Chapter 4
Reversible Chemical Reactions

4.1 Introduction

In the discussion of thermal energy storage in Chap. 3, it was pointed out that energy can be stored in both the *sensible heat* that is related to changes in the temperature of materials and their heat capacities, and the *latent heat* involved in isothermal phase transitions. A common example of such an isothermal phase transition with a significant amount of stored heat is the melting and freezing of water. In such cases, there are no changes in chemical composition. The chemical species below and above the phase transition are the same. Only their physical state is different. Such reactions are said to be *congruent*.

Another type of energy storage involves reversible chemical reactions, in which there is a change in the chemical species present. In many cases, such reactions can also be reversible. An example of this would be the reaction of hydrogen and oxygen to form water, and its reverse, the decomposition of water into hydrogen and oxygen. The energy, or heat, involved in this reversible reaction is the heat of reaction, and is sometimes called *quasi-latent heat*.

As was mentioned in Chap. 3, the amounts of heat involved in latent heat reactions can be much larger than those that are involved in sensible heat. As a result they are typically used in situations in which it is desired to maintain the temperature of a system at, or near, a constant value. As will be seen in this chapter, there are a number of materials in which chemical reactions can take place that can exhibit both *enhanced sensible heat* and *quasi-latent heat*.

R.A. Huggins, *Energy Storage*, DOI 10.1007/978-3-319-21239-5_4

4.2 Types of Non-congruent Chemical Reactions

In addition to the *congruent* reactions mentioned above, there are a number of different types of *chemical reactions* in which one or more materials react to produce products with different compositions. Reactions in which the reactants and products have different compositions are *non-congruent.*

In some cases the result of the reaction is a change in the chemical composition of one or more of the phases present by the addition of another species to it, or deletion of a species from it. Such reactions are called by the general label *insertion reactions*.

There are also a number of important chemical reactions in which some phases grow or shrink, or new phases form and others disappear. The result is that the microstructure of the material gets significantly changed, or reconstituted. Such reactions, of which there are several types, are called *reconstitution reactions*.

In order to see how to make use of them for energy storage, it is important to understand the major types of *reaction mechanisms*, as well as the *driving forces* that tend to cause such reactions to occur.

4.2.1 Insertion Reactions

Changes in the chemical composition of materials can be the result of the *insertion* of guest species into normally unoccupied crystallographic sites in the crystal structure of an existing stable *host material*. The opposite can also occur, in which atoms are *deleted* from crystallographic sites within the host material.

Such reactions, in which the composition of an existing phase is changed by the incorporation of guest species, can also be thought of as a *solution* of the guest into the host material. Therefore, such processes are also sometimes called *solid solution reactions*. In the particular case of the insertion of species into materials with layer-type crystal structures, insertion reactions are sometimes called *intercalation reactions*.

Although the chemical composition of the host phase initially present can be changed substantially, this type of reaction does not result in a change in the identity, the basic crystal structure, or amounts of the phases in the microstructure.

However, in most cases the addition of interstitial species into previously unoccupied locations in the structure, or their deletion, causes a change in volume. This involves mechanical stresses, and absorbs or emits mechanical energy. The mechanical energy related to the insertion and extraction of interstitial species plays a significant role in the *hysteresis*, and thus energy loss, observed in a number of reversible battery electrode reactions.

Generally, the incorporation of such guest species occurs *topotactically*. This means that the guest species tend to be present at specific (low energy) locations inside the crystal structure of the host species.

A simple reaction of this type might be the reaction of an amount x of species A with a phase BX to produce the *solid solution* product A_xBX. This can be written as

$$xA + BX = A_xBX \tag{4.1}$$

4.2.2 Formation Reactions

A different type of reaction results in the formation of a new phase, rather than the modification of an existing one. A simple example can be the reaction of species A with species B to form a new phase AB. This is a *formation reaction*, and can be represented simply by the equation

$$A + B = AB \tag{4.2}$$

Since this modifies the microstructure, this is an example of one type of *reconstitution reaction*.

There are many examples of this type of formation reaction. There can also be subsequent additional formation reactions whereby other phases can be formed by further reaction of the products of an original reaction.

The *driving force* for the simple reaction in Eq. (4.2) is the difference in the values of the *standard Gibbs free energy of formation* of the products, only AB in this case, and the standard Gibbs free energies of formation of the reactants, A and B:

$$\Delta G_r^0 = \sum \Delta G_f^0(\text{products}) - \sum \Delta G_f^0(\text{reactants}) \tag{4.3}$$

The standard Gibbs free energy of formation of all elements is zero, so if A and B are simple elements, the value of the standard Gibbs free energy change, $\Delta G_r^{\,0}$, that results per mol of this reaction is simply the standard Gibbs free energy of formation per mol of AB, $\Delta G_f^{\,0}(AB)$. That is

$$\Delta G_r^0 = \Delta G_f^0(AB) \tag{4.4}$$

Values of the standard Gibbs free energy of formation for many materials can be found in a number of sources, for example, [1]. These values change with the temperature, due to the change in the product of the temperature and the entropy related to the reaction, as was discussed in Chap. 2.

In addition to the change in Gibbs free energy, there is a change in enthalpy, and thus the stored heat, related to such reactions. This is the difference between the enthalpies of the products and the reactants:

$$\Delta H_r^0 = \sum \Delta H_f^0(\text{products}) - \sum \Delta H_f^0(\text{reactants}) \tag{4.5}$$

Values of the enthalpy of most materials are relatively temperature-insensitive, except when phase changes take place that involve structural changes, and therefore changes in the entropy.

