

Chapter 5

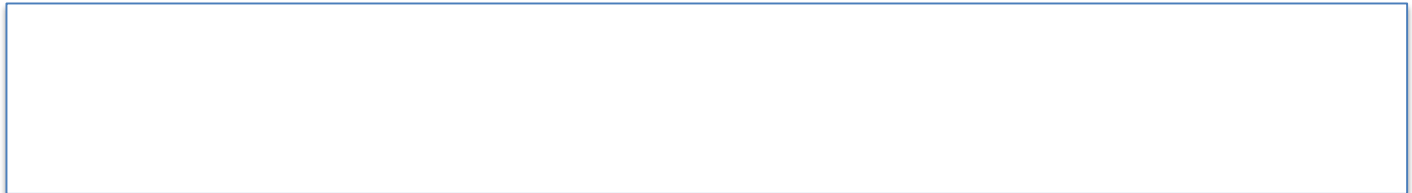
AUXILIARY FUNCTIONS

5.1 Introduction

- The main power of the thermodynamic method stems from its provision of criteria for equilibrium in materials systems
- S and V are an inconvenient choice of independent variables.

5.1 Introduction

- From the theoretician's point of view the most convenient choice of independent variables would be V and T



$$\begin{aligned} G &= (U + PV) - TS \text{ (The Gibbs F.E.)} \\ &= H - TS \end{aligned} \quad \mathbf{(5.2)}$$

5.2 The Enthalpy, H

- For a closed system with const. P

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

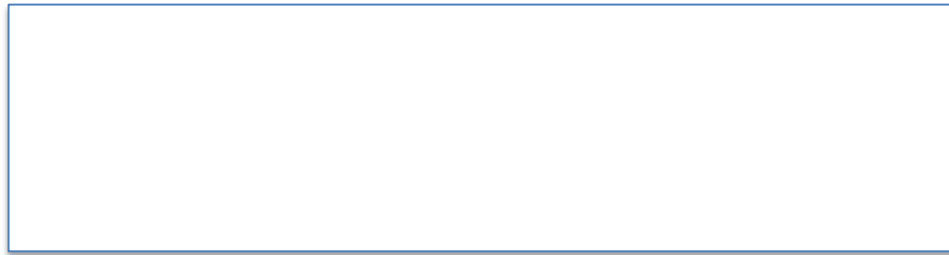
$$(U_2 + PV_2) - (U_1 + PV_1) = q_p$$

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

5.3 THE HELMHOLTZ FREE ENERGY, A

$$(A_2 - A_1) = (U_2 - U_1) - (T_2 S_2 - T_1 S_1)$$

If the system is closed



- If the process is isothermal, $T_2 = T_1 = T$, then, from the 2nd Law

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

5.3 THE HELMHOLTZ FREE ENERGY, A

- Hence

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

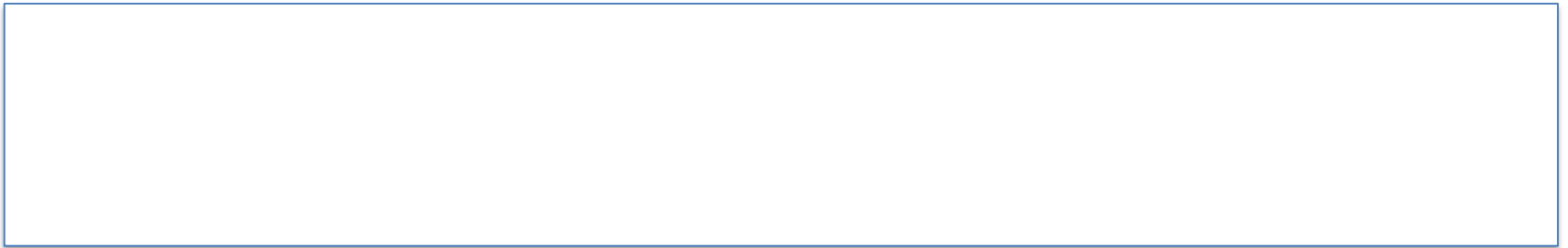
$$(A_2 - A_1) + T\Delta S_{\text{irr}} = -w \quad (5.3)$$

