

CHAPTER 2

UNARY SYSTEMS

Although little used as such in metallurgical work, the phase diagrams of one-component (unary¹) systems are of importance because they provide the foundation upon which the diagrams of all multicomponent systems must be built. An understanding of the concepts of one-component diagrams is, therefore, prerequisite to a full appreciation of the meaning of the more complex phase diagrams. In Fig. 1-2 a typical diagram of this class has been presented.

Of the three externally controllable factors temperature, pressure, and composition, only the first two may be varied in a one-component system, because the composition must always be unity, i.e., the pure metal constitutes 100% of the material under consideration. The two remaining variables, temperature and pressure, may be represented on a two-dimensional diagram, where it is customary to plot the temperature (abscissa) along the horizontal axis and the pressure (ordinate) along the vertical axis (Fig. 2-1). This is called a *PT*, or *pressure-temperature, diagram*. The three states or phases—solid, liquid, and gas—are represented in the three correspondingly labeled areas. Equilibrium between any two phases occurs upon the mutual boundary of the areas concerned, and equilibrium among all three phases occurs at the intersection of the three boundaries.

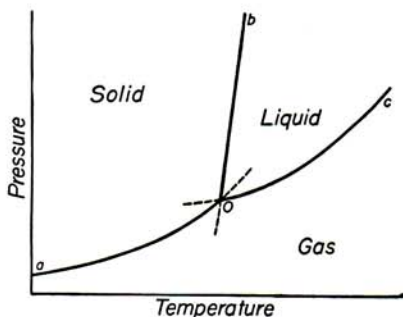


FIG. 2-1

¹ The use of Latin roots in the derivation of names for the systems of various numbers of components is preferred. This leads to the following terminology:

Unary = one component
Binary = two components
Ternary = three components
Quaternary = four components
Quinary = five components

Sexinary = six components
Septenary = seven components
Octanary = eight components
Nonary = nine components
Decinary = ten components

Invariant Equilibrium

According to the phase rule three phases may coexist at equilibrium only at a single point on the diagram, point *O* in Fig. 2-1. This is the *triple point*. It is also an *invariant*¹ *point* because there all the externally controllable factors are fixed, with definite values. If either the temperature or the pressure is caused to deviate from the stated values, one or two of the phases must disappear.

This may be seen more clearly in an example. Suppose that a sample of a pure metal, such as zinc, is confined in a chamber made of a substance toward which the metal is inert. The chamber is sealed with a tightly fitting piston by means of which the enclosed volume may be controlled. Now, if the piston is lifted to provide some vacant space around the metal sample and the whole apparatus is heated until a portion of the metal has melted but is then held at constant temperature without further introduction of heat, the pure metal will come to equilibrium with solid, liquid, and vapor all present together. A slight increase in the temperature would cause the inward flow of heat until the solid portion disappeared by melting; a decrease would cause the liquid to disappear by freezing. If, in another experiment, an attempt were made to raise the pressure by lowering the piston, it would be found that no rise in pressure could be observed until the vapor was entirely condensed, after which further lowering of the piston would result in a pressure increase. Thus, any permanent change in either the temperature or the pressure reduces the number of phases present.

In the above example, particular note should be made of the observation that no increase in the pressure occurred until the gas phase had disappeared; a partial lowering of the piston caused some of the vapor to condense, but there was no change in the number of phases present or in the pressure (or temperature) of the system. Similarly, if at constant volume enough heat had been introduced to melt a part, but not all, of

¹ Terms used to designate the number of degrees of freedom are preferably derived from Latin roots, as follows:

Invariant	= no degrees of freedom
Univariant	= one degree of freedom
Bivariant	= two degrees of freedom
Tervariant	= three degrees of freedom
Quadrivariant	= four degrees of freedom
Quinquevariant	= five degrees of freedom
Sexivariant	= six degrees of freedom
Septevariant	= seven degrees of freedom
Octavariant	= eight degrees of freedom
Nonavariant	= nine degrees of freedom
Decivariant	= ten degrees of freedom

the solid present, the temperature, pressure, and phase count would have remained constant. This serves to illustrate the important fact that the *phase rule is not concerned with the total or relative quantities of the phases present or with their related volumes and heat contents*; it is concerned only with the number of phases present and with their temperature, pressure, and composition.