4.2.3 Decomposition Reactions

A number of materials can undergo *decomposition reactions* in which one phase is converted into two related phases. This is the reverse of *formation reactions*, and can be represented simply as

$$AB = A + B \tag{4.6}$$

There are two general types of these reactions. In one case, one phase decomposes into two other phases when it is cooled, and in the other, a single phase decomposes into two other phases when it is heated. There are specific names for these reactions. If a single liquid phase is converted into two solid phases upon cooling, it is called a *eutectic reaction*. On the other hand, if the high temperature single phase is also solid, rather than being a liquid, this is a *eutectoid reaction*.

In the case of a single solid phase decomposing into a solid phase and a liquid phase when it is heated, the mechanism is called a *peritectic reaction*. Likewise, if all phases are solids, what happens is called a *peritectoid reaction*.

These types of reactions will be discussed in more detail later.

4.2.4 Displacement Reactions

Another type of *reconstitution reaction* involves a *displacement* process that can be simply represented as

$$A + BX = AX + B \tag{4.7}$$

in which species A displaces species B in the simple binary phase BX, to form AX instead. A new phase, consisting of elemental B, will be formed in addition. This will tend to occur if phase AX has a greater stability, i.e., has a more negative value of $\Delta G_f{}^0$, than the phase BX. An example of this type is

$$Li + Cu_2O = Li_2O + Cu \tag{4.8}$$

in which the reaction of lithium with Cu_2O results in the formation of two new phases, Li_2O and elemental copper. In this case

$$\Delta G_r^0 = \Delta G_f^0(Li_2O) - \Delta G_f^0(Cu_2O) \tag{4.9}$$

since the standard Gibbs free energy of formation of all elements is zero.

The thermal effect of such a reaction is therefore

$$\Delta H_r^0 = \Delta H_f^0(Li_2O) - \Delta H_f^0(Cu_2O) \tag{4.10}$$

It is also possible to have a *displacement reaction* occur by the replacement of one interstitial species by another inside a stable host material. In this case, only one additional phase is formed, the material that is displaced. The term *extrusion* is sometimes used in the technical literature to describe this type of process.

In some cases, the new element or phase that is formed by such an *interstitial displacement process* is *crystalline*, whereas in other cases, it can be *amorphous*.

4.3 Phase Diagrams

Phase diagrams are *thinking tools* that are useful to help understand these various types of reactions, and associated phenomena. They are graphical representations that indicate the phases and their compositions that are present in a materials system under equilibrium conditions. They were often called *constitution diagrams* in the past. Thus it is reasonable that reactions in which there is a change in the identity or amounts of the phases present are designated as *reconstitution reactions*.

Phase diagrams are widely used in materials science and materials engineering, and are especially useful in understanding the relationships between thermal treatments, microstructures and the properties of metals, alloys, and other solids.

4.3.1 The Gibbs Phase Rule

The *Phase Rule* was proposed by J. Willard Gibbs, a physicist, chemist, and mathematician, in the 1870s. Gibbs developed much of the theoretical foundations of chemical thermodynamics and physical chemistry, and is often considered to have been one of the greatest American scientists. He introduced the concepts of chemical potential and free energy, made great contributions to statistical mechanics, and also invented vector analysis.

What is now generally called the *Gibbs phase rule* is an especially useful *thinking tool* when considering reactions within and between materials. It will appear a number of times in this text.

For present purposes it can be written as

$$F = C - P + 2 \tag{4.11}$$

in which C is the *number of components* (e.g., chemical elements), and P is the *number of phases present* in a materials system in a given experiment.

A phase is formally described as a distinct and homogeneous form of matter separated by its surface from other forms. That definition may not seem to be very useful. But consider a mixture of salt and pepper. They are different phases, for it is possible to physically separate them as black and white particles. Likewise, water and ice can be identified and separated, even though they have the same chemical composition, H_2O. Therefore, they are separate phases.

The quantity F may also be difficult to understand. It is the *number of degrees of freedom*; that means the number of *intensive thermodynamic parameters* that must be specified in order to *define the system* and *all of its associated properties*.

Intensive parameters have values that are independent of the amount of material present. For this purpose, the most useful intensive thermodynamic parameters are the temperature, the overall pressure, and either the chemical potential or the chemical composition of each of the phases present. In electrochemical systems, the electric potential can also be an important intensive parameter.

4.3.2 Binary Phase Diagrams

As mentioned earlier, *phase diagrams* are figures that graphically represent the equilibrium state of a chemical system. There are various types of phase diagrams, but in the most common case they are two-dimensional figures that indicate the temperature and compositional conditions for the stability of various phases and their compositions under equilibrium conditions.

A *binary phase diagram* is a two-dimensional plot of temperature versus the overall composition for materials (*alloys*) composed of two different components (elements). It shows the temperature-composition conditions for the stability and composition ranges of the various phases that can form in a given system, and is commonly used in materials science and engineering. It will be seen that there are temperature-composition regions in which only a single phase is stable, and regions in which two phases are stable.

A very simple binary system is shown in Fig. 4.1. In this case it is assumed that the two components (elements) A and B are completely miscible; that is, they can dissolve in each other over the complete range of composition, from pure element A to pure element B, both when they are liquids and when they are solids. Thus one can speak of a liquid solution and a solid solution in different regions of temperature-composition space. Since the elements have different melting points, the temperature above which their liquid solution is stable (called the *liquidus*) will vary with composition across the diagram. The temperature below which the material is completely solid (called the *solidus*) is also composition-dependent. At any composition there is a range of temperature between the solidus and the liquidus within which two phases are present, a liquid solution and a solid solution.

