

# THE FIRST LAW OF THERMODYNAMICS AND ENTHALPY

## 2.1 INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS

On the macroscopic scale of observation, a system possesses potential energy,  $E_p$ , by virtue of its position and kinetic energy,  $E_K$ , by virtue of its motion. On the microscopic scale, the *internal energy*,  $U$ , contained *within* a system is the sum of the potential and kinetic energies of the atoms and molecules which comprise the system. Regardless of the scale of observation, potential, kinetic, and internal energies must be measured relative to an arbitrary reference frame. Consequently, *absolute* potential, kinetic, and internal energies are undefined, and only corresponding changes have physical significance.

Let  $\Delta E_p$  and  $\Delta E_K$  designate changes in the macroscopic molar potential and kinetic energies of a system as a consequence of a change from state 1 to state 2. In addition, let  $\Delta U$  represent the molar internal energy change corresponding to this same change in state. The total molar energy change  $\Delta E_T$  of the system is then

$$\Delta E_T = \Delta E_p + \Delta E_K + \Delta U.$$

The last term in this expression,  $\Delta U$ , is of fundamental importance in thermodynamics. Fortunately, the microscopic scale of observation is unnecessary to detect internal energy differences. Using only the macroscopic scale of observation,  $\Delta U$  can be detected by noting differences in the macroscopic properties of a system in different states. For example, molten  $\text{SiO}_2$  at  $1000^\circ\text{C}$  and 1 atm pressure has a different density, viscosity, vapor pressure, and electrical conductivity than molten  $\text{SiO}_2$  at  $1700^\circ\text{C}$  and 1 atm pressure. Hence, the physical and thermodynamic properties of these two states are different.

In accordance with the conservation of energy principle, the relationship between the internal energy, work, and heat of a system must be one in which

- (1) Internal energy is *increased* by work performed *on* and/or heat transferred *into* the system.
- (2) Internal energy is *decreased* by work performed *by* and/or heat transferred *from* the system.

Statements (1) and (2) constitute the *First Law of Thermodynamics*. Expressed mathematically in accordance with the sign conventions for work and heat in Section 1.9, the First Law of Thermodynamics is

$$\Delta U = Q - W \quad [2-1]$$

where  $Q$  is the molar heat absorbed or released by a system and  $W$  is the work performed per mole on or by the same system.

The First Law, written in differential form, becomes

$$dU = \delta Q - \delta W \quad [2-2]$$

While neither  $Q$  nor  $W$  stand alone as thermodynamic properties, the difference between them is a definition of the thermodynamic property,  $\Delta U$ . This difference constitutes a statement of the First Law.

Further insight into the First Law is obtained by considering two special processes involving work and heat:

- (1) *Adiabatic process.*  $Q = 0$ ; from [2-1],  $\Delta U = -W_{ad}$ . In such a case,  $W_{ad}$  or adiabatic work is a state function.  $P, V$ , and  $T$  are variables.
- (2) *Isochoric process.*  $\Delta V = 0$ . Since volume is constant,  $W = \int P dV = 0$ . From [2-1],  $\Delta U = Q_v$ . In such a case,  $Q_v$  is a state function.  $P$  and  $T$  are variables.

Example Problem 2-1 in Section 2.3 illustrates a general application of the First Law as well as special cases (1) and (2) for an ideal gas. The reason that an ideal gas is selected for this example is because the equation of state is simple and easy to use in illustrating a First Law application. However, caution is advised in extrapolating the results of this example to non-ideal gases or condensed states. For example,  $\Delta U$  is a function of temperature only for an ideal gas and is independent of volume change. This simplification is not true in general.

## 2.2 ENTHALPY: A STATE FUNCTION

Substituting [1-10] into [2-2], assuming constant pressure, and integrating:

$$\int_{U_1}^{U_2} dU = Q_p - P \int_{V_1}^{V_2} dV$$

or

$$(U_2 - U_1) = Q_p - P(V_2 - V_1).$$

Upon rearranging,

$$(U_2 + PV_2) - (U_1 + PV_1) = Q_p \quad [2-3]$$

Since  $U + PV$  is an expression involving only state functions, a new thermodynamic property, *enthalpy*, is defined by

$$H = U + PV \quad [2-4]$$

Inserting [2-4] into [2-3],

$$H_2 - H_1 = \Delta H = Q_p \quad [2-5]$$

In differential form,

$$dH = \delta Q_p \quad [2-6]$$

## 2.3 HEAT CAPACITY

Substituting [1-10] into [2-2],

$$dU = \delta Q - PdV \quad [2-7]$$

Expressing the partial derivative form of [2-7] with respect to temperature at constant volume,

$$\left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\delta Q}{\partial T} \right)_V = C_v \quad [2-8]$$

$C_v$ , molar heat capacity at constant volume, is expressed in differential form by

$$dU = C_v dT \quad [2-9]$$

or in integral form by

$$\Delta U = \int_{T_1}^{T_2} C_v dT \quad [2-10]$$

where  $C_v$  is an intensive property (e.g., J/(mol·K)). Also,

$$dU' = C_v' dT$$

where  $C_v'$ , total heat capacity at constant volume, is an extensive property (e.g., J/K).

Expressing the partial derivative form of [2-6] with respect to temperature at constant pressure,

$$\left( \frac{\partial H}{\partial T} \right)_P = \left( \frac{\delta Q_p}{\partial T} \right)_P = C_p \quad [2-11]$$

$C_p$ , molar heat capacity at constant pressure, is expressed in differential form by

$$dH = C_p dT \quad [2-12]$$

or in integral form by

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad [2-13]$$

where  $C_p$  is an intensive property (e.g., J/(mol·K)). Also,

$$dH' = C_p' dT$$

where  $C_p'$ , total heat capacity at constant pressure, is an extensive property

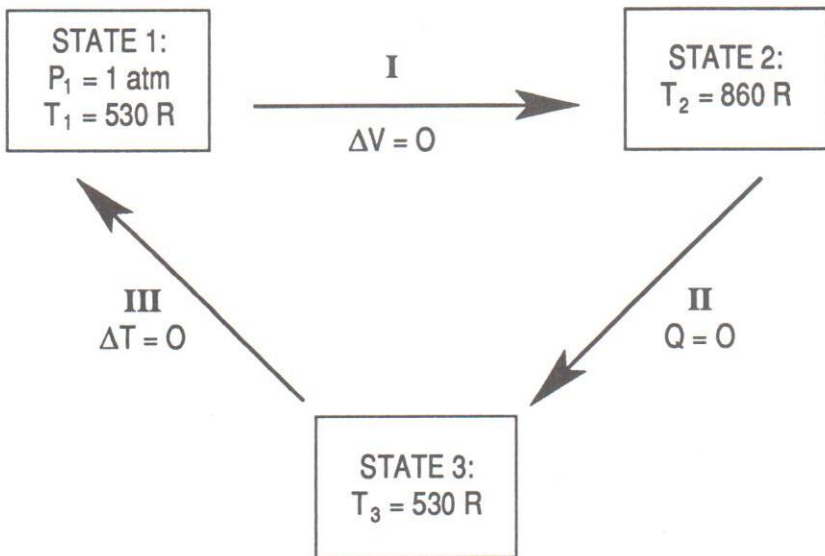
(J/K). It is left to the reader to develop expressions for heat capacity on a mass basis\* (i.e., specific heat capacities  $c_v$  and  $c_p$  at constant volume and pressure respectively).

