

## CHAPTER 1

### CHEMICAL EQUILIBRIUM

#### 1.1 The Definition of Chemical Equilibrium

In any discussion of scientific principles there must be no doubt as to the meaning and usage of the terms employed. This is particularly important for chemical equilibrium, a concept which is too frequently treated by intuition rather than logic. Every equilibrium has to do with a *process*. In *chemical* equilibria the processes involved are changes in chemical composition or in physical state or in both; the materials which can undergo these changes constitute the *system*. Furthermore these processes must be *reversible*. An example of a reversible process is afforded by a system consisting of nitrogen, hydrogen, and ammonia.

It is a well-known fact that gaseous nitrogen and hydrogen can react, at least partially, to form ammonia and that ammonia gas can decompose, at least partially, to form nitrogen and hydrogen, according to the stoichiometric relation  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ . Although a gaseous solution of nitrogen, hydrogen, and ammonia may be homogeneous, its properties may change progressively with time.<sup>1</sup> Some of the nitrogen and hydrogen may react to form ammonia, or the reverse process may occur, but in either event the rate of the reaction will steadily decrease and eventually vanish, as far as any laboratory experiments of reasonable duration can show. There is no assurance, however, that a great lapse of time would show no further reaction and hence there is no assurance that equilibrium with respect to this process has been reached.

An unambiguous test for equilibrium can be made by *changing the conditions* slightly. If a small increase in the *temperature* of the system results in the formation of a little more nitrogen and hydrogen, and a small decrease in the temperature of the system results in the formation of a little more ammonia, then, within the

<sup>1</sup> The presence of a catalyst may accelerate this change.

accuracy of the measurements, it can be said that the system must have been in equilibrium with respect to the process of nitrogen and hydrogen forming ammonia, and ammonia forming nitrogen and hydrogen. Similarly a small increase and decrease in the *pressure* on the system or small changes in the *proportions* of the three gases could be used as alternative criteria for equilibrium.

It should be noted that the decision as to whether or not a system is in equilibrium with respect to a certain process rests on a purely *experimental* basis and in order to show that equilibrium obtains, the state of equilibrium must be upset by changing the conditions which determine it. *A system is said to be in equilibrium with respect to a particular process if it can be shown that the process is reversible for small opposite changes of conditions.* This definition is a general one, applicable to the mechanical equilibrium of physical systems as well as to chemical equilibrium. The factors which must be taken into consideration in dealing with any specific case are (1) the process involved (always including the reverse process) and (2) the conditions affecting the equilibrium.

## 1.2 Conditions Affecting Equilibrium in Homogeneous Systems

In chemical systems the processes with respect to which there can be equilibrium are both numerous and varied, but the conditions affecting equilibrium are small in number. Only because of this fact is it possible to discuss equilibria in general terms. In the equilibrium discussed above, temperature, pressure, and composition were the variables considered as affecting equilibrium. Additional conditions would be gravitational, electrical, and magnetic fields, and radiation; these factors can all be taken into account thermodynamically. In most cases, however, these conditions are either maintained constant or are completely absent; under such circumstances they need not be considered. Although surface-to-volume ratio may be important in some heterogeneous equilibria, this effect belongs properly to the field of surface and colloid chemistry. In an elementary treatise, therefore, the only conditions given consideration are temperature, pressure, and composition. The comprehensive treatment of equilibria in chemical systems was first put on a precise basis by J. Willard Gibbs,<sup>1</sup> who showed that all chemical equilibria are controlled by the first and second laws of thermodynamics.

<sup>1</sup> *Trans. Conn. Acad. Sci.*, 3, 228 (1876).

In discussing the equilibrium among nitrogen, hydrogen, and ammonia it was pointed out that a small change of any one of the conditions resulted in a small change in the proportions of the three substances. The direction in which the reversible process will proceed depends on the direction in which the condition is changed. If no reaction were to occur when heat is added to a system, its temperature would rise. If an endothermic reaction were to occur, the temperature rise would be less. But if an exothermic reaction were to occur, more heat would be produced, which would result in further exothermic reaction until one or more of the reagents was consumed. This last possibility is contrary to all experience with systems initially in equilibrium.