Likewise, at any temperature between the melting points of pure A and pure B, the liquid and solid phases that are in equilibrium with each other have different

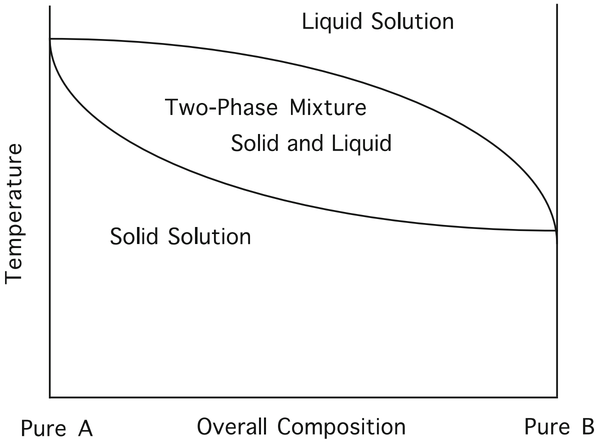

Fig. 4.1 Schematic phase diagram for a binary system with complete miscibility in both the liquid and solid phases

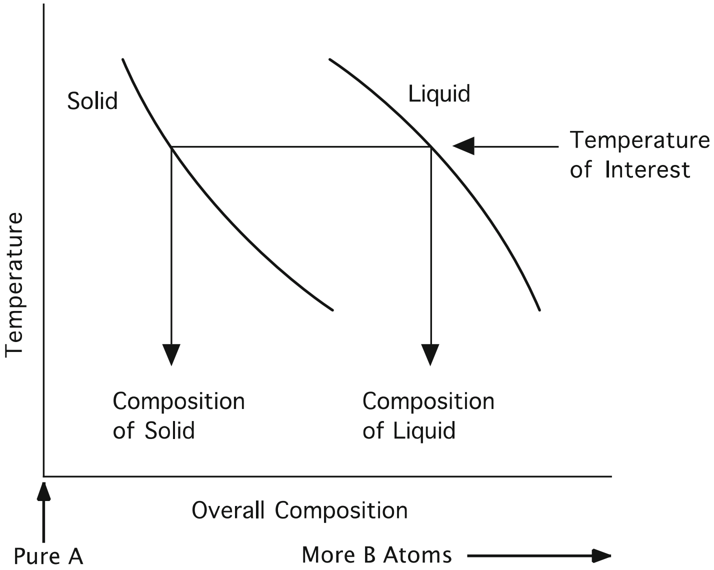

Fig. 4.2 Compositions of liquid and solid phases in equilibrium with each other at a particular temperature between the melting points of the two elements

compositions, corresponding to the compositional limits of the two-phase region in the middle part of this type of phase diagram. This is shown schematically in Fig. 4.2.

The compositions of the solid and liquid phases that are in equilibrium with each other at a particular temperature of interest can be directly read off the composition scale at the bottom of the diagram. It is also obvious that these two compositions will both be different for other temperatures, due to the slopes of the solidus and liquidus curves. At a fixed temperature, the relative amounts, but not the compositions, of the two phases depend upon the overall composition. The overall composition is, of course, not limited to the range within the two-phase mixture region of the phase diagram.

Consider an isothermal experiment, and suppose that the overall composition were to start far to the left at the temperature of interest in the case illustrated in Fig. 4.2, perhaps as far as pure A. Now if more and more atoms of element B are continually added, a solid solution of B atoms in A will be formed whose composition will gradually rise. This can continue over a relatively wide compositional range until the overall composition reaches the solidus line that signifies the one-phase/two-phase border.

Further addition of B atoms causes the overall composition to keep changing, of course. However, the composition of the solid solution can not become indefinitely B rich. Instead, when the overall composition arrives at the *solidus* line, some liquid phase begins to form. Its composition is different from that of the solid solution, being determined by the composition limit of the liquid solution at that temperature, the *liquidus* line. Thus the microstructure contains two phases with quite different local compositions, one solid, and the other liquid. Further changes in the overall composition at this temperature result in the formation of more and more of the fixed-composition liquid solution phase at the expense of the fixed-composition solid solution phase. By the time that the overall composition reaches that of the liquid solution (the liquidus line) there is no more of the solid phase left. Further addition of B atoms then causes the composition of the liquid solution to gradually become more and more B rich.

This same type of behavior also occurs if all of the phases in the relevant part of a phase diagram are solids. The same rules apply. In any two-phase region at a fixed temperature the compositions of the two end phases are constant, and variations of the overall composition are accomplished by changes in the relative amounts of the two fixed-composition phases. It is thus obvious that one-phase regions are always separated by two-phase regions in such binary (two-component) phase diagrams at a constant temperature.

It can readily be seen that this behavior is consistent with the Gibbs phase rule, $F = C - P + 2$. For a binary, 2-component system, $C = 2$. In single-phase regions, $P = 1$. Therefore, $F = 3$. This means that three intensive parameters must be specified to determine such a system, and all of its properties. Thus if the pressure is 1 atm, specification of the composition and the temperature, two more intensive variables, determines all the properties in one-phase regions of this part of the phase diagram.

On the other hand, in a two-phase region, i.e., where a mixture of a solid solution and a liquid solution are both present, $C = 2$, and $P = 2$. Therefore, $F = 2$. This means that if the pressure is fixed, for example, as one atm, only one other parameter must be specified to determine all the properties. This parameter might be the temperature, for example. As shown in Fig. 4.2, that will automatically determine the compositions of each of the two phases. Alternatively, if the composition of the solid solution were specified, that can only occur at one temperature, and with only one composition of the liquid solution.

4.3.3 The Lever Rule

The relation between the overall composition and the amounts of each of the phases present in a two-phase region of a binary phase diagram can be found by use of a simple mechanical analog, and is called the *lever rule*.