### Example Problem 2-1

Consider a quasi-static three step process. The working substance is 1 lb mol of diatomic ideal gas initially at 70°F and 1 atm. The gas is heated at constant volume to 400°F, expanded adiabatically to the initial temperature of 70°F, and finally compressed isothermally to the initial pressure of 1 atm. Confirm the data table illustrated at the end of the solution below.

### Solution

Construct a “closed loop” or graphical scheme of the given and required data. The process and given data are illustrated in Figure 2.1. The method of solution involves three general steps: (a) compute all  $P$ - $V$ - $T$  data possible from the ideal gas equation of state:  $PV = RT$  ( $n = 1$ ), (b) compute process paths I, II, and III; (c) confirm the data table. Note that the cyclic sum for each process serves as a data check.



**Figure 2.1** Quasi-static cyclic process corresponding to the data given in Example Problem 2-1. The data are labeled on the diagram. I: isochoric heating, II: adiabatic expansion; III: isothermal compression.

\* The kinetic theory of gases predicts heat capacity values for ideal gases. For example, for a monatomic gas:  $C_p = (5/2)R$ ,  $C_v = (3/2)R$ , and for a diatomic gas:  $C_p = (7/2)R$ ,  $C_v = (5/2)R$ . When the specific gas is not specified, these values should be used.

(a) Compute all  $P$ - $V$ - $T$  data from the ideal gas equation.

State 1:  $P_1 V_1 = RT_1$ .

$$V_1 = \frac{RT_1}{P_1} = \frac{0.73 \times 530}{1} \text{ ft}^3/(\text{lb} \cdot \text{mol})$$

$$= 386.9 \text{ ft}^3/(\text{lb} \cdot \text{mol})$$

State 2:  $V_2 = V_1 = 386.9 \text{ ft}^3/(\text{lb} \cdot \text{mol})$

$$P_2 V_2 = RT_2$$

$$P_1 V_1 = RT_1$$

$$P_2 = \frac{T_2}{T_1} \times P_1 = \frac{860}{530} \times 1 \text{ atm}$$

$$= 1.623 \text{ atm.}$$

State 3: Since  $P$ ,  $V$ , and  $T$  vary when  $Q = 0$ , relationships specific to an adiabatic process are applicable. These relationships are derived as follows. Beginning with  $U = f(V, T)$  and using the chain rule,

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV.$$

Since  $U = f(T)$  only for an ideal gas,  $(\partial U / \partial V)_T dV = 0$ . Substituting [2-8] into the chain rule expression above and combining with [1-10] and [2-2],

$$dU = C_v dT = -P dV.$$

Differentiating the ideal gas equation of state  $PV = RT$ ,

$$P dV + V dP = R dT,$$

and substituting into the above expression for  $dU$ ,

$$dU = C_v dT = V dP - R dT.$$

Separating variables and substituting for  $V$  from [1-1] for  $n = 1$ ,

$$(C_v + R) \frac{dT}{T} = R \frac{dP}{P}.$$

Integrating,

$$\left( \frac{C_v + R}{R} \right) \int_{T_2}^{T_3} \frac{dT}{T} = \int_{P_2}^{P_3} \frac{dP}{P}$$

$$\left(\frac{T_3}{T_2}\right)^{\frac{(C_v+R)}{R}} = \frac{P_3}{P_2}$$

or

$$P_3 = P_2 \left(\frac{T_3}{T_2}\right)^{\gamma/(\gamma-1)}$$

where  $\gamma = C_p/C_v = 7/5$  ( $C_p = (7/2)R$  for a diatomic ideal gas and  $C_p - C_v = R$ ). Hence,

$$P_3 = 1.623 \left(\frac{530}{860}\right)^{\frac{7/5}{[(7/5)-1]}} = 1.623 \left(\frac{530}{860}\right)^{7/2} = 0.298 \text{ atm.}$$

Using  $P_3V_3 = RT_3$ ,

$$V_3 = \frac{RT_3}{P_3} = \frac{0.73 \times 530}{0.298} = 1298 \text{ ft}^3/(\text{lb} \cdot \text{mol}).$$

(b) Compute remaining data for process paths I, II, and III.

Path I:  $\Delta U = Q - W = Q - 0$  (isochoric)

$$= C_v \int_{T_1}^{T_2} dT = (5/2)R \int_{530}^{860} dT = (5/2)(1.987)(330)$$

$$= 1639 \text{ BTU}/(\text{lb mol}).$$

Path II:  $\Delta U = Q - W = 0$  (adiabatic) -  $W$

$$= C_v \int_{T_2}^{T_3} dT = (5/2)R \int_{860}^{530} dT = (5/2)(1.987)(-330)$$

$$= -1639 \text{ BTU}/(\text{lb} \cdot \text{mol}) \text{ and } W = 1639 \text{ BTU}/(\text{lb} \cdot \text{mol}).$$

Path III:  $\Delta U = Q - W = 0$  (isothermal)

$$Q = W = \int_{V_3}^{V_1} P dV = RT \int_{1298}^{386.9} \frac{dV}{V}$$

$$= 1.987 \times 530 \times \ln \left( \frac{386.9}{1298} \right)$$

Thus  $Q = W = -1275$  BTU/(lb · mol).

(c) The completed data table is illustrated below.

Path	$\Delta U$ BTU/(lb mol)	$Q$ BTU/(lb mol)	$W$ BTU/(lb mol)	$\Delta P$ atm	$\Delta T$ R	$\Delta V$ ft <sup>3</sup> /(lb mol)
I	1639	1639	0	+0.623	+330	0
II	-1639	0	1639	-1.325	-330	+911.1
III	0	-1275	-1275	+0.702	0	-911.1
Cycle	0	364	364	0	0	0

## 2.4 ENTHALPY (HEAT) OF TRANSFORMATION

The term *phase transformation* refers to either a polymorphic solid-solid transformation, a solid-liquid transformation, or a condensed phase-gas transformation. A *polymorphic (allotropic) transformation* occurs when a solid element or compound undergoes a change in crystal structure. There is no change in the chemistry of the solid, and each structural variety of the solid is called a *polymorph* of that solid.

The phase boundaries of Figure 2.2, for example, illustrate the range of pressures and temperatures at which various SiO<sub>2</sub> polymorphic transformations occur. At 1713°C or above, *fusion* occurs and SiO<sub>2</sub> melts to form liquid. Figure 2.3 illustrates the equilibrium phase diagram for pure H<sub>2</sub>O. The range of pressures and temperatures over which fusion occurs is indicated by the inclined solid-liquid phase boundary.