The reaction between nitrogen and hydrogen to form ammonia is exothermic; the reverse process is therefore endothermic. Consequently, if heat is added to a gaseous solution of nitrogen, hydrogen, and ammonia in equilibrium, the proportion of ammonia can decrease but cannot increase. Since an increase in the temperature of the system requires the addition of heat, an increase in temperature is associated with a decrease in the proportion of ammonia. Conversely, a decrease in temperature is associated with an increase in the proportion of ammonia. It follows, therefore, that if a system is in equilibrium with respect to a process, an increase of temperature can only result in that change of proportions required by the endothermic direction of the process, while a decrease of temperature can only result in that change of proportions required by the exothermic direction of the process.

By similar reasoning it can be shown that an increase of pressure on a system at equilibrium can only result in that change of proportions required by the process which diminishes the volume of the system, while a decrease of pressure can only result in that change of proportions required by the process which leads to an increase of volume.

Likewise it can be shown that an increase in the proportion of one of the substances in a homogeneous system at equilibrium can only result in the change of proportions required by the process which diminishes the proportion of that substance. For example, an increase in the proportion of nitrogen will result in the formation of more ammonia. It is always the relative amount of a substance (proportion or concentration), rather than its absolute amount, which affects the equilibrium.

The ability to predict the direction in which changes can take

place in a system initially at equilibrium was recognized by several workers in the latter half of the nineteenth century. Robin (1879) stated the rule for changes of pressure, van't Hoff (1884) for changes of temperature, and in 1888, Le Châtelier stated the rule in general terms.

### 1.3 Heterogeneous versus Homogeneous Equilibria

*Phases* are bodies of matter differing in properties, such as chemical composition, density, refractive index, optical rotation, crystalline form, and physical state (solid, liquid, or gas). Thus homogeneous equilibria pertain to a single phase in which the properties are uniform throughout the system and the substances involved constitute a solution.

Under certain conditions ice and water can exist in equilibrium with respect to the process of ice turning into water and water turning into ice. The properties of ice obviously differ from those of water, and hence the system consists of two phases, water and ice. It may contain many lumps of ice, but since they all have the same properties, they constitute a single phase. The relative amounts of the phases have no bearing on the equilibrium. Systems consisting of more than one phase are said to be heterogeneous; equilibria involving more than one phase are thus heterogeneous equilibria.

Another example of a two-phase equilibrium is that between ice and an aqueous solution of sodium sulfate. Here the equilibrium is with respect to the process of ice dissolving in and crystallizing from the solution. There is an important difference, however, between this case and the ice-water system. While the two phases, ice and water, have the same composition, this is not true for the salt solution and ice. The consequences of this difference will be made apparent in a subsequent portion of this chapter.

### 1.4 Components versus Constituents

The composition of a substance can be expressed in terms of any set of constituents from which it can be quantitatively synthesized or into which it can be quantitatively decomposed. For example, hydrogen and oxygen are an obvious set of constituents of water or ice; hydrogen peroxide and hydrogen are a less obvious choice. Among the possible sets of constituents of sodium sulfate are so-

dium, sulfur, and oxygen; sodium, sulfur dioxide, and oxygen; sodium oxide and sulfur trioxide; sodium sulfide and oxygen. Similarly, possible sets of constituents of an aqueous sodium sulfate solution are sodium, sulfur, oxygen, and hydrogen; sodium sulfate and water; aqueous sodium hydroxide solution and aqueous sulfuric acid of suitable concentrations.

The *elementary composition*, stated in terms of the elements as constituents, is commonly used for pure substances. In describing heterogeneous systems, such as ice and sodium sulfate solution, the *phase constituents*, i.e., the mechanically mixed phases themselves, constitute a set of considerable importance. The chemist can choose any set of constituents appropriate to his particular needs.