Univariant Equilibrium

Equilibrium between two phases in a one-component system occurs with one degree of freedom and is called *univariant equilibrium*.

$$P + F = C + 2$$

$$2 + 1 = 1 + 2$$

This means that either the pressure or the temperature may be freely selected, but not both. Once a pressure is chosen at which two phases are to be held in equilibrium, there will be only one temperature that will satisfy the requirements, or conversely. Since it is permissible to select the pressure (or temperature) willfully, whereupon it is found that the other variable, the temperature (or pressure), has a corresponding dependent value, it is apparent that equilibria between any two phases must be represented on the one-component diagram by a line, or curve.

Three curves of univariant equilibrium issue from the triple point in Fig. 2-1 and are called *triple curves*. They represent the equilibria between the solid phase and gas (line *aO*), between liquid and gas (line *Oc*), and between the solid and liquid (line *Ob*). There are always three, and only three, triple curves issuing from each triple point, because the three phases represented at the triple point can be paired in only three ways.

The *vaporization, or liquid-gas, curve* extends from the triple point to a *critical point* at *c*. There the curve ends; at higher temperature the liquid and gas phases are indistinguishable. If a liquid partially filling a closed container is heated, the pressure will rise in accordance with the demands of line *Oc* and the vapor over the liquid will gradually become denser as the pressure increases. When the temperature and pressure of the critical point are reached, the densities of liquid and gas will be identical, the meniscus (interface between liquid and gas) will have vanished, and the gas and liquid phases will be one. The fact that this two-phase equilibrium can exist over a limited temperature and pressure range only is in no way contradictory to the exercise of a degree of freedom. The "free" choice of pressure or temperature must obviously remain within the ranges where both phases concerned are themselves stable and distinguishable.

Along the triple curve *aO* the solid and gas phases are coexistent. This

is the *sublimation curve*. It proceeds from the triple point always to lower temperature and lower pressure and may be presumed to end at the absolute zero of temperature at zero pressure. The *melting curve* O_b , along which solid and liquid are in equilibrium, has no known terminus (except in those cases where a new type of crystal appears at high pressure, when the curve ends upon another triple point representing the co-existence of liquid and two kinds of solid, Fig. 2-2). If the metal expands upon melting, this curve inclines upward to the right, in accordance with

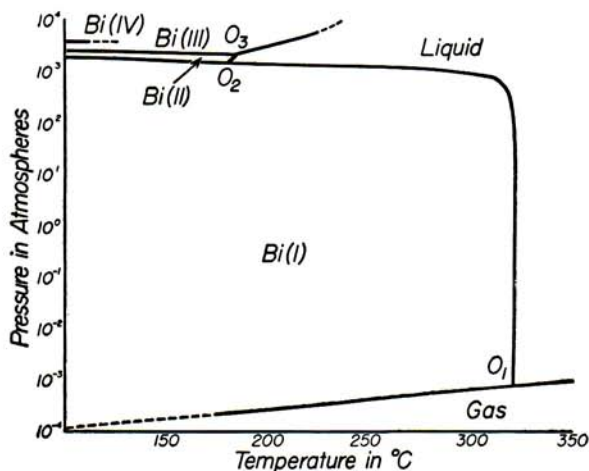


FIG. 2-2. Pressure-temperature diagram of bismuth. The abruptness with which the melting curve bends toward lower temperature at higher pressure is the result of having plotted the pressure upon a logarithmic scale. Three triple points are shown: Bi_I-L-G , $Bi_{II}-Bi_{III}-L$, and $Bi_{II}-Bi_{III}-L$. The full range of existence of the fourth solid phase Bi_{IV} has not been determined. (After P. W. Bridgman.)

the requirements of the theorem of Le Châtelier, or if the metal contracts during melting (bismuth and gallium, for example), the melting curve inclines upward to the left.

Metastable Univariant Equilibria

Each of the triple curves in Fig. 2-1 has been drawn with a dotted portion extending beyond the triple point. This construction, which is normally omitted, serves to demonstrate that the diagram has been drawn in accordance with the demands of the Clausius-Clapeyron equation. As a practical guide in drawing PT (pressure-temperature) diagrams of this kind, it is useful to remember that either the extension of each triple curve should lie within the field of the phase not represented on that triple curve or, equivalently, the angle between adjacent triple curves at their intersection with the triple point should never exceed 180° of arc.