THERMODYNAMIC LOOP APPLICATIONS IN MATERIALS SYSTEMS

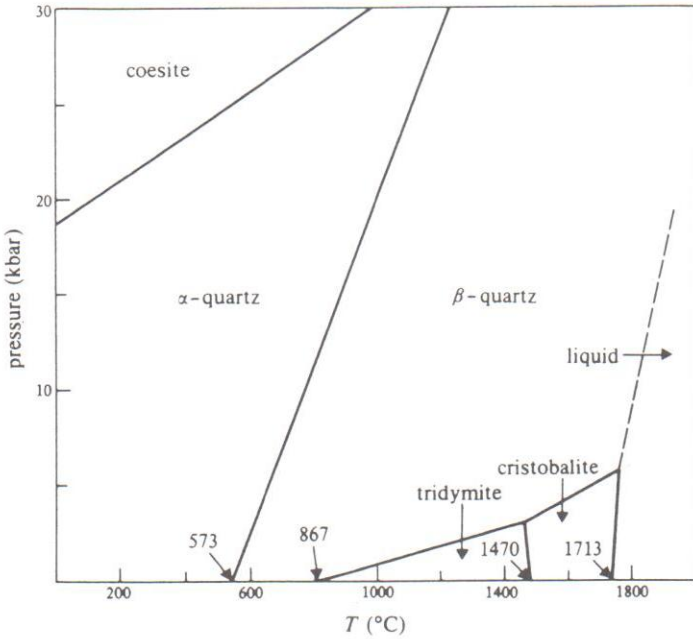


Figure 2.2 Polymorphs of SiO<sub>2</sub>. (After F.R. Boyd and J.L. England, 1960.)

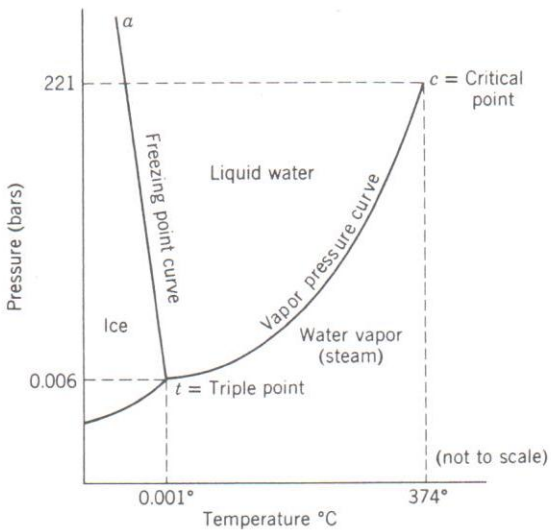


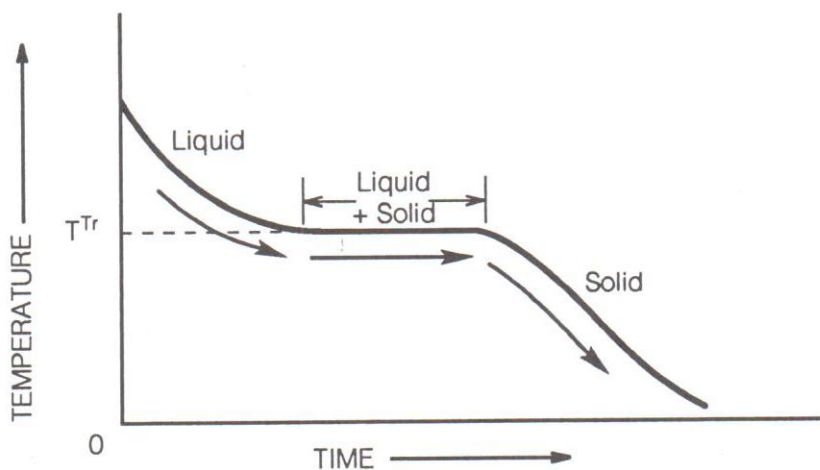
Figure 2.3 A portion of the equilibrium phase diagram of H<sub>2</sub>O, a one component system. (From C. Klein and C.S. Hurlbut, Jr., 1985, *Manual of Mineralogy*, Fig. 4.37. Reprinted by permission of John Wiley and Sons, Inc., Copyright © 1985.)



Two types of condensed phase-gas transformations are shown by the concave upward curves. Above the “triple point” pressure, liquid evaporates to form water vapor. Below the “triple point” pressure, solid evaporates to form water vapor by the process of *sublimation*.

The pressures and temperatures at which a phase transformation occurs are determined experimentally. For example, for a one-component system at constant pressure, cooling curve plots of temperature versus time reveal a “flat” or isothermal hold during the time interval between the start and finish of a liquid to solid transformation, Figure 2.4. The “hold temperature” is identified as the transformation temperature provided the cooling is slow enough to prevent supercooling or non-equilibrium cooling. Heat is released ( $Q_p = -\Delta H_f$  where  $\Delta H_f$  is the *heat or enthalpy of fusion*) during the hold and the temperature cannot decrease until all liquid is solidified. Recalling [2-5], the terms *heat of transformation* and *enthalpy of transformation* are often used interchangeably. Hence for any transformation at constant pressure,

$$\Delta H^{\text{Tr}} = Q_p.$$



**Figure 2.4** Hypothetical temperature-time equilibrium cooling curve for a one component system. At the transformation temperature,  $T^{\text{Tr}}$ , a liquid to solid transformation occurs.

The effect of supercooling on  $-\Delta H_f$  is illustrated later in this chapter. In addition, the phase rule and its application to two component phase diagrams is introduced in Chapter 7.

While Figure 2.3 is only qualitative, vapor-liquid equilibrium data are published for a variety of working substances used in power system design. For example, Appendix D, Table D.1, lists typical vapor-liquid equilibrium data for water. Based on this data, water exerts a vapor pressure of 0.25 bar ( $\approx 0.25$

atm) at 65°C. The heat absorbed when a phase change occurs is  $\Delta h^{\text{Tr}} = h_g - h_l = 2618 - 272 \text{ kJ/kg} = 2346 \text{ kJ/kg}$ . A comparison of data in Appendix D, Table D.2, for potassium at  $\approx 0.25 \text{ bar}$  shows a substantially higher equilibrium temperature of  $\approx 627^\circ\text{C}$  but a similar  $\Delta h^{\text{Tr}} \approx 2009 \text{ kJ/kg}$ . The engineering-materials aspects of these comparisons are significant as will be discussed later. Heats of transformation for selected substances are found in Appendix A, Table A.2.

## 2.5 STANDARD STATE ENTHALPY

Since energy in any form is relative, only changes in enthalpy can be computed or measured. Hence, an arbitrary reference or standard state has been universally accepted. The *standard state enthalpy* or *heat content* of an element or compound is defined for the most *stable* form of that element or compound under the chosen conditions of temperature and pressure. It is denoted by superscript 0 and is defined in Table 2.1 for solids, liquids, and gases in elemental or compound form. By convention, the heat content of an element is zero at 298 K and one atmosphere pressure. The heat of formation of a compound, denoted by  $\Delta H_T^{0,f}$  in Table 2.1, is defined in the next section.

