1 Summary of basic thermodynamic concepts

This chapter provides a summary of the three laws of thermodynamics and the important defined functions and relations for applying these laws to materials systems. It is assumed that the reader has completed an introductory course on thermodynamics. The purpose of this chapter is to bring the reader back "up to speed". An extensive reference list of thermodynamic data sources is also provided.

1.1 Basic thermodynamics

The subject of thermodynamics is based on three empirical laws and their application, generally through the use of specially defined functions. A summary of the three laws and the various defined functions follows. The reader is referred to one of the many comprehensive texts on thermodynamics for a more detailed treatment [1–4].

1.1.1 Extensive and molar properties of a thermodynamic system

The properties (state functions) which refer to the entire system and, therefore, are dependent on size (e.g. mass, volume) are termed *extensive* and may be represented by a generic quantity, Q'. Those properties which are independent of the size of the system (e.g. temperature, pressure) are termed *intensive*. The ratio of any two extensive properties becomes an intensive property. A particularly useful quantity of this type arises when a particular Q' is divided by the number of moles of material in

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the system, yielding a *molar quantity*, Q:

$$Q = \frac{Q'}{n} \tag{1.1}$$

For example, $V = V'/n$ is the molar volume of the system.

The contribution of each component to an extensive property of the system under isobaric and isothermal conditions is described by the *partial molar quantities*, $\bar{Q}_i$:

$$\bar{Q}_i \equiv \left(\frac{\partial Q'}{\partial n_i}\right)_{T,P,n_j} \tag{1.2}$$

where n_i represents the number of moles of component i and n_j represents the numbers of moles of the other components in the system. $\bar{Q}_i$ is that part of Q' which is contributed by one mole of component i. This is expressed as follows:

$$Q' = \sum_i n_i \bar{Q}_i \tag{1.3}$$

The important *Gibbs–Duhem* relation between the partial molar quantities [5] is obtained by combination of the definition of Q' in differential form,

$$dQ' = \sum_i n_i \, d\bar{Q}_i + \sum_i \bar{Q}_i \, dn_i \tag{1.4}$$

with the mathematical properties of $Q'(T, P, n_1, n_2, \ldots.)$

$$dQ' = \left(\frac{\partial Q'}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial Q'}{\partial P}\right)_{T,n_i} dP + \sum_i \bar{Q}_i \, dn_i \tag{1.5}$$

to yield

$$-\left(\frac{\partial Q'}{\partial T}\right)_{P,n_i} dT - \left(\frac{\partial Q'}{\partial P}\right)_{T,n_i} dP + \sum_i n_i \, d\bar{Q}_i = 0 \tag{1.6}$$

Similarly, the molar and partial molar quantities may be related and for the simple case of a binary system A–B with the mole fraction of

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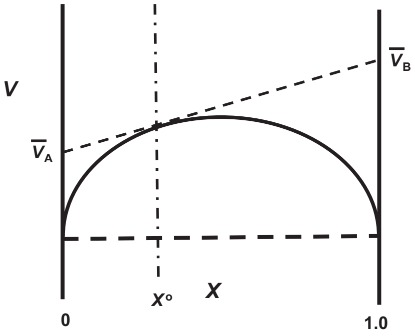

Figure 1.1 Plot of molar volume versus mole fraction for a hypothetical binary system A–B. The intercepts of the tangent drawn at $X°$ are the partial molar volumes.

component B represented by X the relations are

$$\bar{Q}_A = Q - X\frac{dQ}{dX} \tag{1.7}$$

$$\bar{Q}_B = Q + (1 - X)\frac{dQ}{dX} \tag{1.8}$$

These relations [5] have the simple graphical interpretation that the intercepts of a tangent to a plot of Q versus X at $X = 0$ and $X = 1$, respectively, are $\bar{Q}_\mathrm{A}$ and $\bar{Q}_\mathrm{B}$. The use of these relationships is illustrated in Figure 1.1 for a hypothetical binary system A–B. In this case Q represents the molar volume of the system, V. The tangent line drawn at composition X^0 has intercepts $\bar{V}_\mathrm{A}$ at $X = 0$ and $\bar{V}_\mathrm{B}$ at $X = 1.0$, which are the partial molar volumes of A and B, respectively, for a solution of that particular composition.

1.1.2 The first law

The *first law of thermodynamics* is a formulation of the *law of conservation of energy*. For a closed system without chemical reaction it may be written as

$$dE' = \delta q + \delta w \tag{1.9}$$

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where E' is the extensive *internal energy* of the system and is a state function, q is the *heat absorbed by the system* and w is the *work done on the system*. The heat and work are non-state functions (i.e. they are path-dependent), hence the symbol δ is used, rather than the usual d, for their differentials.