The extensions of the triple curves do, in fact, have physical significance in certain cases. Suppose, for example, that a body of liquid, in equilibrium with its vapor, is cooled through the triple point and undercooling occurs, i.e., the solid phase fails to appear. When this happens, the vapor pressure, in equilibrium with the undercooled liquid, is that shown by the dotted extension of the liquid-gas curve Oc . The system is said to be in a state of *metastable equilibrium*. A similar metastability may exist in the event that the solid fails to melt when heated through the triple point. Here the equilibrium is represented upon the extension of the solid-gas curve. In each case the metastable portion of the curve lies at higher pressure than does the curve of stable equilibrium at the same temperature. This is a general rule, namely: *the vapor pressure of a metastable phase is, at a given temperature, always greater than that of the stable phase.*

Bivariant Equilibrium

If the temperature and pressure are each fixed arbitrarily and independently, this condition corresponds to the exercise of two degrees of freedom, *bivariant equilibrium*, and only one phase can exist in a stable state.

$$P + F = C + 2$$

$$1 + 2 = 1 + 2$$

Points on the phase diagrams designated by an independent selection of pressure and temperature values will occupy an area whereby it is seen that the areas between the triple curves in Fig. 2-1 must represent the existence of single phases.

Interpretation of the One-component Phase Diagram

A list of estimated triple points of some of the more common metals is given in Table 1. For the majority of the metals the disposition of the triple curves is such that the triple point lies far below atmospheric pressure and the critical point well above atmospheric pressure, as in Fig. 2-3, where the pressure at P_2 is considered to be 1 atmosphere.

The behavior of such a metal during heating under a constant pressure of 1 atmosphere (isobaric heating) may be predicted by following the line P_2 from left to right. At the minimum temperature (left end, point 1), the solid phase is surrounded by a gas phase exhibiting a partial pressure a of metal vapor plus a much larger partial pressure $1a$ of air, to make a total pressure of 1 atmosphere. If the system is enclosed, this equilibrium will be maintained; if open to the free passage of air, the metal vapor will

drift away and the partial pressure of the metal will be maintained only to the extent that sublimation from the metal surface can keep pace with the loss of metal vapor.¹ As the temperature is increased, the solid phase

TABLE 1. TRIPLE POINTS OF COMMON METALS (COMPUTED)

Metal	Temperature, °C	Pressure, atmospheres
Arsenic	814	36
Barium	704	0.001
Calcium	850	0.0001
Copper	1083	0.00000078
Iron (δ)	1535	0.00005
Lead	327	0.0000001
Manganese	1240	0.001
Mercury	-38.87	0.0000000013
Nickel	1455	0.0001
Platinum	1773	0.000001
Silver	960	0.0001
Strontium	770	0.0001
Zinc	419	0.05

remains unchanged, while the partial pressure of the metal vapor increases along the curve aO to that of the triple point. At nearly the same temperature the metal melts isothermally (point 2). The physical properties,

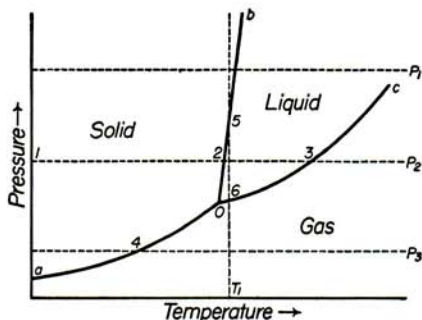


FIG. 2-3

such as density and electrical conductivity, as well as the mechanical properties suffer discontinuous change. Above the melting temperature the partial pressure of the metal vapor continues to rise, but more slowly at first, until the vaporization curve Oc intersects at atmospheric pressure (point 3). This is the boiling point; at higher temperatures only metal vapor can exist.

During cooling, the same changes occur in reverse order: condensation of gas to liquid (point 3), freezing of the liquid (point 2), and a reduction of the partial pressure of the gas phase along the corresponding triple curves.

The metal arsenic has its triple point at a pressure of 36 atmospheres.

¹ With most metals the vapor pressure is so low at room temperature as to be entirely negligible; indeed, it has been calculated that the vapor pressure of tungsten would be equivalent to one atom in the entire solar system. In a few cases, however, the pressure is significant.

In this case, 1 atmosphere of pressure lies far below the triple point, as at P_3 in Fig. 2-3. Upon heating, the partial pressure of arsenic vapor reaches 1 atmosphere at 350°C (point 4). Here, given time, the solid phase will be converted directly to gas; i.e., it will sublime. The rate of sublimation is low, however, and it is possible to heat arsenic to and above the temperature of the triple point before it has evaporated. When this is done, melting occurs near the temperature of the triple point.

Another conceivable case is that in which 1 atmosphere of pressure lies above the critical point c , as at P_1 . Here, conditions are similar to those described for the case where 1 atmosphere lay at P_2 , except that no boiling point will be observed. No examples of this kind have as yet been identified among the metals.