To assess properly the conditions affecting a heterogeneous equilibrium the chemist uses a particular set of constituents, namely the set having the least number necessary to describe the composition of every phase present. The constituents in such a set are termed *components*. Ice and water have the same composition and therefore constitute a one-component system. Ice and an aqueous solution of sodium sulfate constitute a two-component system. For the heterogeneous system ice-sodium sulfate solution, a possible set of constituents is sodium, sulfur, hydrogen, and oxygen. However, in the ice phase the relative proportions of hydrogen and oxygen are always the same (in accordance with the law of reacting weights), and hence one constituent, water, is sufficient to describe the composition of this phase. Two constituents, water and sodium sulfate, are sufficient to describe the composition of the solution. The constituents sodium, sulfur, hydrogen, and oxygen are clearly not a set of components since they are four in number. Moreover, if the proportions of any pair (except the pair sodium and sulfur) are specified, the composition of the solution is established. The proportions of the two remaining constituents are known by virtue of the two relations

$$\text{Weight of sulfur} = \text{weight of sodium} \times \frac{32}{2 \times 23} \quad (a)$$

$$\begin{aligned} \text{Weight of oxygen} = \text{weight of sulfur} \times \frac{4 \times 16}{32} \\ + \text{weight of hydrogen} \times \frac{16}{2 \times 1} \quad (b) \end{aligned}$$

It should be noted that equation (b) applies to the ice phase as well as to the solution. For any set of constituents greater in number than the components there will always be interrelating stoichiometric equations of this type. The number of such relations will be equal to the difference between the number of constituents and the number of components. Thus by broader definition, applicable to homogeneous as well as heterogeneous systems, a set of components is a set of composition variables (constituents) among which there exist no interrelating equations. A gaseous solution of nitrogen, hydrogen, and ammonia in general requires three components; however, if equilibrium exists, so that the mass law serves as one relation among the three constituents, then only two components are necessary; the proportion of the third constituent is fixed by the mass law.

The number of components may be less than the number of phases. For example, sodium sulfate, steam, and an aqueous solution of sodium sulfate can coexist at the boiling point of a solution saturated with respect to sodium sulfate. In this instance the solution can be in equilibrium with steam with respect to the process of steam dissolving in and being liberated from the solution, and in equilibrium with sodium sulfate with respect to the process of sodium sulfate dissolving in and crystallizing from the solution. Although three phases are present the system is two-component.

The *number* of components is more important than the *choice* of components. At 760 mm pressure and 32.384°C the three phases, sodium sulfate, Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), and a solution (33.2% sodium sulfate, 66.8% water)<sup>1</sup> can coexist in equilibrium with respect to three processes. (These processes will be discussed at some length in Chapter 3.) Although three phases are present, two constituents are sufficient to describe their compositions. Three choices of components for this two-component system are shown in Table 1.1.

Although the composition of sodium sulfate expressed in *B* may appear artificial, it simply records the fact that 100 g of sodium sulfate can be obtained by removing 127 g of water from 227 g of Glauber's salt. Whether a substance can be made by adding various things together or by removing one substance from another

<sup>1</sup> Throughout this book percentages are to be interpreted as percentages by weight unless otherwise stated.

is unimportant. It will be found necessary in later portions of this book to use choices such as *B* or *C*.

TABLE 1.1 CHOICE OF COMPONENTS FOR A SYSTEM HAVING THE PHASE CONSTITUENTS SODIUM SULFATE, GLAUBER'S SALT, AND SATURATED SOLUTION

A. Components: Sodium Sulfate-Water		
PHASE	COMPOSITION	
	% sodium sulfate	% water
Sodium sulfate.....	100	0
Glauber's salt.....	44.1	55.9
Solution.....	33.2	66.8

B. Components: Glauber's Salt-Water		
	% Glauber's salt	% water
Sodium sulfate.....	227	-127
Glauber's salt.....	100	0
Solution.....	75.3	24.7

C. Components: Sodium Sulfate-Glauber's Salt		
	% sodium sulfate	% Glauber's salt
Sodium sulfate.....	100	0
Glauber's salt.....	0	100
Solution.....	-19.5	119.5

### 1.5 Degrees of Freedom in Heterogeneous Systems

Just as in the case of homogeneous systems, the conditions affecting equilibrium in heterogeneous systems are temperature, pressure, and the compositions of the phases.<sup>1</sup>