5.3 THE HELMHOLTZ FREE ENERGY, A

- For an isothermal process conducted at const. V, no P-V work,

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

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



- For a reversible process, $dA = 0$, **reversible means equilibrium!**

5.3 THE HELMHOLTZ FREE ENERGY, A

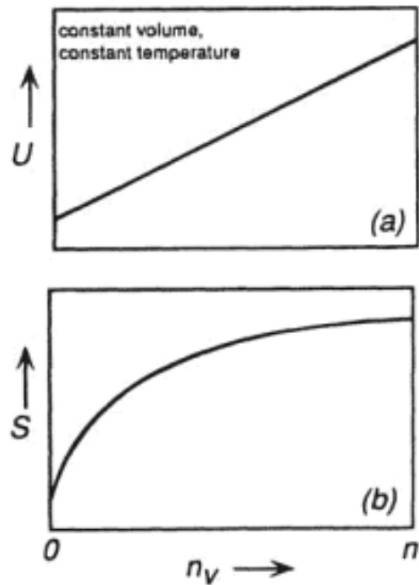


Figure 5.1 The variations of (a) internal energy, U , and (b) entropy, S , with the number of atoms in the vapor phase of a closed solidvapor system at constant temperature and constant volume.

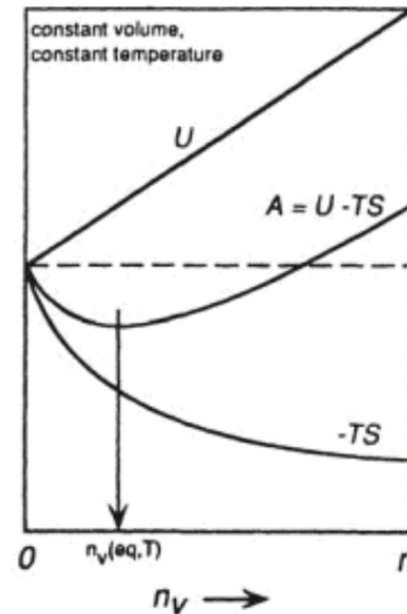


Figure 5.2 Illustration of the criterion for equilibrium in a closed solidvapor system at constant temperature and constant volume.

5.3 THE HELMHOLTZ FREE ENERGY, A

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

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

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

$$\ln p (\text{atm}) = \frac{-3166}{T} + 16.01$$

$$\Delta A = -T\Delta S_{\text{irr}}$$

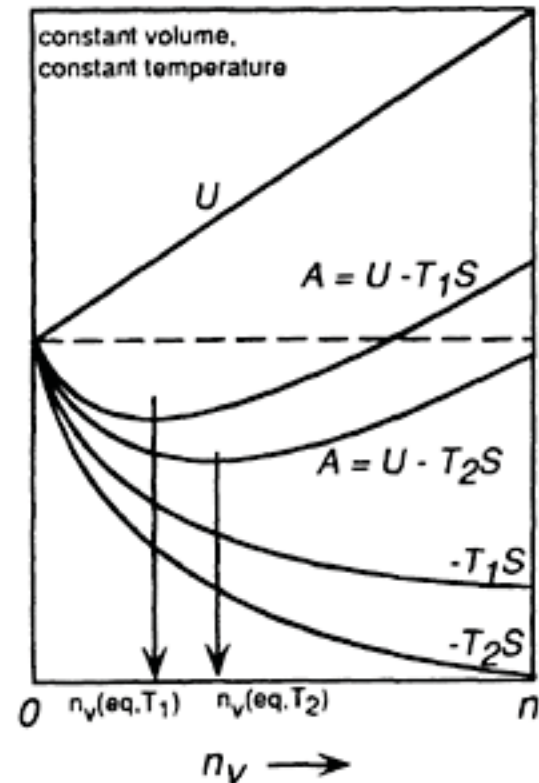


Figure 5.3 The influence of temperature on the equilibrium state of a closed solid-vapor system of constant volume.