If two different masses M_1 and M_2 are hung on a bar that is supported by a fulcrum, the location of the fulcrum can be adjusted so that the bar will be in balance. This is shown in Fig. 4.3. The condition for balance is that the ratio of the lengths L_2 and L_1 is equal to the ratio of the masses M_1 and M_2. That is,

$$M_1/M_2 = L_2/L_1 \tag{4.12}$$

Analogously, the amounts of the two phases in a two-phase region can be found from the lengths L_1 and L_2 on the composition scale. The ratio of the amounts of phases 1 and 2 is related to the ratio of the deviations of their compositions L_2 and L_1 from the overall composition on the composition scale. This is illustrated in Fig. 4.4, and can be expressed as

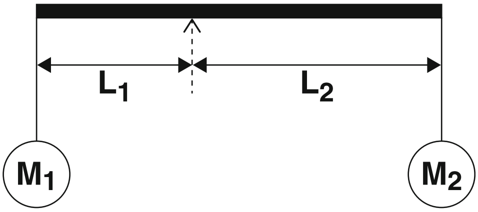

Fig. 4.3 Mechanical lever analog

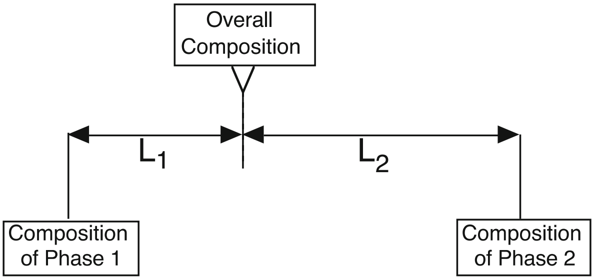

Fig. 4.4 Application of the lever rule to compositions in a two-phase region of a binary phase diagram

$$Q_1/Q_2 = L_2/L_1 \tag{4.13}$$

in which Q_1 and Q_2 represent the amounts of phases 1 and 2.

4.3.4 Three-Phase Reactions in Binary Systems

It was mentioned in Sect. 4.2.3 that a number of materials undergo decomposition reactions, i.e., peritectic, eutectic, or their all-solid analogs, peritectoid and eutectoid, reactions upon changes in the temperature. These reactions all must involve three phases, *A*, *B*, and *AB*, or more generally, α, β, and γ.

Again considering the Gibbs phase rule, in a binary system where $C = 2$, and $P = 3$, F must be 1. At a fixed pressure of one atmosphere, no more parameters can be varied. What this means is that three phases can only be in equilibrium under one set of conditions. The compositions of each of the phases present can only have a single value, and the temperature must also be fixed.

Thus when three phase reactions take place at a fixed pressure in binary systems all of the phases must be present and in equilibrium with each other at a specific temperature, and with particular compositions. Two will touch the isothermal composition line at the ends, and the third will do so at a single composition between them. Both above and below the unique peritectic temperature only one-phase and two-phase regions are possible.

In peritectic reactions one of the phases at the ends must be a liquid, whereas the other two phases are solids. This situation can be understood by consideration of the simple binary system containing a peritectic reaction shown in Fig. 4.5. In this case the terminal (end) phases on the *A* and *B* component sides of the phase diagram are labeled *α* and *β*.

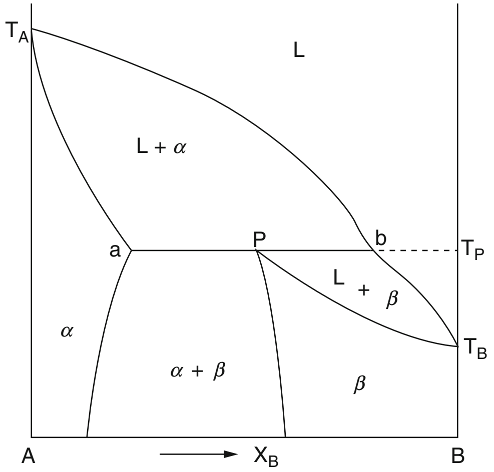

Fig. 4.5 Generalized configuration showing the isothermal arrangement of phases in a peritectic reaction

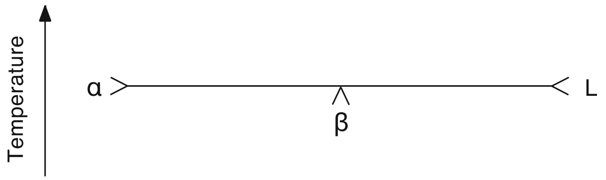

Fig. 4.6 Simple schematic representation of a peritectic reaction

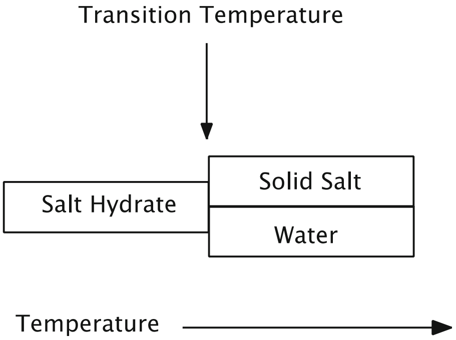

Fig. 4.7 Schematic representation of a salt hydrate decomposition reaction

The melting points of components *A* and *B* are indicated by T_A and T_B, whereas the temperature of the peritectic reaction is T_P. At this temperature phase α has a composition *a*, phase *β* has a composition *P*, and the liquid a composition *b*.

The situation at the peritectic temperature can also be represented schematically as shown in Fig. 4.6.

4.3.5 Examples of Materials Systems with Peritectic Reactions

An example of a group of materials that undergo peritectic reactions is the family of salt hydrates. Upon heating, they form two product phases, a saturated aqueous solution plus a solid salt phase, at a specific transition temperature. This type of reaction could be represented as shown in Fig. 4.7. The transition temperature is the peritectic temperature.