1.1.2.1 Work

Work can be done on the system by a variety of forces but can always be written according to the mechanics definition of the force multiplied by the distance through which it acts,

$$\delta w_i = F_i \, dx_i \tag{1.10}$$

In the case where the only work involves the system expanding against an external pressure, this expression becomes

$$\delta w = -P_{\text{ext}} \, dV' \tag{1.11}$$

This expression occurs in many applications, so other forms of work are referred to as "non-PV work" and are represented by $\delta w'$. Thus the total work done on the system is written as

$$\delta w = -P_{\text{ext}} \, dV' + \delta w' \tag{1.12}$$

An important example of non-PV work is *surface work*, which will be introduced in Chapter 2 and will play a major role in most of this book.

1.1.2.2 Heat

Heat is energy, which is in motion under the influence of a driving force, which is a temperature difference. Two important special cases are heat transport under conditions of constant volume and constant pressure. In the former case, in the absence of $\delta w'$, the path-dependent function q becomes the change in the state function E, following Equation (1.9).

Under these conditions the parameter relating q to the temperature difference is the constant-volume heat capacity,

$$C_V \equiv \left(\frac{\partial E}{\partial T}\right)_V \tag{1.13}$$

Thus, the heat flow associated with changing the temperature of a system from T_1 to T_2 is

$$q = \Delta E' = n \int_{T_1}^{T_2} C_V \, dT \tag{1.14}$$

The constant-pressure case is conveniently formulated in terms of the state function known as the *enthalpy*:

$$H' \equiv E' + PV' \tag{1.15}$$

The first law in terms of enthalpy becomes

$$dH' = dE' + P\,dV' + V'\,dP = q + V'\,dP + \delta w' \tag{1.16}$$

In the case of constant pressure and the absence of $\delta w'$, the path-dependent function q becomes the change in the state function H. Under these conditions the parameter relating q to the temperature difference is the constant-pressure heat capacity,

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P \tag{1.17}$$

Thus, the heat flow associated with changing the temperature of a system from T_1 to T_2 at constant pressure is

$$q = \Delta H' = n \int_{T_1}^{T_2} C_P \, dT \tag{1.18}$$

1.1.3 The second law

The question of whether or not a process can occur is answered by the *second law of thermodynamics*. The mathematical statement of the

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second law, which follows directly from the empirical statements, is, for an isolated system,

$$dS' \geq 0 \tag{1.19}$$

where S is the state function known as *entropy*, which is defined by

$$dS' \equiv \frac{\delta q_{\text{rev}}}{T} \tag{1.20}$$

The inequality in Equation (1.19) pertains to a process that will tend to occur irreversibly (spontaneously), whereas the equality pertains to a *reversible process*, i.e. one in which the system is never displaced from equilibrium by a finite amount. An equivalent expression for the second law, which does not require the constraint of an isolated system, is

$$dS'_{\text{system}} + dS'_{\text{surroundings}} \geq 0 \tag{1.21}$$

The surroundings are presumed to behave reversibly, so that Equation (1.21) may be written as

$$dS'_{\text{system}} + \frac{\delta q_{\text{surroundings}}}{T} \geq 0 \tag{1.22}$$

or, noting that $\delta q_{\text{surroundings}} = -\delta q_{\text{system}}$,

$$\delta q_{\text{system}} \leq T\, dS'_{\text{system}} \tag{1.23}$$

Note that, for the special case of constant pressure and $\delta w' = 0$, Equation (1.20) may be written as

$$dS' = \frac{dH'}{T} = \frac{nC_P\, dT}{T} \tag{1.24}$$

1.1.4 The third law

The third law is based on the observation that the entropy change for some reactions approaches zero as the temperature approaches 0 K. If

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the entropy of the component elements is arbitrarily set to zero then the entropy of a compound formed from those elements would also be zero. This has been discussed in detail by Lupis in Section I.3 of Reference [3]. The third law may then be expressed as follows:

> If the entropy of each element in complete thermodynamic equilibrium is taken as zero at zero Kelvin the entropy of every other substance becomes zero at zero Kelvin if the substance is in complete thermodynamic equilibrium.

In equation form this may be expressed as

$$S^{\circ}_{0\mathrm{K}} = 0 \tag{1.25}$$

and the entropy of the substance at any temperature, T, is just the entropy increment for heating the substance from 0 K to T, i.e. absolute values of the entropy may be calculated.