The properties of water are defined once the temperature and pressure are fixed, since they are single-valued functions of these variables. Liquid water can exist over a wide range of temperature and pressure, either of which can be varied independently. A system consisting of water and steam can also exist over a wide

<sup>1</sup> Phases of variable composition are of necessity solutions, since the composition of a pure substance (element or compound) is invariant.

range of temperature and pressure and yet be in equilibrium with respect to the process  $\text{water} \rightleftharpoons \text{steam}$ . Only one of these variables can be independent, however. If the temperature is arbitrarily fixed at  $25^{\circ}\text{C}$  water can exist in equilibrium with steam only at the pressure fixed by nature, 23.756 mm. If the pressure were fixed at 17.535 mm this equilibrium could obtain only at the temperature  $20^{\circ}\text{C}$ . Equilibrium is also possible between ice and water or between ice and steam, but if one of the variables (either temperature or pressure) is chosen, the other is fixed by nature. The three phases, water, steam, and ice, can coexist in equilibrium simultaneously with respect to the three processes  $\text{water} \rightleftharpoons \text{steam}$ ,  $\text{ice} \rightleftharpoons \text{water}$ , and  $\text{ice} \rightleftharpoons \text{steam}$ , but only at  $0.0098^{\circ}\text{C}$  and 4.576 mm pressure, *i.e.*, neither the temperature nor the pressure can be chosen at will.

In a one-component system composition is clearly not one of the conditions affecting equilibrium. The only variables to be considered are temperature and pressure; whether both, only one, or neither of them be independently variable depends on the number of phases involved. The independent variables are usually referred to as the degrees of freedom of the system, *i.e.*, the quantities which must be stated in order to define the system. The terms invariant, univariant, bivariant, etc., are used to indicate the number of degrees of freedom. The relation between the number of phases and the variance of a one-component system is summarized in Table 1.2.

TABLE 1.2 DEGREES OF FREEDOM IN ONE-COMPONENT SYSTEMS

Number of phases.....	1	2	3
Number of independent variables.....	2	1	0

The properties of an aqueous solution of sodium sulfate are uniquely defined only when the temperature, the pressure, and the composition of the solution are stated. As long as the solution is the only phase involved these conditions can be varied independently. Three numbers are sufficient to define the state of this system: the temperature, the pressure, and the proportion of *one* of the components. In Table 1.1 composition was expressed in terms of two percentages, but once the components are stated only one need be specified, since the two must always total 100. In general, the number of composition variables requiring speci-



fication is *one less* than the number of components. In a system having  $C$  components, composition can be expressed in terms of  $C - 1$  of the components; for once the components are stated, the proportion of the unspecified one can be obtained by subtraction.

For the two-component system consisting of ice and an aqueous solution of sodium sulfate in equilibrium, only two of the three variables, temperature, pressure, and composition, are independent. At a pressure of 1 atm the freezing point of a 3% sodium sulfate solution (97% water) is fixed by nature at  $-0.84^{\circ}\text{C}$ . Similarly, the particular solution having the freezing point  $-1.0^{\circ}\text{C}$  at 1 atm has a composition fixed by nature at 3.5% sodium sulfate (96.5% water); and if one should wish to have an equilibrium between ice and a 1.00% sodium sulfate solution (99.00% water) at  $-0.29^{\circ}\text{C}$ , it would be possible at a pressure of 1 atm, but not at 2 atm. For a two-phase equilibrium in a two-component system there are, then, only two degrees of freedom. Any two of the variables may be chosen at will,<sup>1</sup> but the value of the third is dependent on the other two; it is, in fact, a *dependent* variable in the mathematical sense.

