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Chapter 5

Auxiliary Functions

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5.1 INTRODUCTION

Combination of the First and Second Laws of Thermodynamics leads to the derivation of Eq. (3.12)

$$dU = TdS - PdV$$

In this chapter the thermodynamic functions A (the Helmholtz free energy), G (the Gibbs free energy), and μ_i (the chemical potential of the species i) are introduced, and their properties and interrelationships are examined. The functions A and G are defined as

$$A = U - TS \tag{5.1}$$

and

$$\begin{aligned} G &= U + PV - TS \\ &= H - TS \end{aligned} \tag{5.2}$$

5.2 THE ENTHALPY *H*

A closed system undergoing a change of state at constant pressure, *P*, from the state 1 to the state 2, the First Law gives

$$U_2 - U_1 = q_p - P(V_2 - V_1)$$

which, on rearrangement, gives

$$(U_2 + PV_2) - (U_1 + PV_1) = q_p$$

or

$$\Delta H = H_2 - H_1 = q_p$$

5.3 THE HELMHOLTZ FREE ENERGY *A*

For a system undergoing a change of state from state 1 to state 2, Eq. (5.1) gives

$$(A_2 - A_1) = (U_2 - U_1) - (T_2S_2 - T_1S_1)$$

and, if the system is closed,

$$(U_2 - U_1) = q - w$$

in which case

$$(A_2 - A_1) = q - w - (T_2S_2 - T_1S_1)$$

If the process is isothermal, that is, $T_2=T_1=T$, the temperature of the heat reservoir which supplies or withdraws heat during the process, then, from the Second Law, Eq. (3.4a),

$$q \leq T(S_2 - S_1)$$

and hence

$$(A_2 - A_1) \leq -w$$

Comparison with Eq. (3.11) shows that the equality can be written as

$$(A_2 - A_1) + T\Delta S_{irr} = -w \tag{5.3}$$

and thus, during a reversible isothermal process, for which ΔS_{irr} is zero, the amount of work done by the system w_{max} is equal to the decrease in the value of the Helmholtz free energy. Furthermore, for an isothermal process conducted at constant volume, which, necessarily, does not perform *P-V* work, Eq. (5.3) gives

$$(A_2 - A_1) + T\Delta S_{irr} = 0 \tag{5.4}$$

or, for an increment of such a process,

$$dA + TdS_{irr} = 0$$

As dS_{irr} is always positive during a spontaneous process it is thus seen that A decreases during a spontaneous process, and as $dS_{irr}=0$ is a criterion for a reversible process, equilibrium requires that

$$dA = 0 \tag{5.5}$$

Thus in a closed system held at constant *T* and *V*, the Helmholtz free energy can only decrease or remain constant, and equilibrium is attained in such a system when *A* achieves its minimum value.
The Helmholtz free energy thus provides a criterion for equilibrium in a system at constant temperature and constant volume.

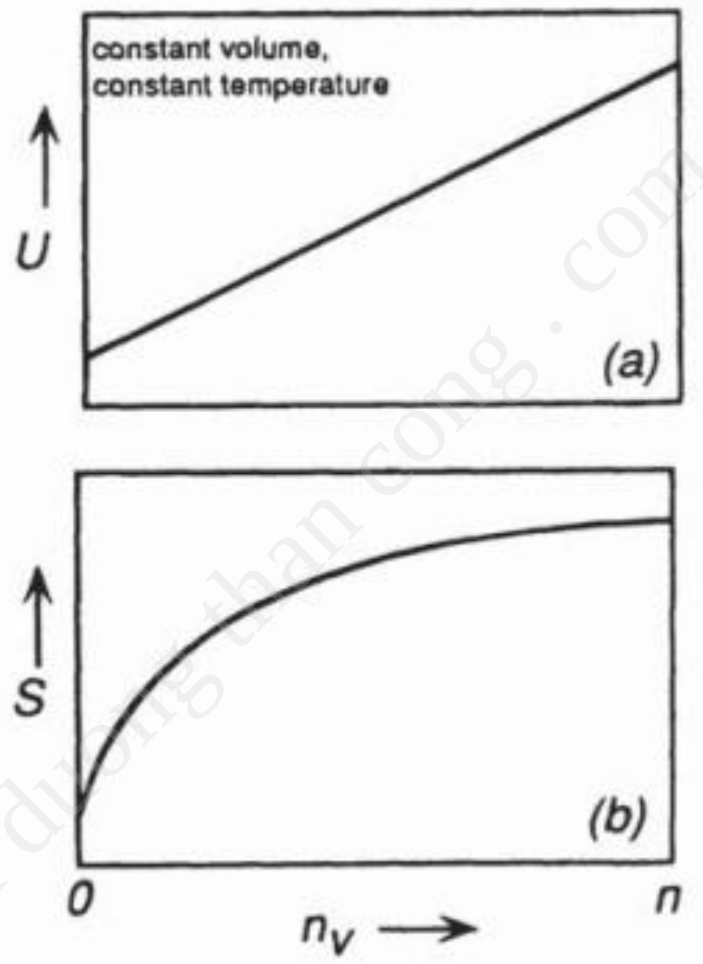

Figure 5.1 The variations of (a) internal energy, U, and (b) entropy, S, with the number of atoms in the vapor phase of a closed solidvapor system at constant temperature and constant volume.