The phase diagram for this type of system, in which the salt forms a monohydrate, is shown in Fig. 4.8.

Some examples of materials that can undergo this type of structural change at modest temperatures are included in Table 4.1. It can be seen that they can store a rather large amount of heat per unit volume.

The properties of some salt ammoniates that also undergo congruent reactions are presented in Table 4.2.

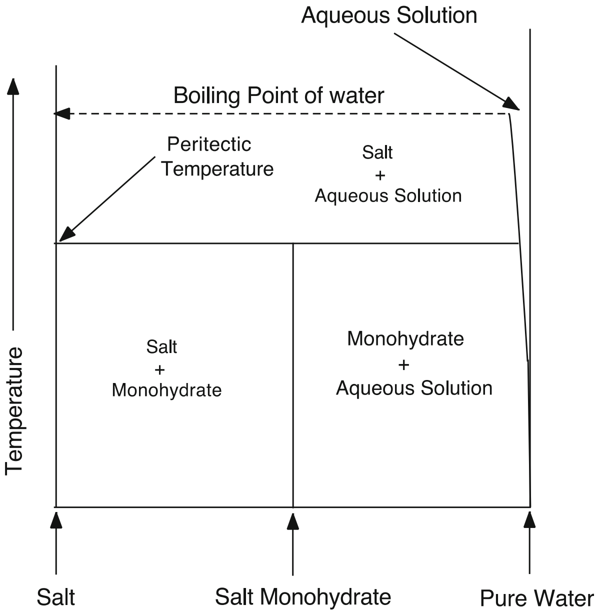

Fig. 4.8 Phase diagram of a salt-water system in which a salt monohydrate forms at low temperatures

Table 4.1 Data on several salt hydrates

Hydrate	Temperature (°C)	Heat of fusion ($kJ\ kg^{-1}$)	Latent heat density ($MJ\ m^{-3}$)
$CaCl_2 \bullet 6\ H_2O$	29	190.8	281
$Na_2SO_4 \bullet 10\ H_2O$	32		342
$Na_2CO_3 \bullet 10\ H_2O$	33		360
$CaBr_2 \bullet 6\ H_2O$	34	115.5	
$Na_2HPO_4 \bullet 12\ H_2O$	35		205
$Zn(NO_3)_2 \bullet 6\ H_2O$	36	146.9	
$Na_2HPO_4 \bullet 7\ H_2O$	48		302
$Na_2S_2O_3 \bullet 5\ H_2O$	48		346
$Ba(OH)_2 \bullet 8\ H_2O$	78	265.7	655
$Mg(NO_3)_2 \bullet 6\ H_2O$	89	162.8	162.8
$MgCl_2 \bullet 6\ H_2O$	117	168.6	168.6

Table 4.2 Data on several salt ammoniates

Reaction	Dissociation temp. at 1 bar (°C)	ΔH (kJ per mol)
$CaCl_2 \bullet 8\ NH_3 = CaCl_2 \bullet 4\ NH_3 + 4\ NH_3$	27	184
$BaBr_2 \bullet 4\ NH_3 = BaBr_2 \bullet 2\ NH_3 + 2\ NH_3$	40	86
$LiCl \bullet 3\ NH_3 = LiCl \bullet 2\ NH_3 + NH_3$	56	46
$BaBr_2 \bullet 2\ NH_3 = BaBr_2 \bullet NH_3 + NH_3$	66	46
$MnCl_2 \bullet 6\ NH_3 = MnCl_2 \bullet 2\ NH_3 + 4\ NH_3$	87	200
$CuSO_4 \bullet 5\ NH_3 = CuSO_4 \bullet 4\ NH_3 + NH_3$	100	60

4.3.6 Binary Systems That Contain Eutectic Reactions

The discussion thus far has been about materials systems containing peritectic reactions. There are a number of cases in which eutectic reactions are present, in which a liquid phase decomposes to form two solid phases, α and β upon cooling. This can be represented schematically as shown in Fig. 4.9.

A real example of this is the lead–tin metallurgical system, whose phase diagram is shown in Fig. 4.10. In this case, the liquid phase reacts to form the terminal lead and tin solid solutions at the eutectic temperature, 185 °C.

The discussion thus far has assumed that the overall composition of the liquid is the same as the eutectic composition. This is, of course, not necessary.

If the overall composition does not coincide with the *eutectic composition*, or the *peritectic composition* in the case of phase diagrams containing peritectic reactions,