Table 2.1: Standard State Enthalpy

State of Aggregation	Pure Elements $P^0 = 1 \text{ atm}^*$ Stable <sup>†</sup> at 298 K	Pure Compounds $P^0 = 1 \text{ atm}^*$ Stable <sup>†</sup> at $T$ (K)
Solid	$\Delta H_{298}^0 = 0$	$\Delta H_T^0 = \Delta H_T^{0,f}$
Liquid	$\Delta H_{298}^0 = 0$	$\Delta H_T^0 = \Delta H_T^{0,f}$
Gas (ideal)	$\Delta H_{298}^0 = 0$	$\Delta H_T^0 = \Delta H_T^{0,f}$

\* *Standard state pressure* is an arbitrarily adopted unit and some tables of thermodynamic data (e.g., Robie et al., 1979 and Holland, 1990) are based on a standard pressure of 1 bar (1 bar = 1.01325 atm). Changing the reference pressure from 1 atm to 1 bar has a negligible effect on the thermodynamic properties tabulated in this book.

† For diatomic gases such as hydrogen,  $\text{H}_2$ ,  $\Delta H_{298}^0 = 0$ . For monatomic hydrogen, H,  $\Delta H_{298}^0 \neq 0$ .

## 2.6 ENTHALPY (HEAT) OF FORMATION AND REACTION Heat of Formation

*Heat or enthalpy of formation*,  $\Delta H_T^{0,f}$ , is defined as the heat associated with the formation of a *compound* from its *elements* at *any temperature* at which the compound and its component elements are *stable*. Hence, at  $P^0 = 1 \text{ atm}$  and  $T = 298 \text{ K}$  for which data is readily available in the literature,

$$\int_{\text{Reactants}}^{\text{Products}} dH = \Delta H_{298}^{0,f} = \Delta H_{298}^0 (\text{Product}) - \sum n \Delta H_{298}^0 (\text{Elements})$$

$$\text{or } \Delta H_{298}^{0,f} = \Delta H_{298}^0 (\text{Product})$$

where  $n$  is the number of moles of each element and  $\Delta H_{298}^{0,f}$  is the *standard state heat of formation*. Values of  $\Delta H_{298}^{0,f}$  for selected compounds are given in Appendix A, Table A.1. From Table 2.1,  $\sum n \Delta H_{298}^0 (\text{Elements}) = 0$ .

### Heat of Reaction

The *heat or enthalpy of reaction*,  $\Delta H_T$ , at temperature  $T$  is defined as the heat released or absorbed when reactants form products in a *balanced* chemical reaction.

Hence, at  $P^0 = 1 \text{ atm.}$  and  $T = T(\text{K})$ ,

$$\int_{\text{Reactants}}^{\text{Products}} dH = \Delta H_T^0$$

$$\text{or } \Delta H_T^0 = \sum n \Delta H_T^{0,f} (\text{Products}) - \sum n \Delta H_T^{0,f} (\text{Reactants}) \quad [2-14]$$

where  $\Delta H_T^0$  is the standard heat of reaction and  $n$  is the number of moles of each reactant or product. Note that the superscript  $f$  applies to compounds but not to elements.

As an example of the application of [2-14], consider the chemical reaction occurring in the standard state ( $P^0 = 1 \text{ atm, } T = T(\text{K})$ ) for reactants A and B forming products C and D:



The standard state heat of reaction is

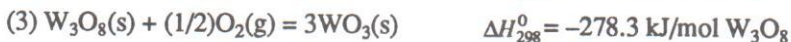
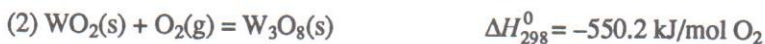
$$\Delta H_T^0 = n_C \Delta H_{T,C}^{0,f} + n_D \Delta H_{T,D}^{0,f} - n_A \Delta H_{T,A}^{0,f} - n_B \Delta H_{T,B}^{0,f}$$

where  $\Delta H_{T,A}^{0,f}$ ,  $\Delta H_{T,B}^{0,f}$ ,  $\Delta H_{T,C}^{0,f}$ , and  $\Delta H_{T,D}^{0,f}$  are the standard state molar heats or enthalpies of formation of A, B, C, and D respectively, at temperature  $T$ . If A, B, C, or D are elements at 298 K, then  $\Delta H_{298}^{0,f} = 0$ . The *number of moles* (corresponding to  $n_A$ ,  $n_B$ ,  $n_C$ , and  $n_D$ ) in the chemical reaction are incorporated into the summation formula. Note that  $\Delta H_T^0$  is written on a per-mole basis corresponding to  $n_A$  moles of A,  $n_B$  moles of B, etc. If  $\Delta H_T^0 = 50 \text{ kJ/mol}$ , then  $\Delta H_T^0$  is  $50 \text{ kJ}/n_A = (50/n_A) \text{ kJ/mol}$  of A,  $50 \text{ kJ}/n_B = (50/n_B) \text{ kJ/mol}$  of B, etc.

It is possible to compute the enthalpy change of a reaction even if all of the enthalpies of formation of the products and reactants are unknown. Suppose the reaction in question is written as a combination of two or more reactions for which enthalpy changes are known at the *same* pressure and temperature as the desired reaction. The enthalpy change of the desired reaction can then be computed by combining the enthalpies of the constituent reactions. The enthalpies are combined in a manner analogous to that in which the reactions themselves must be combined to produce the desired reaction. This important fact, known as *Hess's law*, applies to all *thermodynamic* functions. Application of Hess's law to calculation of standard state reaction enthalpy is illustrated in Example Problem 2-2.

**Example Problem 2-2**

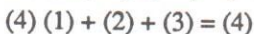
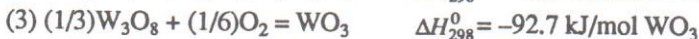
Given:  $T = 298 \text{ K}$ ,  $P = 1 \text{ atm}$  and



Find:  $\Delta H_{298}^{0,f}, \text{WO}_3$ .

**Solution**

Equations and enthalpies are additive.

**Example Problem 2-3**

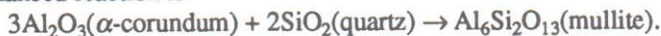
The standard enthalpies of formation of several minerals at 968 K are as follows:



Calculate  $\Delta H^0$  for the production of mullite from  $\alpha$ -corundum and quartz at 968 K.

*Solution*

The balanced reaction is



The enthalpy change of the reaction is calculated from [2-14],

$$\Delta H_{968}^0 = (1) \Delta H_{\text{mull}}^{0,f} - (3) \Delta H_{\alpha\text{-cor.}}^{0,f} - (2) \Delta H_{\text{qz}}^{0,f}.$$

Substituting the formational enthalpy values for the products and reactants,

$$\Delta H_{968}^0 = \{(1)(42.2) - (3)(31.8) - (2)(-15.3)\} \text{ kJ/mol.}$$

Since  $n = 1$  for mullite,

$$\Delta H_{968}^0 = \underline{-22.6 \text{ kJ/mol mullite.}}$$

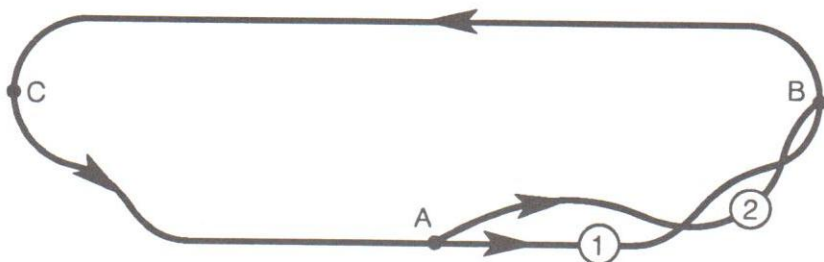
Note that  $\Delta H_{968}^0$  is not equal to  $\Delta H_{\text{mull}}^{0,f}$  in this example because mullite in the above reaction is not produced from its elements.