At a pressure of 1 atm, ice, Glauber's salt, and an aqueous solution of sodium sulfate can coexist in equilibrium with respect to the process of ice dissolving in and crystallizing from the solution, as well as with respect to the process of Glauber's salt dissolving in and crystallizing from the solution. However, at 1 atm this equilibrium can obtain only when the temperature is  $-1.10^{\circ}\text{C}$  and the composition of the solution is 3.85% sodium sulfate (96.15% water). If some other pressure were chosen, equilibrium among the three phases would still be possible; the temperature and the composition of the solution would be somewhat different, but their numerical values would be determined once the pressure was chosen. In this example the pressure is the only degree of freedom. It should be clear, however, that any one of the variables (temperature, pressure, or composition of the solution) can be made the independent one; but once the independent variable has been selected, the other two become dependent. For a three-phase equilibrium in a two-component system there is, therefore, only one degree of freedom.

<sup>1</sup> It should be clear that equilibrium between any number of specified phases will be possible only over a *range* of conditions. The fact that this range is finite in no way invalidates the arguments set forth here.

In addition to the three phases, ice, Glauber's salt, and solution, which can exist in equilibrium with respect to the processes enumerated above, it is possible to have a fourth phase involved, namely water vapor. The additional processes would be water vapor dissolving in and being liberated from the solution and ice  $\rightleftharpoons$  water vapor. There would be no degrees of freedom in this four-phase equilibrium, however, since the pressure exerted by the water vapor (the common vapor pressure of the solution and the ice) would be fixed by nature. The dependence of the variance of a two-component system on the number of phases is given in Table 1.3.

TABLE 1.3 DEGREES OF FREEDOM IN TWO-COMPONENT SYSTEMS

Number of phases.....	1	2	3	4
Number of independent variables.....	3	2	1	0

It can be seen from Table 1.2 that for a one-component system the sum of the number of phases  $\mathcal{P}$  and the number of degrees of freedom  $\mathcal{F}$  is always equal to 3. For a two-component system it can be seen from Table 1.3 that  $\mathcal{P} + \mathcal{F}$  is always equal to 4. In both cases it is seen that  $\mathcal{P} + \mathcal{F} = \mathcal{C} + 2$ , an equation that has been shown to be valid for systems at equilibrium having any number of components; it is usually written in the form  $\mathcal{F} = \mathcal{C} + 2 - \mathcal{P}$ . This expression is the *phase rule*. The number 2 arises from the two variables, temperature and pressure.

While the form of the phase rule has been developed here with reference to only two systems, its applicability is perfectly general for any case of heterogeneous equilibrium. Since the phase rule has never been found to be in disagreement with experiment, it can be accepted as one of those laws of nature which, by the scientific method, are established through inductive reasoning. The first and second laws of thermodynamics have been established in the same way. Because of their comprehensive nature Gibbs was able to deduce the phase rule from them.<sup>1</sup> In the chapters that follow, the phase rule will be used as a basis for the discussion of heterogeneous equilibria in a wide variety of systems. It not only predicts the number of degrees of freedom in any given system, but also the maximum number of phases which can participate in

<sup>1</sup> A derivation is given in Appendix I.

equilibrium; since  $\mathcal{F}$  cannot be less than zero, the maximum number of phases which can participate in equilibrium will be  $\mathcal{C} + 2$ .

### EXERCISES

1. State whether or not equilibrium could exist among the phases in the following sets:

- a. Water and solid sodium chloride
- b. Solid sodium chloride and an aqueous solution of sodium chloride
- c. Solid sodium chloride and a liquid solution consisting of sodium chloride, copper sulfate, and water
- d. Water vapor and an aqueous solution of sodium chloride
- e. Water vapor and Glauber's salt
- f. Water vapor, Glauber's salt, and anhydrous sodium sulfate
- g. Glauber's salt and anhydrous sodium sulfate

For those sets in which equilibrium is possible, state the process or processes with respect to which there could be equilibrium.

2. Ammonium chloride vaporizes on being heated. State the number of components in a system consisting of solid ammonium chloride and its vapor. Would the number of components be changed by admitting ammonia gas from a cylinder? Would the number of phases be altered? Would an equilibrium still be possible?

3. At elevated temperatures calcium carbonate can exist in equilibrium with its dissociation products:  $\text{CaCO}_3(\text{solid}) \rightleftharpoons \text{CaO}(\text{solid}) + \text{CO}_2(\text{gas})$ . State the number of phases and the number of components in this system. Would the number of components be changed by admitting carbon dioxide from a cylinder? Would the number of phases be altered?