1.1.5 Combined first and second laws

Many of the useful applications of thermodynamics result from combining the first and second laws in terms of appropriate functions under the assumption of reversible conditions. The second law may be combined with the first law by substituting Equation (1.23) for the heat absorbed by the system into Equation (1.9), giving

$$dE' \leq T\,dS' - P\,dV' + \delta w' \tag{1.26}$$

The combined first and second laws may also be written in terms of other state functions, which are defined for convenience in solving certain types of problems. These include the *enthalpy* (Equation (1.15)) such that

$$dH' = dE' + P\,dV' + V'\,dP \leq T\,dS' + V'\,dP + \delta w' \tag{1.27}$$

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the *Helmholtz free energy*,

$$F' \equiv E' - TS' \tag{1.28}$$

which yields

$$dF' \leq -P\,dV' - S'\,dT + \delta w' \tag{1.29}$$

and the *Gibbs free energy*,

$$G' \equiv H' - TS' \tag{1.30}$$

which yields

$$dG' \leq V'\,dP - S'\,dT + \delta w' \tag{1.31}$$

Two useful relations result from Equations (1.29) and (1.31). Firstly, under isothermal conditions Equation (1.29) becomes

$$dF' \leq -P\,dV' + \delta w' = \delta w_{\text{tot}} = -\delta w_{\text{by system}} \tag{1.32}$$

The relation in Equation (1.32) indicates that the work done by the system will always be less than or equal to the negative of the change in Helmholtz free energy. Thus the maximum isothermal work which can be obtained from the system will correspond to the equality, i.e. reversible conditions. Similarly under isothermal, isobaric conditions Equation (1.31) becomes

$$dG' \leq \delta w' \tag{1.33}$$

Multicomponent and open systems require additional terms in Equations (1.26), (1.27), (1.29) and (1.31) to include the contributions to the various functions made by adding or removing matter from the system. These terms are the chemical potentials of each component in the system, defined by

$$\mu_i \equiv \left(\frac{\partial E'}{\partial n_i}\right)_{S',V',n_1,n_2,\ldots} \tag{1.34}$$

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Thus, Equation (1.26) becomes

$$dE' \leq T\,dS' - P\,dV' + \sum_{i=1}^{N} \mu_i\,dn_i + \delta w' \tag{1.35}$$

for a multicomponent system. Addition of the identity

$$d(PV' - TS') = P\,dV' + V'\,dP - T\,dS' - S'\,dT \tag{1.36}$$

to Equation (1.35) yields

$$dG' \leq V'\,dP - S'\,dT + \sum_{i=1}^{N} \mu_i\,dn_i + \delta w' \tag{1.37}$$

Thus, the chemical potential of a component is equivalent to its *partial molar Gibbs free energy*,

$$\mu_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n_1,n_2,\ldots} = \bar{G}_i \tag{1.38}$$

Similar operations yield

$$\mu_i = \left(\frac{\partial H'}{\partial n_i}\right)_{S',P,n_1,n_2,\ldots} = \left(\frac{\partial F'}{\partial n_i}\right)_{T,V',n_1,n_2,\ldots} \tag{1.39}$$

It should be noted that the chemical potentials written in terms of E', H' and F' do not correspond to partial molar quantities.

1.1.5.1 A note on Maxwell reciprocal relations

The combined first and second laws all have the same mathematical form. If reversible conditions are invoked, the general form is that of a perfect differential,

$$dQ' = \left(\frac{\partial Q'}{\partial x_1}\right)_{x_2,x_3,\ldots} dx_1 + \left(\frac{\partial Q'}{\partial x_2}\right)_{x_1,x_3,\ldots} dx_2 + \left(\frac{\partial Q'}{\partial x_3}\right)_{x_1,x_2,\ldots} dx_3 + \cdots \tag{1.40}$$

where x_1, x_2, x_3, etc. are appropriate state variables. The mathematical properties of Equation (1.40) are such that the mixed second partial

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derivatives of Q' are independent of the order of differentiation. For example,

$$\left(\frac{\partial^2 Q'}{\partial x_1\,\partial x_2}\right) = \left(\frac{\partial^2 Q'}{\partial x_2\,\partial x_1}\right) \tag{1.41}$$

where all variables other than the differentiation variable are held constant in each operation. Equation (1.41) is the general form of the *Maxwell reciprocal relations*, which are useful for implementing changes of variable in various calculations. As an example, if $\delta w' = 0$ in Equation (1.37) and T and P are the variables of differentiation, Equation (1.41) becomes

$$\left(\frac{\partial V}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial S}{\partial P}\right)_{T,n_i} \tag{1.42}$$

This expression is useful in that it converts the pressure dependence of entropy to a simple quantity,

$$\left(\frac{\partial V}{\partial T}\right)_{P,n_i}$$

which is directly related to the coefficient of thermal expansion. Clearly there are many Maxwell relations, which arise from the different forms of the combined first and second laws depending on the operative system state variables. A more extensive discussion of these relations is presented in Chapter 5 of Reference [2].

1.2 Multicomponent systems – solution thermodynamics

The changes in properties when a solution is formed from its components are described by the mixing quantities. The partial molar mixing quantities for each component are given by

$$\Delta \bar{Q}_i^{\mathrm{M}} = \bar{Q}_i - Q_i^{\circ} \tag{1.43}$$