the phase change, i.e., solid to liquid, liquid to vapor, etc., usually given in calories per mole, and ΔV = the change in specific volume accompanying the phase change, usually given in cubic centimeters per mole.

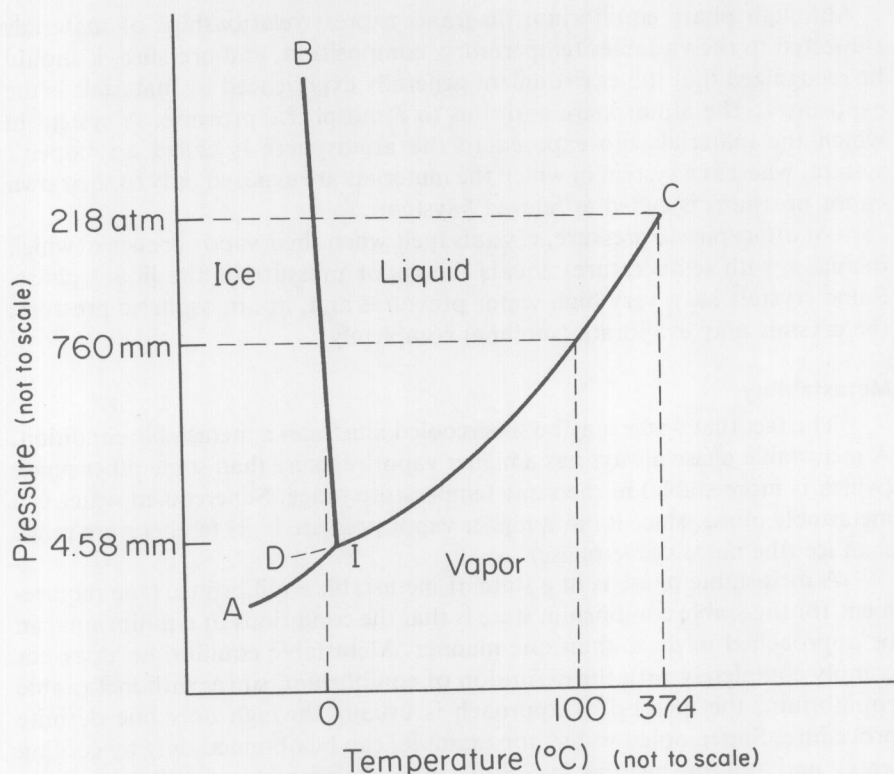


Fig. 2.2. Schematic diagram of part of the water system.

The slopes of the boundary lines are usually positive because, in going from a low to a higher temperature, the enthalpy change is positive and the volume change is most often positive. There are several exceptions involving solid-liquid transformation in which the change in specific volume on heating is not positive and consequently the slopes of the melting point curves are negative. The substances water, bismuth, and antimony exhibit such behavior.

2.2. The Water System

A good example for the discussion of the one-component system is the water system. Such a common material as water is well known, and its different phases, water (the liquid form), ice (the crystalline form), and water vapor (the gaseous form), are very familiar to us at atmospheric pressure. Figure 2.2 shows a schematic diagram of part of the water system. The change at atmospheric pressure on heating ice crystals is noted on the constant pressure (isobaric) line across the diagram. Ice changes to water at 0°C.* Water boils at 100°C.

As pressure on the system is increased, the temperature at which liquid changes to vapor is increased; thus, water boils at a lower temperature at high altitudes where pressure is lower. Decreasing pressure, while it lowers the boiling point, causes the melting point to increase. Generally, however, liquids are less dense than their crystalline form, and the melting points increase with increasing pressure.

The boundary line between liquid and vapor represents the temperature and pressure of boiling points of the liquid or the condensation points of the vapor. As pressure is increased, the boiling point is increased, as is indicated by the line *IC* in Fig. 2.2. Liquid and vapor are in equilibrium on this line. At point *C*, called the critical point, the distinction of the two phases is lost; the vapor and liquid have become homogeneous under such high temperatures and pressures. This critical temperature for water is 374.0°C at a critical pressure of 217.7 atm.

*In a closed system and with pure water (i.e., water containing no air in solution), the freezing point of water is actually 0.0099°C at a pressure of 760 mm.