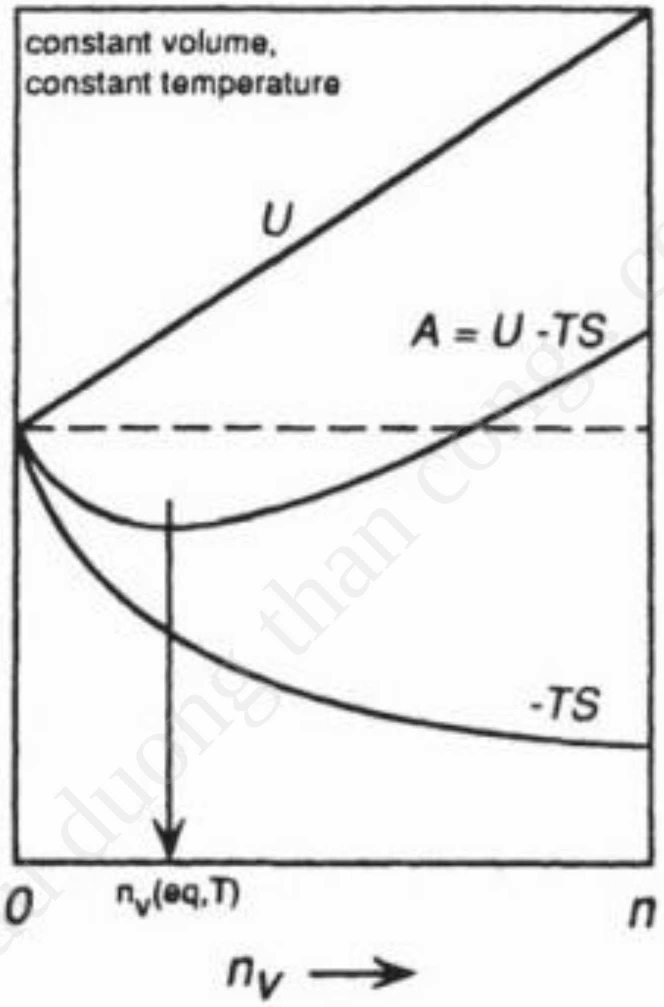

Figure 5.2 Illustration of the criterion for equilibrium in a closed solidvapor system at constant temperature and constant volume.

The saturated vapor pressure, is given by

$$p = \frac{n_{v(\text{eq},T)} kT}{(V - V_S)}$$

in which *V* is the volume of the containing vessel, *Vs* is the volume of the solid phase present, and *k* is Boltzmann's constant

An increase in the temperature from T_1 to T_2

$$p_{(\text{at } T_1)} = \frac{n_{v(\text{eq},T_1)} kT_1}{(V - V_{S(\text{at } T_1)})}$$

to

$$p_{(\text{at } T_2)} = \frac{n_{v(\text{eq},T_2)} kT_2}{(V - V_{S(\text{at } T_2)})}$$

5.4 THE GIBBS FREE ENERGY *G*

For a system undergoing a change of state from 1 to 2, Eq. (5.2) gives

$$\begin{aligned}(G_2 - G_1) &= (H_2 - H_1) - (T_2S_2 - T_1S_1) \\ &= (U_2 - U_1) + (P_2V_2 - P_1V_1) - (T_2S_2 - T_1S_1)\end{aligned}$$

For a closed system, the First Law gives

$$(U_2 - U_1) = q - w$$

and thus

$$(G_2 - G_1) = q - w + (P_2V_2 - P_1V_1) - (T_2S_2 - T_1S_1) \tag{5.6}$$

If *T*1=*T*2=*T*, the constant temperature of the heat reservoir which supplies or withdraws heat from the system,
and if *P*1=*P*2=*P*, the constant pressure at which the system undergoes a change in volume,
Then

$$(G_2 - G_1) = q - w + P(V_2 - V_1) - T(S_2 - S_1)$$

The First Law the work *w* is the *total* work done on or by the system during the process. Thus if the system performs chemical or electrical work in addition to the work of expansion against the external pressure, then these work terms are included in *w.*
Thus *w* can be expressed as

$$w = w' + P(V_2 - V_1)$$

in which *P*(*V*2–*V*1) is the *P*-*V* work done by the change in volume at the constant pressure*P* and *w*' is the sum of all of the non-*P*-*V* forms of work done.