## CHAPTER 2

### ONE-COMPONENT SYSTEMS

#### 2.1 Polymorphism and Isomerism

Pure substances of the same elementary composition can be classed as polymorphs<sup>1</sup> or as isomers.<sup>2</sup> They are classed as polymorphs of one another if they give rise to the same solid, liquid, or gas by simple phase transitions. For example, there are several crystalline modifications of ice known, but all of these are convertible, one to the other, by simple phase transitions; they all give rise to the same liquid, water, and to the same vapor, steam. These various forms of ice are therefore polymorphs of the pure substance water. Solid polymorphs are distinguished by difference in crystalline form, density, refractive index, solubility, and other properties. Since all vapors and most liquids are amorphous,<sup>3</sup> the term polymorphs is not always extended to include them. No pure substance is known to exist in more than one vapor phase. A few pure substances are known to exist in more than one liquid phase; those which show some regularity of structure are referred to as "liquid crystals."

Pure substances of the same elementary composition which do not give rise to a common phase by simple phase transition are classed as isomers, *e.g.*, the structural isomers butane and isobutane, ethanol and dimethyl ether; the geometrical isomers *cis*- and *trans*-butene-2; the optical isomers *d*- and *l*-tartaric acid. This class also includes those polymeric<sup>4</sup> forms which cannot be classed as polymorphs, *e.g.*, acetylene and benzene, styrene and polystyrene, formaldehyde and trioxane. Polymerism is a special case of isomerism arising from the concept of molecular weight, a concept which plays no part in distinguishing isomers from polymorphs.

<sup>1</sup> From *polys*, many, and *morphe*, form.

<sup>2</sup> From *isos*, equal, and *meros*, parts.

<sup>3</sup> From *a*, negative, and *morphe*, form.

<sup>4</sup> From *polys*, many, and *meros*, parts.

In the case of elements the term allotropes<sup>1</sup> is applied to both polymorphs and isomers, regardless of whether one form can be turned into another by simple phase transition. The allotropes rhombic and monoclinic sulfur are polymorphic; the allotropes oxygen and ozone are not. For compounds the term "allotropes" is synonymous with "polymorphs."

The treatment of one-component systems concerns the simple phase transitions among polymorphs. The only conditions affecting equilibrium among polymorphs are temperature and pressure. These two parameters are conventionally represented as the coordinates of a diagram with mutually perpendicular axes. Such a diagram is used to present, in graphical form, information about freezing points, boiling points, vapor pressures, and transition temperatures of pure substances (elements or compounds).

## 2.2 The Freezing Point of Water

The freezing point of water is the temperature at which ice and water can exist in equilibrium with respect to the process of ice turning into water and water turning into ice. The effect of pressure on the freezing point is shown in Table 2.1. It should

TABLE 2.1 FREEZING POINTS OF WATER ( $\rightleftharpoons$  ICE I)

Pressure	Freezing point, °C
5 mm.....	+ 0.0098
760 mm.....	+ 0.0023
590 atm.....	- 5.00
1090 atm.....	-10.00
1540 atm.....	-15.00
1910 atm.....	-20.00

be noted that the freezing point of water at 1 atm is *not* zero on the centigrade scale; on this scale zero has been defined as the temperature at which ice can exist in equilibrium with water saturated with air at 1 atm pressure. The liquid is then not pure water, but a solution, and its freezing point has been found to be 0.0023° lower than that of pure water. The accuracy of most freezing-point determinations is such that the effect of dissolved air can be neglected.

It is seen from Table 2.1 that increase of pressure lowers the

<sup>1</sup> From *allos*, another, and *tropos*, condition.

freezing point of water; this is true for any liquid which *expands* on freezing. If the specific volume of the solid is *less* than that of the liquid (*e.g.*, benzene), the freezing point is raised with increase of pressure.