## 2.7 INTRODUCTION TO THE THERMODYNAMIC LOOP (TL)

Although Hess's law is useful, it is limited in application to constant pressure and temperature reactions. A more general and useful analytical tool is direct application of Kirchhoff's law to solve a wide variety of thermodynamic problems. Kirchhoff's law is referred to in this book by the term *thermodynamic loop* (TL). The TL represents an effective way to organize and simplify the solution of more complex problems in chemical thermodynamics (personal communication, 1959, R. Schuhmann, Jr., Department of Metallurgical Engineering, Purdue University, West Lafayette, Indiana). The TL approach is described (Stracher and Johnson, 1990) by the property

$$\sum \Delta\theta \Big|_{\text{Loop}} = 0$$

where  $\Delta\theta$  is the change in value of the state function  $\theta$  between any two points along the loop (see, for example, Fine and Geiger, 1979, and Hamill et al., 1966). Figure 2.5 illustrates a thermodynamic loop with a *state function path* defined by the property  $\sum \Delta\theta_{\text{TL}} = 0 = \Delta\theta_{\text{A} \rightarrow \text{B}} + \Delta\theta_{\text{B} \rightarrow \text{C}} + \Delta\theta_{\text{C} \rightarrow \text{A}}$ . In addition, the path taken between any two points along any segment of the loop results in the same  $\Delta\theta$ . For example,  $\Delta\theta_{\text{A} \rightarrow \text{B}, \text{path 1}} = \Delta\theta_{\text{A} \rightarrow \text{B}, \text{path 2}}$ . As an illustration of thermodynamic loop analysis, an expression will be derived for the enthalpy change of a reaction as a function of temperature in the following problem.



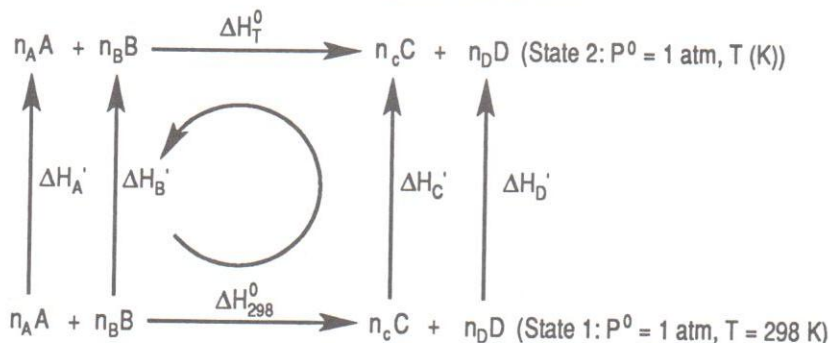
**Figure 2.5** Thermodynamic loop with state function path A-A. (From G.B. Stracher and D.L. Johnson, 1990.)

### Example Problem 2-4

Derive an expression for the standard enthalpy change of the general chemical reaction  $n_A A + n_B B \rightarrow n_C C + n_D D$  as a function of temperature at  $P^0 = 1$  atm.

#### Solution

An isobaric thermodynamic loop is set up as follows:



$\Delta H_{298}^0$  and  $\Delta H_T^0$  are *reaction enthalpies* for states 1 and 2 respectively.  $\Delta H_A'$ ,  $\Delta H_B'$ ,  $\Delta H_C'$ , and  $\Delta H_D'$  are the *total enthalpy changes* from state 1 to 2 for reaction components A, B, C, and D respectively. Summing around the loop in an *arbitrary counterclockwise* direction,

$$\sum \Delta H_{TL} = 0 = \Delta H_{298}^0 + \Delta H_C' + \Delta H_D' - \Delta H_T^0 - \Delta H_A' - \Delta H_B'.$$

Applying [2-13] to each reaction component and rearranging,

$$\Delta H_T^0 = \Delta H_{298}^0 + n_C \int_{298}^T C_p^C dT + n_D \int_{298}^T C_p^D dT - n_A \int_{298}^T C_p^A dT - n_B \int_{298}^T C_p^B dT$$

or

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^T \Delta C_p dT \quad [2-15]$$

In general,

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^T \Delta C_p dT \quad [2-16]$$

where  $\Delta C_p = n_C C_p^C + n_D C_p^D - n_A C_p^A - n_B C_p^B$ . For a reaction involving any number of components,

$$\Delta C_p = \sum n_i C_p^i (\text{Products}) - \sum n_i C_p^i (\text{Reactants}) \quad [2-17]$$

where  $n_i$  and  $C_p^i$  are the number of moles of component  $i$  in the reaction and the molar heat capacity of component  $i$  respectively.

Equations [2-15] and [2-16] are normally found in thermodynamics textbooks for the case in which no phase changes occur. Phase changes are incorporated into the TL in Example Problem 2-5.

The solution to [2-16] now becomes one of evaluating  $C_p$  for each component in the reaction. In Appendix A, Table A.3A,  $C_p$  is expressed by the empirical equation

$$C_p = a + bT + cT^{-2} + dT^{-0.5} \quad [2-18]$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are constants. Examination of [2-16] and [2-18] reveals two simplifying cases:

Case I: If  $a = b = c = d = 0$ ,  $\Delta C_p = 0$ , hence

$$\Delta H_T^0 = \Delta H_{T_1}^0 \quad [2-19]$$

Case II: If  $b = c = d = 0$ ,  $\Delta C_p = a$  (constant), hence

$$\Delta H_T^0 = \Delta H_{T_1}^0 + a(T - T_1) \quad [2-20]$$

It should be noted that for many engineering applications, the assumption  $\Delta C_p \approx 0$  simplifies computations without compromising the engineering accuracy of the result. Further reference to these simplifying cases will be made in subsequent chapters.

A suggested procedure for organizing a thermodynamic loop can be remembered in terms of *The Four S's Of Thermodynamic Loop Analysis*: (1) Setup, (2) Sum, (3) Substitute, and (4) Solve. Each procedure is performed as follows:

- (1) **Set Up:** Write down the reaction for which data is known (typically the standard state), balance and label it state 1. Write down the same reaction for which information is desired and label it state 2. Connect the corresponding reactants and products in each state with vertical arrows. The direction of these arrows (up or down) is arbitrary. If a reactant or product changes phase between states 1 and 2, the phase change must be incorporated into the proper loop segment.
- (2) **Sum:** The direction chosen for summation is arbitrary and is indicated by a single clockwise or counterclockwise arrow drawn between the reactions for each state. Counterclockwise summation is used for all examples in this book, hence, the right hand is used with the thumb pointing up. The remaining fingers of the right hand are curled in the direction chosen for summation. Sum properties around the loop and set the sum equal to zero. Loop segments pointing in the summation direction imply a plus sign in the sum, and loop segments pointing opposite to the summation direction imply a minus sign in the sum. Rearrange the resulting equation and solve algebraically for the desired unknown.
- (3) **Substitute:** Obtain numerical data from the problem statement and/or the literature and incorporate this data into the appropriate loop segments. Although data may be readily available in tables, charts, or nomographs, a more extensive search may be required for complex non-metallic and metallic systems. Carefully examine the problem statement to insure that no important restrictions or assumptions are overlooked.
- (4) **Solve:** Solve the derived equation for the unknown.