Substituting into Eq. (5.6) gives

$$(G_2 - G_1) = q - w' - T(S_2 - S_1)$$

and again, as

$$q \leq T(S_2 - S_1)$$

then

$$w' \leq -(G_2 - G_1) \qquad (5.7)$$

Again, the equality can be written as

$$-w' = (G_2 - G_1) + T\Delta S_{irr}$$

Thus, for an isothermal, isobaric process, during which no form of work other than P-V work is performed, i.e., $w'=0$

$$(G_2 - G_1) + T\Delta S_{irr} = 0 \qquad (5.8)$$

As $dS_{irr}=0$ is a criterion for thermodynamic equilibrium, then an increment of an isothermal isobaric process occurring at equilibrium requires that

$$dG = 0 \qquad (5.9)$$

5.5 SUMMARY OF THE EQUATIONS FOR A CLOSED SYSTEM

Eq. (3.12) gives

$$dU = TdS - PdV$$

Now,

$$H = U + PV \text{ and thus } dH = TdS + VdP \qquad (5.10)$$

$$A = U - TS \text{ and thus } dA = -SdT - PdV \qquad (5.11)$$

$$G = H - TS \text{ and thus } dG = -SdT + VdP \qquad (5.12)$$

5.6 THE VARIATION OF THE COMPOSITION AND SIZE OF THE SYSTEM

The Gibbs free energy, *G*, is thus a function of *T*, *P*, and the numbers of moles of all of the species present in the system, i.e.,

$$G = G(T, P, n_i, n_j, n_k, \ldots) \qquad (5.13)$$

in which *ni*, *nj*, *nk*, *nk*, …are the numbers of moles of the species *i*, *j*, *k*, …present in the system and the state of the system is only fixed when all of the independent variables are fixed

Differentiation of Eq. (5.13) gives

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i,n_j,\ldots} dt + \left(\frac{\partial G}{\partial P}\right)_{T,n_i,n_j,\ldots} dP + \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,n_k,\ldots} dn_i + \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_i,n_k,\ldots} dn_j + \text{etc.} \qquad (5.14)$$

If the numbers of moles of all of the individual species remain constant during the process, Eq. (5.14) simplifies to Eq. (5.12), i.e.,

$$dG = -SdT + VdP$$

from which it is seen that

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_i,n_j,\ldots} = -S$$

and

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

Substitution into Eq. (5.14) gives

$$dG = -SdT + VdP + \sum_{i=1}^{i=k} \left(\frac{\partial G}{dn_i} \right)_{T,P,n_j,\ldots} dn_i \qquad (5.15)$$

where

$$\sum_{i=1}^{i=k} \left(\frac{\partial G}{dn_i} \right)_{T,P,n_j,\ldots} dn_i$$

is the sum of *k* terms (one for each of the *k* species) each of which is determined by partial differentiation of *G* with respect to the number of moles of the *i*th species at constant *T*, *P*, and n_j, where *nj* represents the numbers of moles of every species other than the ith species.

5.7 THE CHEMICAL POTENTIAL

The term $(\partial G/\partial n_i)_{T,p,nj,\ldots}$ is called *the chemical potential of the species i* and is designated as μ_i, i.e.,

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,\ldots} = \mu_i \qquad (5.16)$$

Eq. (5.15) can thus be written as

$$dG = -SdT + VdP + \sum_{1}^{k} \mu_i dn_i \qquad (5.17)$$

in which from *G* is expressed as a function of *T*, *P*, and composition

$$dU = TdS - PdV + \sum_{1}^{k} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j,\ldots} dn_i \qquad (5.18)$$

$$dH = TdS - VdP + \sum_{1}^{k} \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j,\ldots} dn_i \qquad (5.19)$$

$$dA = -SdT + PdV + \sum_{1}^{k} \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j,\ldots} dn_i \qquad (5.20)$$

Inspection of Eqs. (5.16), (5.18), (5.19), and (5.20) shows that

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} \qquad (5.21)$$

and, hence, the complete set of equations is

$$dU = TdS - PdV + \sum \mu_i dn_i \tag{5.22}$$

$$dH = TdS + VdP + \sum \mu_i dn_i \tag{5.23}$$

$$dA = -SdT - PdV + \sum \mu_i dn_i \tag{5.24}$$

$$dG = -SdT + VdP + \sum \mu_i dn_i \tag{5.25}$$

The First Law gives

$$dU = \delta q - \delta w$$

which, on comparison with Eq. (5.22), indicates that, for a closed system undergoing a process involving a reversible change in composition (e.g., a reversible chemical reaction),

$$\delta q = TdS$$

and

$$\delta w = PdV + \sum \mu_i dn_i$$

The term $\Sigma\, \mu_i dn_i$ is thus the chemical work done by the system which was denoted as w' in Eq. (5.8), and the total work w is the sum of the P-V work and the chemical work.

5.8 THERMODYNAMIC RELATIONS

The following relationships are obtained from Eqs. (5.22)–(5.25).

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,\mathrm{comp}} = \left(\frac{\partial H}{\partial S}\right)_{P,\mathrm{comp}} \tag{5.26}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,\mathrm{comp}} = -\left(\frac{\partial A}{\partial V}\right)_{T,\mathrm{comp}} \tag{5.27}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,\mathrm{comp}} = \left(\frac{\partial G}{\partial P}\right)_{T,\mathrm{comp}} \tag{5.28}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,\mathrm{comp}} = -\left(\frac{\partial G}{\partial T}\right)_{P,\mathrm{comp}} \tag{5.29}$$