That the foregoing statements are correct can be made clear by considering the following cases. At  $0^{\circ}\text{C}$  and 1 atm pressure a mixture of ice and water will be at equilibrium. If this temperature is maintained constant while the pressure is increased to, say, 10 atm, the ice will all melt, in keeping with the fact that an increase in pressure on a system in equilibrium can only result in the process which leads to a decrease of volume. However, if at this new pressure the temperature is lowered, ice can be made to form again (an exothermic process) and to participate in a new equilibrium with water at the lower temperature. Clearly an increase of pressure lowers the freezing point of water. On the other hand, if the pressure on a system consisting of liquid and solid benzene in equilibrium is increased, the liquid benzene will solidify (with a consequent decrease in the volume of the system) and at this new pressure liquid can only be made to form again (an endothermic process) by increasing the temperature. Thus it is seen that the freezing point of benzene is raised by an increase in pressure.

### 2.3 Determination of Freezing (Melting) Points of Pure Substances

From the phase rule it is clear that at a specified pressure the solid and liquid forms of a pure substance (one component) can exist in equilibrium only at a definite temperature fixed by nature. Since this is true regardless of the amounts of the two phases present, it is clear that pure substances must have “sharp” freezing or melting points, *i.e.*, the temperature of the system must remain constant throughout the freezing or melting process, under equilibrium conditions. The “sharpness” of the freezing or melting temperature is frequently taken as a criterion of purity; if the temperature of a system varies continuously throughout the process of phase transition, the system is obviously not one-component.<sup>1</sup> This criterion must be applied with caution, first since

<sup>1</sup> Variation of temperature during phase transitions in two-component systems will be treated in Chapter 3.

the effect of impurities may be small, and secondly since poly-component systems of certain compositions are known to have sharp melting points. Melting points of compounds at atmospheric pressure are frequently used for purposes of identification, particularly by the organic chemist. Melting and freezing points are also widely used as fixed points in thermometry.

While in general liquids can be cooled below their freezing points (undercooled), it is a peculiarity of solids that almost without exception they cannot be heated above their melting points (superheated). For one-component systems the temperature obtained from a freezing-point determination must obviously be the same as that obtained from a melting-point determination. Freezing points are commonly determined by cooling the liquid and following the temperature of the system through its phase transition. A typical cooling curve for a pure substance is shown in Figure 2.1. Solidification starts in the undercooled liquid at  $a$ ; with the liberation of latent heat the temperature rises to  $b$ , remains constant until solidification is complete at  $c$ , and then falls. The temperature corresponding to the interval  $bc$  is the freezing point. If the system is not one-component, *i.e.*, if impurities are present, cooling will give rise to a curve such as that shown in Figure 2.2. Here the portion  $bc$  is not horizontal and hence the solidification of the main constituent is seen to occur over a "freezing range." The length of the time interval  $bc$  in both figures depends on the rate of heat removal and the latent heat of solidification. Pronounced undercooling, *e.g.*, to  $a'$ , may shorten this interval to such an extent that an accurate determination is not possible. Freezing-point determinations are difficult in the case of substances which have small latent heats of solidification or which show pronounced undercooling, or if the amount of sample is small.

In determining *melting points*, curves such as shown in Figures 2.3 and 2.4, respectively, are found for pure substances and those containing small amounts of impurities. The latter shows a "melting range." The interpretation of Figures 2.2 and 2.4 rests on the consideration of two-component systems, to be treated in Chapter 3.

If the specific latent heat of solidification is small or if the chemist has a limited amount of material for the determination, it is preferable to place the substance in a bath having a relatively high heat capacity. The bath is slowly cooled or heated and the bath

temperature noted during the phase transition. Solidification or liquefaction is usually accompanied by a marked change of such properties as volume, electrical resistance, optical transmission, etc. The choice of a property to indicate phase change will depend on the particular nature of the system. The organic chemist frequently makes use of an apparatus such as that shown in Figure 2.5. A small portion of material is placed in a thin-walled capil-

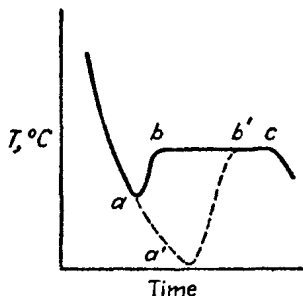


FIG. 2.1 Freezing curve for a pure substance.