5.4 THE GIBBS FREE ENERGY, G

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

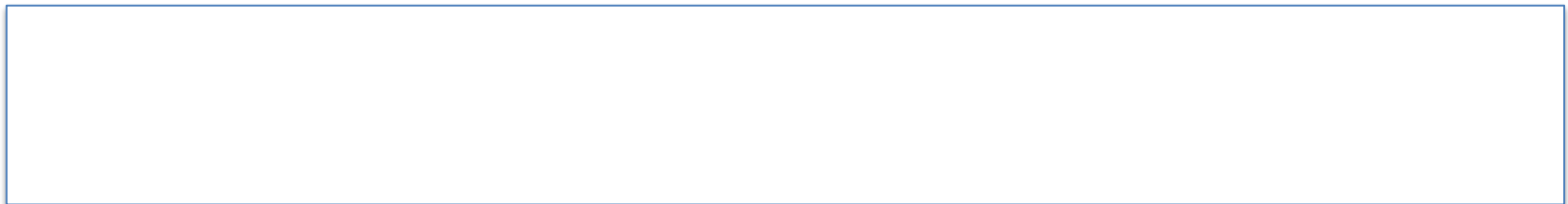
For a closed system, $(U_2 - U_1) = q - w$

If $T_1 = T_2 = T$, and $P_1 = P_2 = P$

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

w is the total work

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

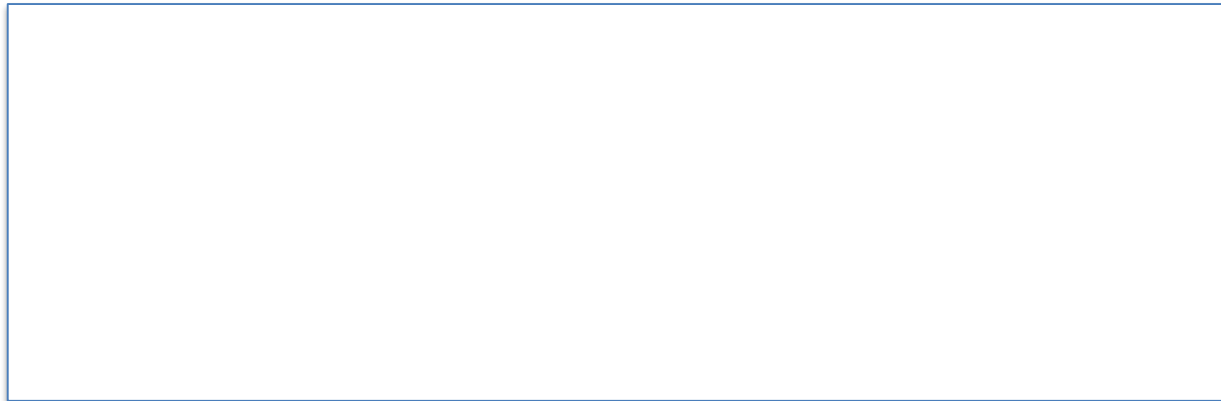


5.4 THE GIBBS FREE ENERGY, G

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

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

$$w' \leq -(G_2 - G_1) \tag{5.7}$$



(5.8)

(5.9)