Changes accompanying *isothermal* (constant temperature) pressure change follow a similar pattern. Consider the case represented in Fig. 2-3, when the temperature is maintained at T_1 and the pressure is gradually reduced from its maximum value. At point 5 melting takes place. (Actually this is a very improbable event, because the slope of the melting curve is usually so slight that the liquid-solid change cannot be observed within the ordinarily attainable range of pressure.) Further decrease in pressure through point 6 would result in the ultimate vaporization of the metal. The latter condition is sometimes observed in vacuum systems.

Allotropy

Some metals are capable of existing in more than one crystalline form. The metal is then said to be *allotropic*, and the individual crystal varieties are known as *allotropes* or *allotropic modifications*. The transformation from one allotrope to another is *allotropic transformation*. This may occur either with pressure change or with temperature change. Bismuth, which exists in only one solid form at normal pressures, has been found to be capable of stable existence in at least two other crystalline forms at very high pressures (Fig. 2-2). Iron, on the other hand, passes through two allotropic transformations when it is heated from room temperature to its melting point (Fig. 2-4).

The PT diagram of an allotropic metal always has more than one triple point, because no more than three phases may be brought into simultaneous equilibrium in a one-component system. Only one of the triple points can involve both liquid and gas; all others represent equilibrium between two crystalline phases and gas, two crystalline phases and liquid, or three crystalline phases. It is noteworthy that successive triple points involving the gas phase (Fig. 2-4) must occur *at ascending temperature and pressure*. No equivalent generalization is possible in the case of triple points involving the liquid phase.

Concerning the Gas Phase in Higher-order Systems

In the treatment of binary, ternary, and higher-order systems immediately following, discussion of equilibria involving the gas phase will generally be omitted. This is done in order to avoid complications which might obscure the principal subject matter. It should be understood, however, that there is always a gas phase present, except when a liquid or solid material is enclosed within and completely fills a sealed container.

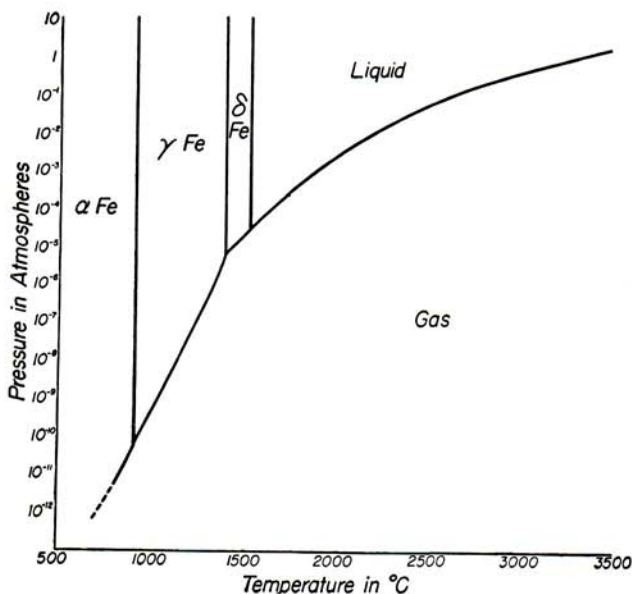


FIG. 2-4. Estimated pressure-temperature diagram of iron.

Since it is customary to handle metals in the open, where the gas phase can exist, the representation of the corresponding phase equilibria without reference to the gas phase constitutes an incomplete expression of the state of equilibrium. For most purposes this omission is inconsequential. Where it is significant, the use of diagrams involving the pressure variable is required (see Chap. 20).

PRACTICE PROBLEMS

1. Draw upon the same coordinate scale estimated PT diagrams for: arsenic, zinc, manganese, silver, lead, copper, and mercury.
2. The metal cobalt freezes at 1478°C to the face-centered cubic crystal form, which in turn transforms at 420°C to the close-packed hexagonal crystal form; its vapor pressure approximates that of its sister metals nickel and iron. Draw an estimated PT diagram for cobalt.

3. A metal is sealed in a completely inert and pressure-tight container. Initially the metal half fills the container, the balance of the space being filled with an inert gas at a pressure of 1 atmosphere. The phase diagram is similar to that given in Fig. 2-3. What changes will occur within the container as this system is heated?

4. A piece of pure iron is held in a continuously pumped vacuum of 0.000001 atmosphere and is heated, during a period of 10 min, to a temperature of 1550°C. What changes will the iron undergo? What difference in behavior should be noticed if the heating rate were reduced to one-thousandth that of the first experiment?