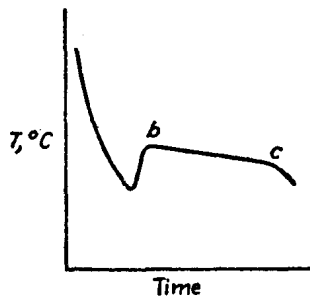


FIG. 2.2 Freezing curve for an impure substance.

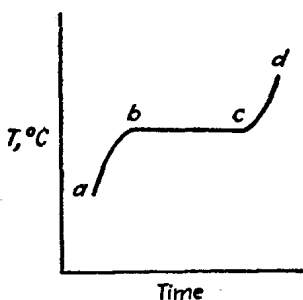


FIG. 2.3 Melting curve for a pure substance.

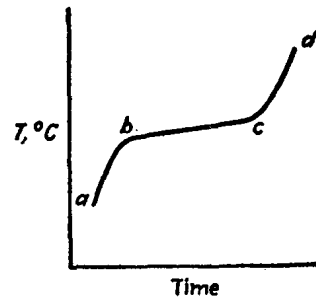


FIG. 2.4 Melting curve for an impure substance.

lary tube which is attached to a thermometer and immersed in a bath as shown. The bath is heated *slowly* and its temperature noted when melting occurs. If the bath is heated too rapidly an *apparent* melting range will be obtained even for a pure substance. Reducing the rate of heating will not diminish a *true* melting range.

## 2.4 Determination of Vapor Pressures of Pure Substances

The vapor pressure of a substance is the pressure of its vapor at which there can be equilibrium with respect to the process of



the substance vaporizing and condensing from the vapor. To ensure that equilibrium obtains, measurements can be made with an apparatus similar to that shown in Figure 2.6. The closed limb  $T$  of the manometer is first evacuated by lowering the mercury-leveling bulb  $L$  and exhausting through  $S$ . The leveling bulb is then raised to the position shown (leaving a Torricellian vacuum in  $T$ ). The pump is temporarily disconnected from  $S$  and the liquid or solid substance introduced into  $B$ . The system is

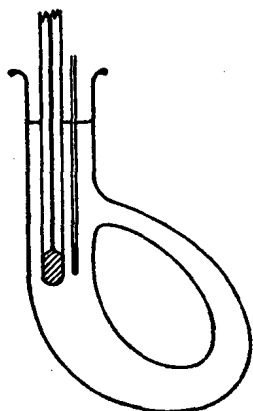


FIG. 2.5 Thiele-Dennis melting-point apparatus.

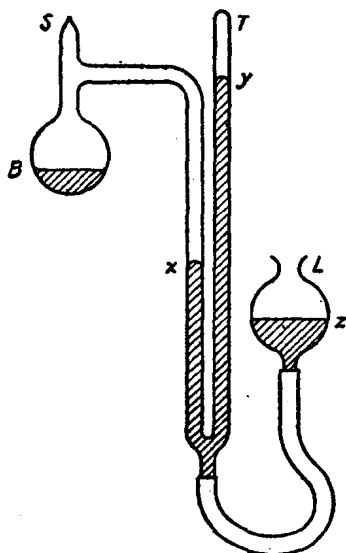


FIG. 2.6 Apparatus for determining the vapor pressure of a pure substance.

again pumped down to remove air and sealed off at  $S$ . For precise determinations it is necessary to remove all dissolved or trapped gases from the substance as well as from the manometer. The bulb  $B$  is maintained at the desired temperature; to avoid distillation the manometer must be maintained at a temperature higher than that of the bulb. The pressure of the vapor is given by the difference in levels  $y - x$ , regardless of changes in atmospheric pressure,  $y - z$ . If the substance and its vapor were in equilibrium,  $y - x$  would be its vapor pressure and should be independent of the volume of the system. On raising the leveling bulb  $L$  the volume of the system is decreased and vapor will condense;