5.5 SUMMARY OF THE EQ. FOR A CLOSED SYS.

$$dU = TdS - PdV$$

$$H = U + PV, \quad (5.10)$$

$$A = U - TS, \quad (5.11)$$

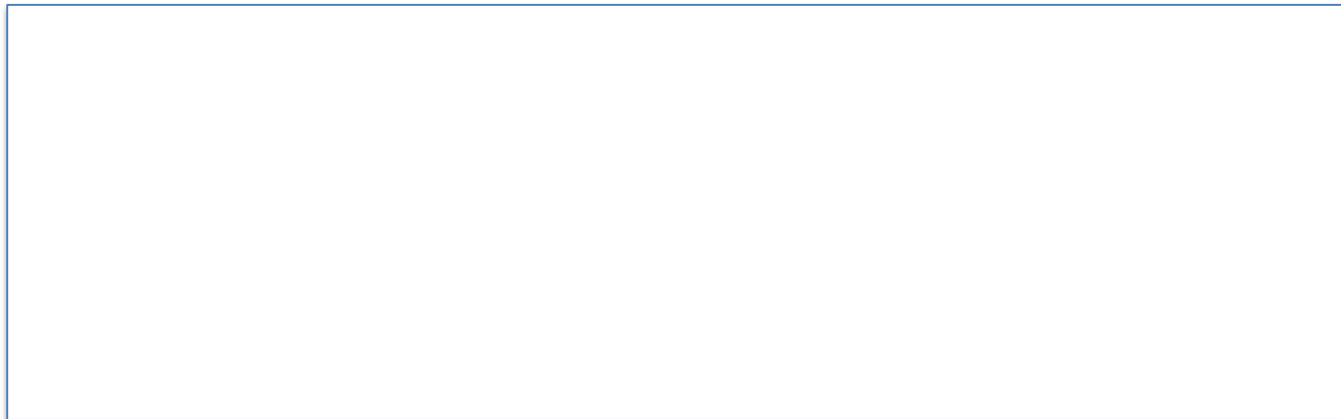
$$G = H - TS, \quad (5.12)$$

5.6 THE VARIATION OF THE COMPO. & SIZE OF THE SYS.

- If the size & composition can vary during a process, then the specification of only two variables is no longer sufficient to fix the state of the system

$$G=G(T,P,n_i,n_j,n_k,\dots) \quad (5.13)$$

- Differentiation of Eq.(5.13)



(5.14)

5.6 THE VARIATION OF THE COMPO. & SIZE OF THE SYS.

$$dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \dots} = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots} = V$$

(5.15)

5.7 The Chemical Potential

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

μ_i is the amount by which the capacity of the system for doing work, other than the work of expansion, is increased, per mole of i added at const. T , P and $i \neq j$.

$$dG = -SdT + VdP + \sum_1^k \mu_i dn_i \quad (5.17)$$

Applicable to open system which exchange matter as well as heat with surrounding, to closed system which undergoes compositional change.

To open system

$$dU = TdS - PdV + \sum_1^k \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j,\dots} dn_i \quad (5.18)$$

$$(5.19)$$

$$(5.20)$$

5.7 The Chemical Potential

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

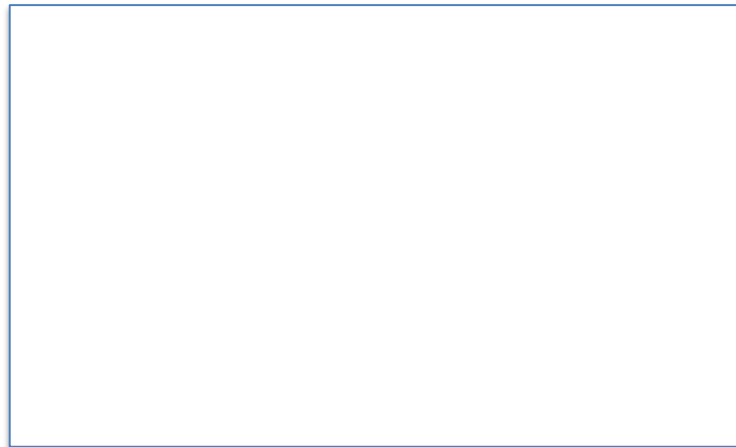
(5.22)

(5.23)

(5.24)

(5.25)

Fundamental Eq.