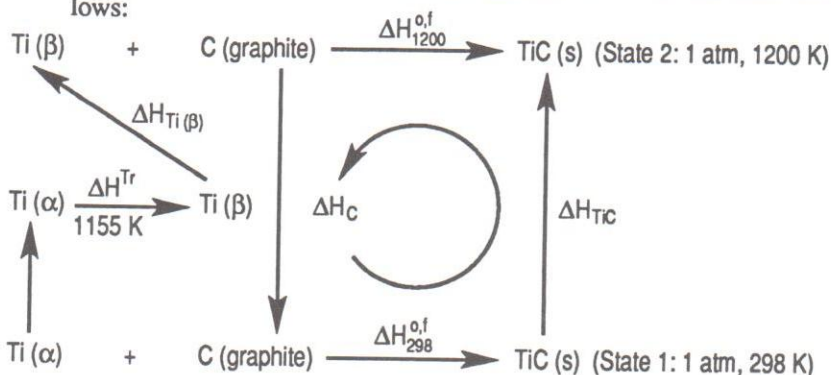
This chapter concludes with numerical examples using TL analysis.

### Example Problem 2-5

Calculate the standard enthalpy of formation of TiC at 1200 K. The data necessary to solve this problem is tabulated in Tables A.1, A.2, and A.3A.

#### Solution

- (1) **Setup.** A TL incorporating the reaction in question is structured to include the  $\text{Ti}(\alpha) \rightarrow \text{Ti}(\beta)$  polymorphic transformation at 1155 K as follows:





(2) **Sum.** Summing in the counterclockwise direction,

$$\Sigma \Delta H_{TL} = 0 = \Delta H_{298}^{0,f} + \Delta H_{TiC} - \Delta H_{1200}^{0,f} + \Delta H_C - \Delta H_{Ti(\beta)} - \Delta H^{Tr} - \Delta H_{Ti(\alpha)}$$

Rearranging and solving for  $\Delta H_{1200}^{0,f}$ ,

$$\Delta H_{1200}^{0,f} = \Delta H_{298}^{0,f} + \Delta H_{TiC} + \Delta H_C - \Delta H_{Ti(\beta)} - \Delta H^{Tr} - \Delta H_{Ti(\alpha)}$$

(3) **Substitute.** Inserting the heat capacity and transformation enthalpy data into the above expression,

$$\begin{aligned} \Delta H_{1200}^{0,f} \text{ (J/mol)} &= -183.70 \times 10^3 \\ &+ \int_{298}^{1200} (1)(49.50 + 3.35 \times 10^{-3}T - 14.98 \times 10^5 T^{-2}) dT \\ &+ \int_{1200}^{298} (1)(17.15 + 4.27 \times 10^{-3}T - 8.79 \times 10^5 T^{-2}) dT \\ &- \int_{1155}^{1200} (1)(28.91) dT - (1)3473 - \int_{298}^{1155} (1)(22.09 + 10.04 \times 10^{-3}T) dT \end{aligned}$$

(4) **Solve.** Integration, left to the reader, gives

$$\Delta H_{1200}^{0,f} = \underline{-186.7 \text{ kJ/mol}}$$

The negative enthalpy of formation of TiC in state 2 implies that the reaction is exothermic. Since both state 1 and state 2 reactions occur at constant pressure ( $P^0 = 1 \text{ atm}$ ), enthalpy changes are equal to the heat evolved. For state 1, the heat evolved is  $Q_1 = -183.7 \text{ kJ/mol}$  and for state 2 the heat evolved is  $Q_2 = -186.7 \text{ kJ/mol}$ ; hence, more heat is evolved at the higher temperature. Note that for each integral, the *lower* temperature limit of integration corresponds to the temperature of the phase at the *tail* of each arrow, while the *upper* temperature limit of integration corresponds to the temperature of the phase at the *head* of each arrow. In addition, as with Hess's law, it is necessary in thermodynamic loop analysis that *all* reactions be properly balanced.

### Example Problem 2-6

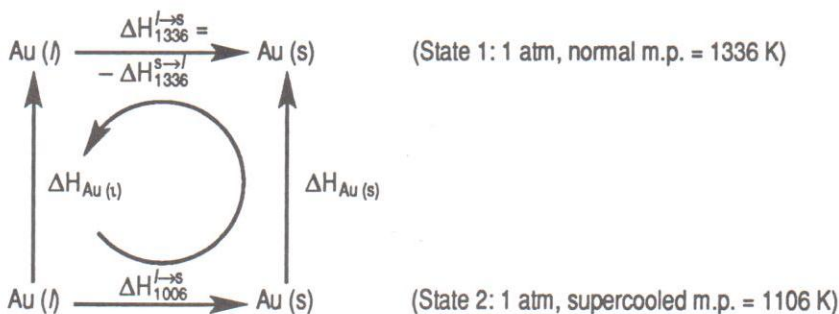
Small droplets of gold are observed to *supercool* (remain liquid)  $230^\circ\text{C}$  below the normal freezing point at atmospheric pressure. Calculate the transformation enthalpy or heat of transformation associated with solidification in

the supercooled state. The data necessary to solve this problem is tabulated in Tables A.2 and A.3A.

### Solution

Since the heat of solidification is the opposite of the heat of fusion,  $\Delta H(l \rightarrow s) = -\Delta H(s \rightarrow l) = -\Delta H_f$ . The directions of the arrows in the TL are set up to yield  $\Delta H(l \rightarrow s)$  directly. Since  $C_p$  for liquid gold at 1 atm pressure is available only from the melting point to 1600 K,  $C_p$  is extrapolated to 1106 K in order to solve this problem.

#### (1) Set Up.



(2) Sum. Summing in the counterclockwise direction,

$$\sum \Delta H_{TL} = 0 = \Delta H_{1106}^{l \rightarrow s} + \Delta H_{Au(s)} - (-\Delta H_{1336}^{s \rightarrow l}) - \Delta H_{Au(l)}$$

Rearranging and solving for  $\Delta H_{1106}^{l \rightarrow s}$ ,

$$\Delta H_{1106}^{l \rightarrow s} = -\Delta H_{Au(s)} - \Delta H_{1336}^{s \rightarrow l} + \Delta H_{Au(l)}$$

(3) Substitute. Inserting heat capacity and transformation enthalpy data into the above expression,

$$\begin{aligned} \Delta H_{1106}^{l \rightarrow s} \text{ (J/mol)} &= - \int_{1106}^{1336} (1)(23.68 + 5.19 \times 10^{-3} T) dT - 12.76 \times 10^3 \\ &\quad + \int_{1106}^{1336} (1)29.29 dT. \end{aligned}$$

(4) Solve. Integrating,

$$\begin{aligned} \Delta H_{1106}^{l \rightarrow s} &= -23.68(1336 - 1106) - (5.19 \times 10^{-3}/2) \\ &\quad \times (1336^2 - 1106^2) - 12.76 \times 10^3 + 29.29(1336 - 1106) \end{aligned}$$

which reduces to

$$\Delta H_{1106}^{l \rightarrow s} = -12.93 \text{ kJ/mol.}$$

Since the phase changes occur at constant pressure (1 atm), the heat of transformation for state 2 is

$$Q^{\text{Tr}} = \Delta H_{1106}^{l \rightarrow s} = -12.93 \text{ kJ/mol.}$$

The liquid to solid phase changes occurring in states 1 and 2 result in negative transformation enthalpies or heats of transformation. This change implies that heat energy is released to the surroundings as liquid gold solidifies. Note that the difference in  $\Delta H_{\text{Au}}^{l \rightarrow s}$  between 1106 K and 1336 K is only 170 J/mol or 1.3%.