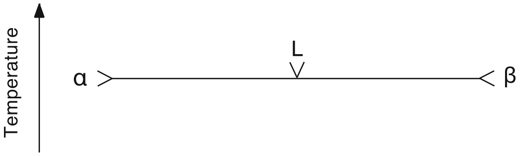

Fig. 4.9 Simple schematic representation of a eutectic reaction

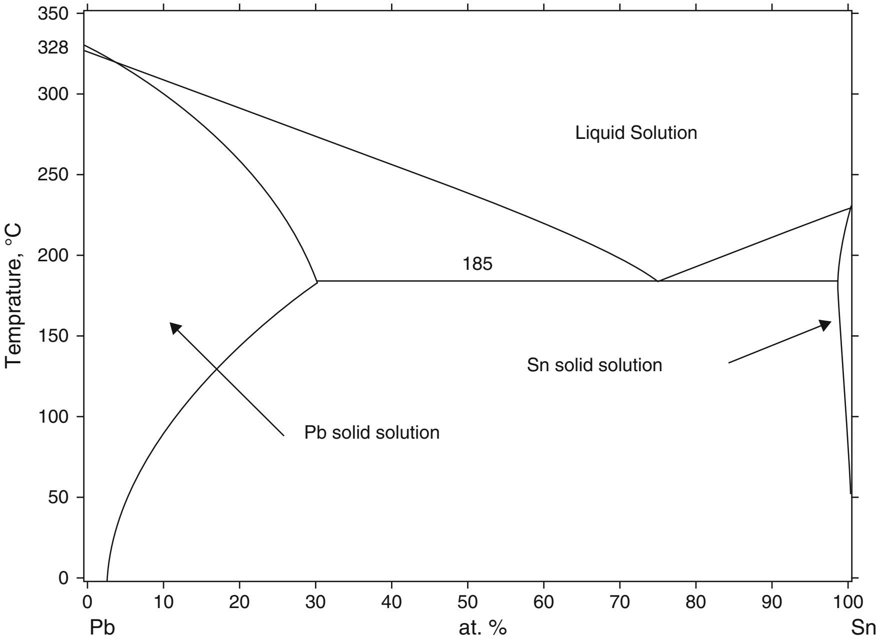

Fig. 4.10 Phase diagram of the lead–tin binary system

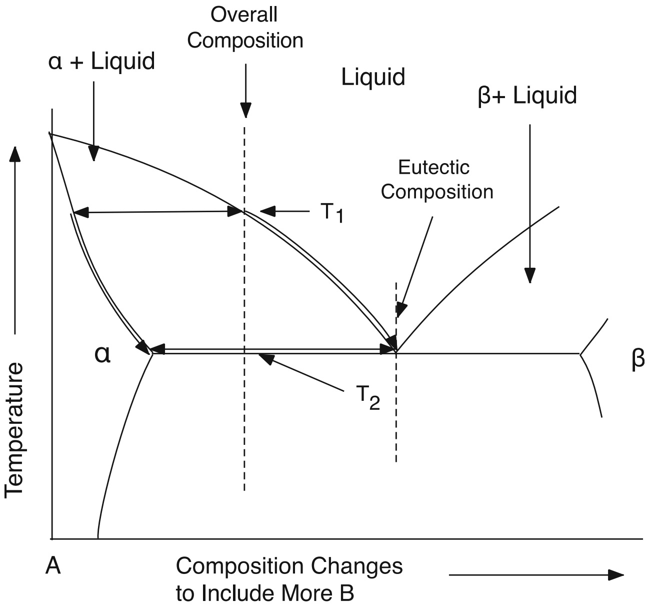

Fig. 4.11 Illustration showing how the compositions of both the solid phase α and the remaining liquid change with temperature above the eutectic temperature

the overall composition traverses a two-phase field during cooling (or heating). This is illustrated in Fig. 4.11 for a eutectic system.

Consider the case of a material with an overall composition on the A-rich side of the eutectic composition that is cooled from a temperature at which it is entirely liquid. When its temperature reaches T_1 the phase α begins to form from the liquid. The composition of the α phase that initially forms is indicated by the left end of the arrow at that temperature. As the temperature decreases further, the compositions of both the solid α phase and the liquid continuously change, both incorporating more B atoms, as shown by the curved arrows along the phase boundaries. The compositional changes of both phase α and the remaining liquid in this temperature region are the result of a chemical reaction in which

$$Liquid_1 = \alpha + Liquid_2 \tag{4.14}$$

where the composition of α has a lower B content, and $Liquid_2$ has a higher B content, than $Liquid_1$. As with all chemical reactions, there are associated changes in Gibbs free energy and enthalpy, i.e., heat. The implications of this are discussed in the following section.

4.4 Thermal Effects Related to Liquid and Solid Reactions

An experimental method that is often used to study phase transformations of materials is commonly called *thermal analysis*. In a simple example, the temperature is raised to a high value, the material is allowed to cool, and the temperature recorded as a function of time.

Changes in the slope of the resulting temperature-time *cooling curve* give information about the type of reactions that are taking place, and over what temperature intervals they occur. If the rate of extraction of heat is maintained constant, it is also possible to get quantitative thermodynamic information in this way.

As discussed in Chap. 3, the amount of heat given off during the cooling of a given mass of material is proportional to the product of the heat capacity and the temperature change. This can be expressed as

$$\int dq = \rho V C_P \int dT \tag{4.15}$$

where q is the heat evolved, ρ the density, V the volume, C_P the heat capacity at constant volume, and T the temperature, if no chemical changes take place.

But when a chemical change also takes place as the temperature is changed in a cooling reaction, an additional heat term must be added to this relation. If the temperature-dependent reaction causes the evolution of heat, the *effective heat capacity* will be greater, with the result that the material will cool at a slower rate. This is illustrated schematically in Fig. 4.12 for a material with an overall

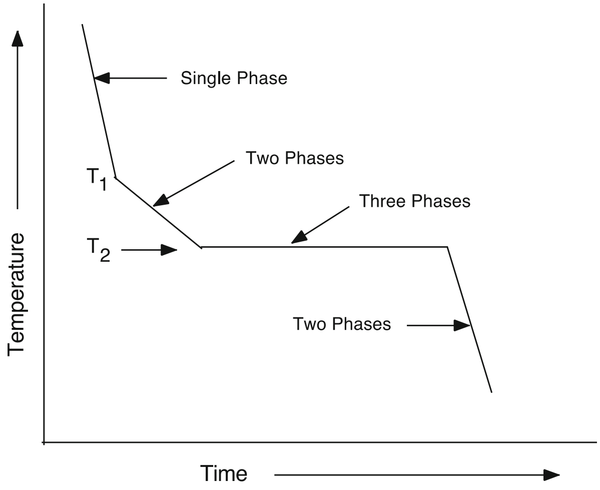

Fig. 4.12 Schematic temperature-time cooling curve showing changes in slope during a constant rate of heat extraction experiment with a material with the overall composition indicated in Fig. 4.11

composition shown in Fig. 4.11. The cooling curve has a relatively steep slope when the material is entirely liquid. When temperature T_1 is reached upon cooling, the reaction indicated in Eq. (4.14) begins to take place, causing the generation of heat. Thus the effective heat capacity is increased, and the rate of cooling, the slope of the cooling curve, decreases. When temperature T_2, the eutectic temperature, is reached, the composition of the remaining liquid is $Liquid_{eut}$, the eutectic composition, and there is no further cooling as the eutectic reaction

$$Liquid_{\text{eut}} = \alpha + \beta \tag{4.16}$$

takes place. When that reaction has come to completion, and there is no more liquid left, the slope of the cooling curve again increases.