## 2.8 DISCUSSION QUESTIONS

- (2.1) Can the change in a state function be equal to the difference of two nonstate functions? Give an example.
- (2.2) The internal energy change of a system is related to the performance of adiabatic work as follows:

$$(1) \Delta U = -W_{\text{Ad.}} > 0$$

$$(2) \Delta U = -W_{\text{Ad.}} < 0.$$

In which case is work done *by* the system? Explain.

- (2.3) Derive the formulas listed below for a *PVT* system.

(a) Constant volume process, *PV* work only:

$$\Delta U' = Q'_v = \int_{T_1}^{T_2} mc_v dT.$$

(b) Constant pressure process, *PV* work only:

$$\Delta H' = Q'_p = \int_{T_1}^{T_2} mc_p dT.$$

- (2.4) Many compounds have two or more polymorphs. For example,  $\text{SiO}_2$  has 6 polymorphs shown in Figure 2.2, while the two polymorphs of  $\text{CaCO}_3$  are the high pressure variety aragonite and the low pressure variety calcite. Give examples of polymorphic phase transformations using Figure 2.2.
- (2.5) Two phase transformations occur at a temperature  $T$  and pressure  $P$ . The phases involved are  $A$  and  $A'$ , and the transformations and enthalpy changes are:



How is  $\Delta H_{(1)}$  related to  $\Delta H_{(2)}$ ? How is  $Q_{(1)}$  related to  $Q_{(2)}$ ?

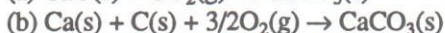
- (2.6) From the definition of standard state enthalpy of a diatomic gas at 298 K,

(a) Is  $\Delta H_{N(g)}^0 = 0$ ?

(b) Is  $\Delta H_{N_2(g)}^0 = 0$ ?

Explain both answers.

- (2.7) For which of the reactions below is  $\Delta H^0 = \Delta H_{CaCO_3}^{0,f}$ ? Explain.



## 2.9 EXERCISE PROBLEMS

- [2.1] Calculate the transformation enthalpy for the isothermal transformation of  $Ti(\beta)$  to  $Ti(\alpha)$  if the transformation occurs 200°C below the equilibrium transformation temperature during cooling.

Ans:  $\Delta H_{955}^{Tr} = -4227$  J/mol.

- [2.2] Derive an expression for the heat of fusion of Si as a function of temperature at 1 atm pressure.

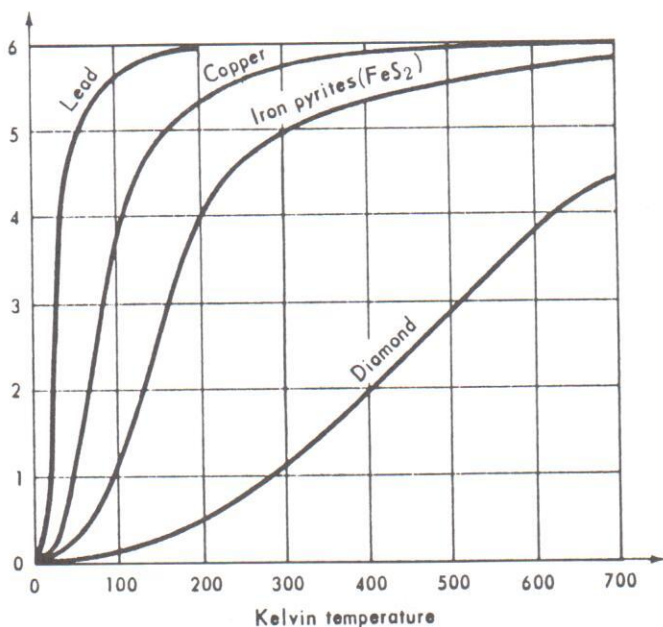
$$\text{Ans: } \Delta H_{T^f}^f \text{ (J/mol)} = 51,157 + 1.51T^f \\ - 0.00117T^{f^2} + 4.56 \times 10^5/T^f.$$

- [2.3] Modified austempering is an isothermal transformation heat treatment used to produce bainite and pearlite (a mixture of ferrite ( $\alpha$ ) and cementite  $Fe_3C$ ). The process involves austenitizing the steel to 100% austenite ( $\gamma$ ) and then quenching to a temperature slightly below the nose of the "I-T" curve and holding at that temperature until the transformation is complete. Estimate the transformation enthalpy for the transition of a 1050 steel at the austempering temperature. Refer to the I-T diagram for 1050 steel, Appendix E, Figure E.1, to select an austempering temperature. Assume carbon solubility has a negligible effect on the result in either phase. Do not include  $Fe_3C$  in the calculations.

Ans:  $\Delta H_{773}^{Tr} = -6855$  J/mol.

- [2.4] The results of constant volume molar heat capacity calculations for several solids are illustrated in Figure 2.6. For each substance,  $C_v$  approaches zero as the absolute temperature approaches zero. In addition,  $C_v$  asymptotically approaches a constant value of 6 cal/(mol·°C) as temperature increases. This constant, known as the *Dulong and Petit value*, is best approximated for each solid in a different temperature range. For lead, this temperature range begins at about 180 K and for Cu, at about 500 K.

## THE FIRST LAW OF THERMODYNAMICS AND ENTHALPY



**Figure 2.6** Variation of  $C_v$  of solids with Kelvin temperature. (From M.W. Zemansky and H.C. Van Ness, 1966, *Basic Engineering Thermodynamics*, Fig. 11.16. Reprinted by permission of McGraw Hill, Inc., New York.)

Calculate the molar heat transferred to or from the surroundings and the molar internal energy change occurring at constant volume when:

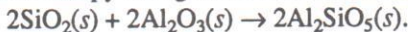
(a) Cu undergoes a temperature increase from 600 to 700 K.

*Ans:*  $Q_v = \Delta U_v = +600$  cal/mol Cu, from the surroundings.

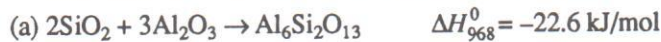
(b) Pb undergoes a temperature decrease from 210 to 180 K.

*Ans:*  $Q_v = \Delta U_v = -180$  cal/mol Pb, to the surroundings.

**[2.5]** Calculate the enthalpy change at 968 K for the reaction

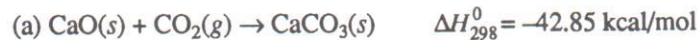


Use the following information (all phases are solids):



*Ans:*  $\Delta H_{968}^0 = 8.4$  kJ/mol  $\text{SiO}_2$ .