The characteristics of the cooling curve will change as the overall composition is varied. This is shown schematically in Figs. 4.13 and 4.14 for three different values of the overall composition.

The thermal behavior of materials with this type of reaction can be used for temperature control or maintenance purposes. By changing the overall composition of the material being used, it is possible to vary the relative effects of the isothermal latent heat reaction and the enhanced sensible heat reaction that takes place over a range of temperature.

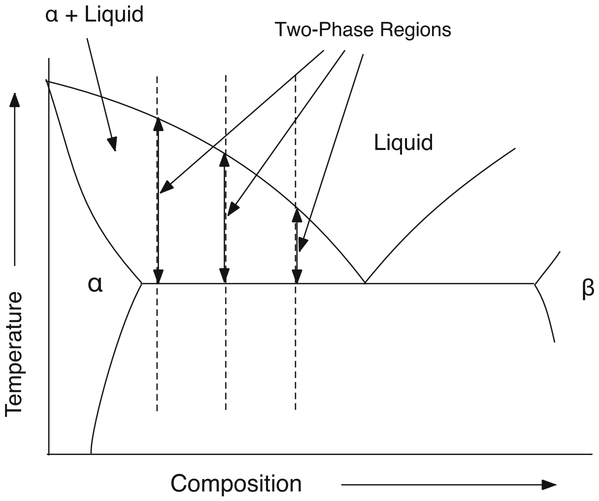

Fig. 4.13 Illustration of the temperature ranges over which the two-phase (a + liquid) structure is formed for three different overall compositions

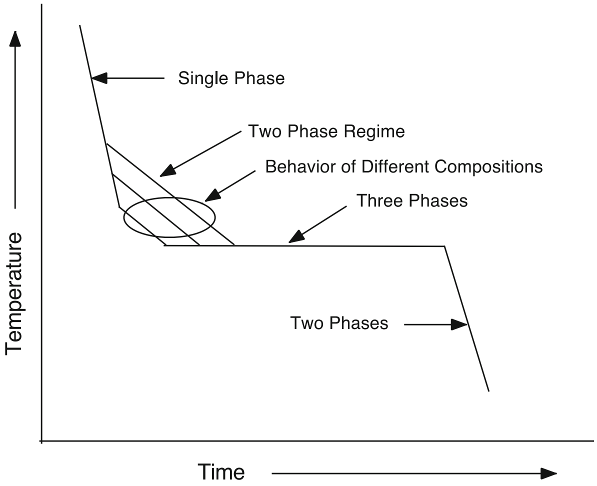

Fig. 4.14 Changes in the cooling curve as the initial overall composition is varied

4.5 Thermal Effects Related to Reversible Gas Phase Reactions

There are a number of simple gas phase reactions of the type

$$A + B = C + D \tag{4.17}$$

The relation between the Gibbs free energy, the enthalpy, and the temperature

$$G = H - TS \tag{4.18}$$

was introduced in Chap. 2. Changes in G constitute the driving forces for all reactions, whereas changes in H indicate changes in heat content.

As has been mentioned earlier, the change in the Gibbs free energy resulting from a reaction of the type in Eq. (4.17) under standard conditions, ΔG_r^0, is the difference between the standard Gibbs free energies of formation of the products and of the reactants. Likewise, the change in enthalpy resulting from such a reaction, ΔH_r^0, is the difference between the standard enthalpies of formation of the products and the reactants.

Reactions such as Eq. (4.17) can generally take place over a substantial range of temperatures. The driving forces for such reactions can sometimes be reversed by changes in the temperature, depending upon the magnitudes of the entropy values of the species involved on both sides of the reaction, according to Eq. (4.18).

On the other hand, the magnitude of the heat generated or absorbed, determined by the enthalpies of the reactants and products, is relatively temperature-independent. However, it goes in the opposite direction if the reaction is reversed.

The first example of the use of this phenomenon to store and transmit heat involves the reaction of methane with steam, generally described as the *steam reforming of natural gas* [2, 3]. It is discussed further in Chap. 8, for it is commonly used to produce hydrogen from natural gas:

$$CH_4 + H_2O = CO + 3H_2 \tag{4.19}$$

The temperature dependence of the direction of this reaction can be understood by calculation of the standard Gibbs free energy change ΔG_r^0 from information about the variation of the standard Gibbs free energies of formation of the species involved with temperature

$$\Delta G_r^0 = \Delta G_f^0(CO) + 3\Delta G_f^0(H_2) - \Delta G_f^0(CH_4) - \Delta G_f^0(H_2O) \tag{4.20}$$

Values of the standard Gibbs free energy of formation of the species in this reaction for three different temperatures are given in Table 4.3.

From these data it is possible to obtain the standard Gibbs free energy of reaction as a function of temperature. The results are listed in Table 4.4, and are plotted in Fig. 4.15. It is seen that this reaction will go forward at temperatures above about 900 K, and in the reverse direction at lower temperatures.

The thermal effects of this reaction can be obtained from information on the standard enthalpies of the species involved. These are shown in Table 4.5. From these data, the temperature dependence of the standard enthalpy change of the reaction can be obtained. The results are listed in Table 4.6, and plotted in Fig. 4.16. As expected, there is not very much variation of the heat effect with temperature. But the important point is that the reaction tends to go forward, and is endothermic, at high temperatures, and in the reverse, exothermic, direction at low temperatures.

Table 4.3 Temperature dependence of the standard Gibbs free energies of formation of species in reaction (Eq. (4.20))

Species	ΔG_f^0 (400 K) (kJ mol^{-1})	ΔG_f^0 (800 K) (kJ mol^{-1})	ΔG_f^0 (1200 K) (kJ mol^{-1})
CO	−146.4	−182.5	−217.8
H_2O	−224.0	−203.6	−181.6
CH_4	−42.0	−2.1	+41.6
H_2	0	0	0

Table 4.4 Temperature dependence of standard Gibbs free energy of reaction (Eq. (4.20))

Temperature (K)	ΔG_r^0 (kJ mol^{-1})
400	+119.6
800	+23.2
1200	−77.8

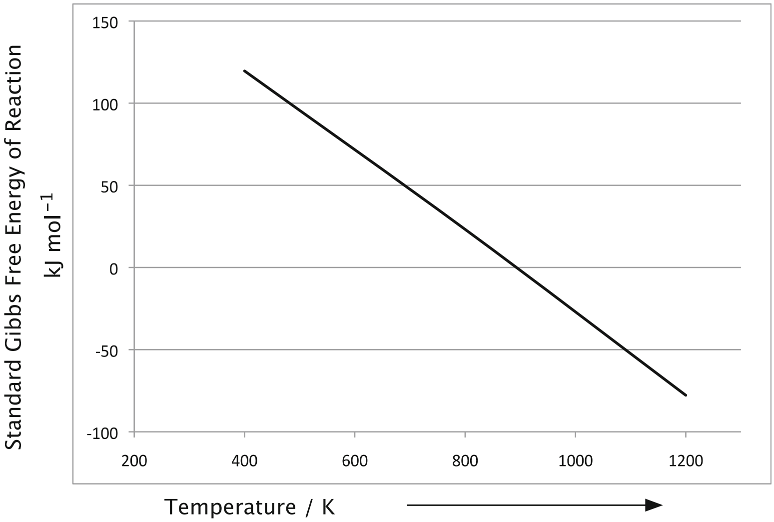

Fig. 4.15 Temperature dependence of the standard Gibbs free energy of reaction (4.20)

Table 4.5 Temperature dependence of the standard enthalpies of species in reaction (Eq. (4.20))

Species	ΔH_f^0 (400 K) (kJ mol^{-1})	ΔH_f^0 (800 K) (kJ mol^{-1})	ΔH_f^0 (1200 K) (kJ mol^{-1})
CO	−110.1	−110.9	−113.2
H_2O	−242.8	−246.4	−249.0
CH_4	−78.0	−87.3	−91.5
H_2	0	0	0

Table 4.6 Temperature dependence of standard enthalpy of reaction (Eq. (4.20))

Temperature (K)	ΔH_r^0 (kJ mol^{-1})
400	+210.7
800	+222.8
1200	+227.3

Use can be made of the temperature-dependent reversal of this reaction, for it can be driven at high temperatures at one location, where it is endothermic, and the product gases sent through pipes to a distant location, where the reaction is caused to react exothermically in the reverse direction, giving off heat. The same thing could be done in a single location, of course, using heat when it is available, and supplying it when it is needed.

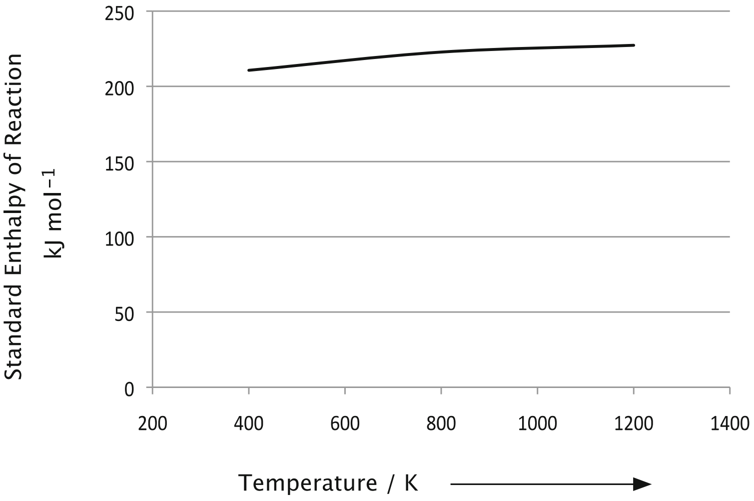

Fig. 4.16 Temperature dependence of the standard enthalpy of reaction (4.20)

Table 4.7 Reversible chemical reactions in the C-H-O system

System	Enthalpy of reaction, ΔH_r^0, kJ mol^{-1}	Temperature range (K)
$C_{10}H_{18} = C_{10}H_8 + 5\ H_2$	314	450–700
$C_7H_{14} = C_7H_8 + 3\ H_2$	213	450–700
$C_6H_{12} = C_6H_6 + 3\ H_2$	207	500–700
$CH_4 + 2\ H_2O = CO_2 + 4\ H_2$	165	500–700
$CH_4 + CO_2 = 2\ CO + 2\ H_2$	247	700–1200
$CH_4 + H_2O = CO + 3H_2$	225	700–1200

A number of other reactions in the carbon–hydrogen–oxygen system can also be used for this purpose. Some of these are listed in Table 4.7.

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