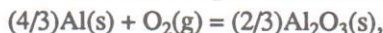
**[2.6]** Calculate the standard enthalpy of formation of  $\text{CaCO}_3$  at 298 K in kcal/mol and kJ/mol from the following data:





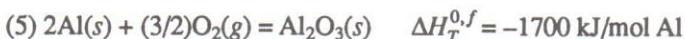
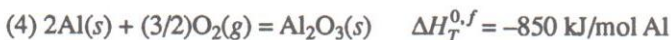
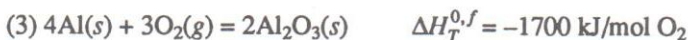
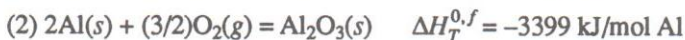
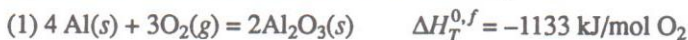
$$\text{Ans: } \Delta H_{298}^{0,f} = -288.4 \text{ kcal/mol} = -1207 \text{ kJ/mol.}$$

[2.7] Given  $\Delta H_T^{0,f} = -1133 \text{ kJ/mol O}_2$  for the reaction



(a) Show  $\Delta H_{298}^{0,f} = -1133 \text{ kJ/mol}$  if  $\Delta C_p \approx 0$ .

(b) Select the correct alternatives below for  $\Delta H_T^{0,f}$ .



Ans: (1) and (4).

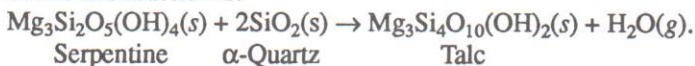
[2.8] Fifty grams of the mineral ilmenite,  $\text{FeTiO}_3$ , are heated in an insulated furnace and then quenched in a 500 gm copper vessel containing 200 gm of water. The temperature of the water and vessel both rise from  $30^\circ\text{C}$  to  $65^\circ\text{C}$ . To what temperature was the ilmenite heated prior to quenching?

Ans:  $T = 924^\circ\text{C}$ .

[2.9] Calculate the final temperature and enthalpy change of the mineral galena,  $\text{PbS}$ , when 253.62 gm of the mineral at  $80^\circ\text{C}$  are placed into 58.73 gm of adiabatically contained water initially at a temperature of  $27^\circ\text{C}$ . Express the enthalpy change in cal/mol  $\text{PbS}$ .

Ans:  $T = 36^\circ\text{C}$ ,  $\Delta H_{\text{PbS}} = -499 \text{ cal/mol}$ .

[2.10] Calculate the heat absorbed and standard enthalpy change at (a) 373 K and (b)  $373 \text{ K} < T < 800 \text{ K}$  resulting from the dehydration of the mineral serpentine,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ , in the presence of quartz to form talc,  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ . Use the heat capacity for  $\text{H}_2\text{O}(l)$  in Appendix A, Table A.3A and the heat capacity for  $\text{H}_2\text{O}(g)$  in Appendix A, Table A.3B. The reaction is:



Ans: (a)  $Q = \Delta H_{373}^0 = 1787 \text{ J/mol}$ ; (b)  $\Delta H_T^0 \text{ (J/mol)} = -69.42 \times 10^{-8}T^3 - 2.59T^2 + 4672.2T - 3.70 \times 10^7T^{-1} - 131,264T^{0.5} - 82,315$ .

[2.11] A high pressure mineral reaction occurring in some rocks buried to depths of 30 km or more within the earth involves the decomposition of the mineral albite (Ab) to form the minerals jadeite (Jd) and quartz

(Qz). Calculate the standard enthalpy change at 298 K for the albite decomposition reaction:



$$\text{Ans: } \Delta H_{298}^0 = -5 \text{ kJ/mol.}$$

- [2.12] Using the standard enthalpy change computed for the reaction in Exercise Problem [2.11], calculate the standard enthalpy change of this reaction at  $T$  where  $298 \text{ K} < T < 844 \text{ K}$ . No phase changes occur.

$$\text{Ans: } \Delta H_T^0 \text{ (J/mol)} = 53.21 \times 10^3 - 238.21T + 7.04 \times 10^{-2}T^2 - 7.57 \times 10^{-6}T^3 + 4.92 \times 10^6T^{-1} + 8.74 \times 10^3T^{0.5}.$$

- [2.13] At 1356 K and 1 atm pressure, the following exothermic reaction occurs:



Calculate the heat evolved and enthalpy of formation of  $\gamma\text{Cu}_2\text{S}(\text{s})$  at 1356 K and 1 atm pressure. Use the heat capacity for  $\text{S}_2(\text{g})$  in Appendix A, Table A.3B. Hint: begin with the reaction



$$\text{Ans: } Q_{1 \text{ atm}} = \Delta H_{1356}^{0,f} = -108 \text{ kJ/mol.}$$

- [2.14] Calculate the standard enthalpy of formation of methane,  $\text{CH}_4(\text{g})$ , at 298 K in kJ/mol and kcal/mol from the following information:



$$\text{Ans: } \Delta H_{298}^{0,f} = 13.22 \text{ kJ/mol} = 3.12 \text{ kcal/mol.}$$

- [2.15] The enthalpy increment for element A at two temperatures is given as follows:

$T$ (K)	$H_T^0 - H_{500}^0$ (J/mol)
1000	1750
700	640

Determine the heat capacity of A which most accurately reflects the data given.

$$\text{Ans: } C_p^A \text{ (J/mol)} = 2.0 + 2 \times 10^{-3}T.$$

- [2.16] Derive the formula

$$\Delta H_{T_2} = \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_p dT$$

where

- (a)  $\Delta H_{T_1}$  and  $\Delta H_{T_2}$  are the constant pressure molar enthalpy changes of a reaction in states 1 and 2 respectively.  
 (b) No phase changes occur between states 1 and 2.  
 (c) All reaction components exist as one mole in the balanced reaction.

- [2.17] Confirm the internal energy change for the transformation of potassium from liquid to vapor phase at 1000 K and 0.753 bar.

Ans:  $\Delta u = 1753$  kJ/kg.

- [2.18] A 20 kg mass falls 10 meters at constant velocity, thereby causing a paddle wheel to stir 500 g of adiabatically contained water initially at 25°C. Assume for the water a negligible change in volume and that  $C_v \approx C_p$ .
- (a) Find the internal energy change and temperature of the water after the weight has fallen 2,4,6,8, and 10 meters.  
 (b) Plot both internal energy change and gravitational potential energy versus temperature. What does the plot suggest?

Ans: (a):

Distance Fallen (m)	$E_p$ (J)	$\Delta U' = -W'_{Ad.}$ (J)	$T(^{\circ}\text{C})$
0.0	1962.0	0.0	25.0
2.0	1570.0	392.4	25.2
4.0	1177.0	784.8	25.4
6.0	784.8	1177.0	25.6
8.0	392.4	1570.0	25.8
10.0	0.0	1962.0	25.9

- (b) Linear plot is consistent with  $C_v = \text{constant}$ .