From the 1st & 2nd laws

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

$$\delta q = TdS$$

The comparison gives

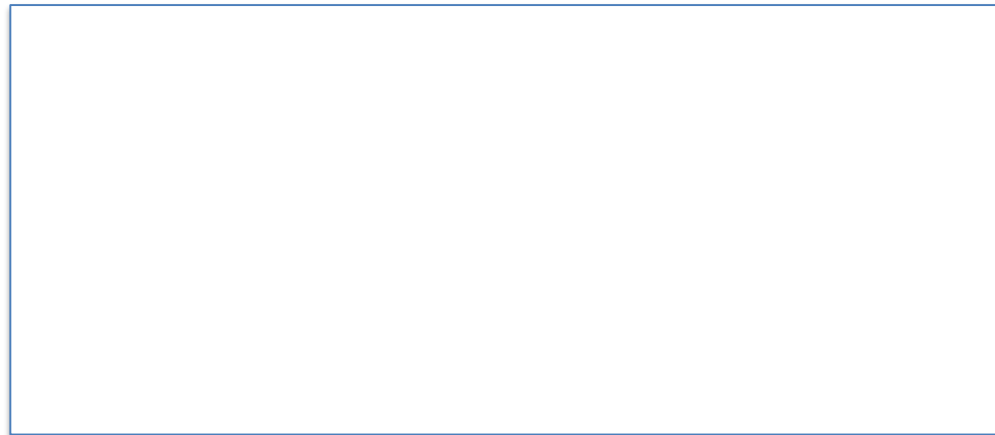
$$\delta w = PdV + \sum \mu_i dn_i$$

= w' = chemical work

5.8 Thermodynamic Relations

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

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



(5.28)

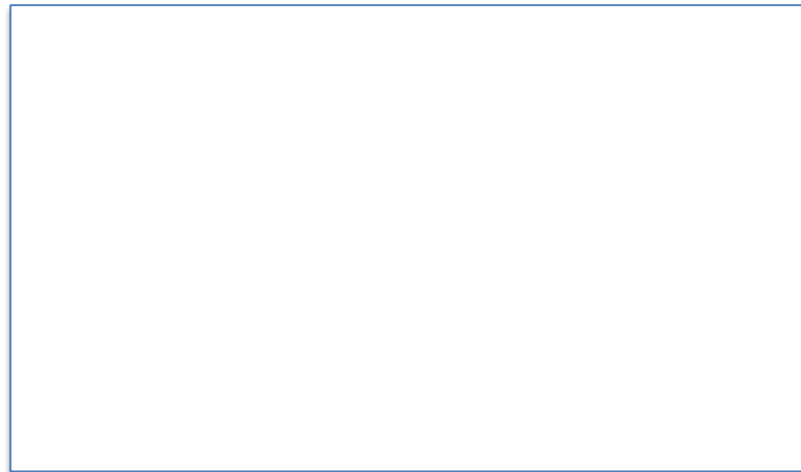
(5.29)

5.9 Maxwell's Equations

If Z is a state function, then $Z = Z(x,y)$

$$dZ = \left(\frac{\partial Z}{\partial x} \right)_y dx + \left(\frac{\partial Z}{\partial y} \right)_x dy$$

$$dZ = Ldx + Mdy$$



5.9 Maxwell's Equations

If Z is a state function, the change in Z is indep. of the order of differentiation.

$$\left[\frac{\partial}{\partial y} \left(\frac{\partial Z}{\partial x} \right)_y \right]_x = \left[\frac{\partial}{\partial x} \left(\frac{\partial Z}{\partial y} \right)_x \right]_y = \frac{\partial^2 Z}{\partial x \partial y}$$

$$\left(\frac{\partial L}{\partial y} \right)_x = \left(\frac{\partial M}{\partial x} \right)_y \quad (5.30)$$

$$dU = TdS - PdV \quad (5.31)$$

$$dH = TdS + VdP \quad (5.10) \quad (5.32)$$

$$dA = -SdT - PdV \quad (5.11) \quad (5.33)$$

$$dG = -SdT + VdP \quad (5.12) \quad (5.34)$$

(5.33) & (5.34) are measurable quantities!

5.9 Maxwell's Equations

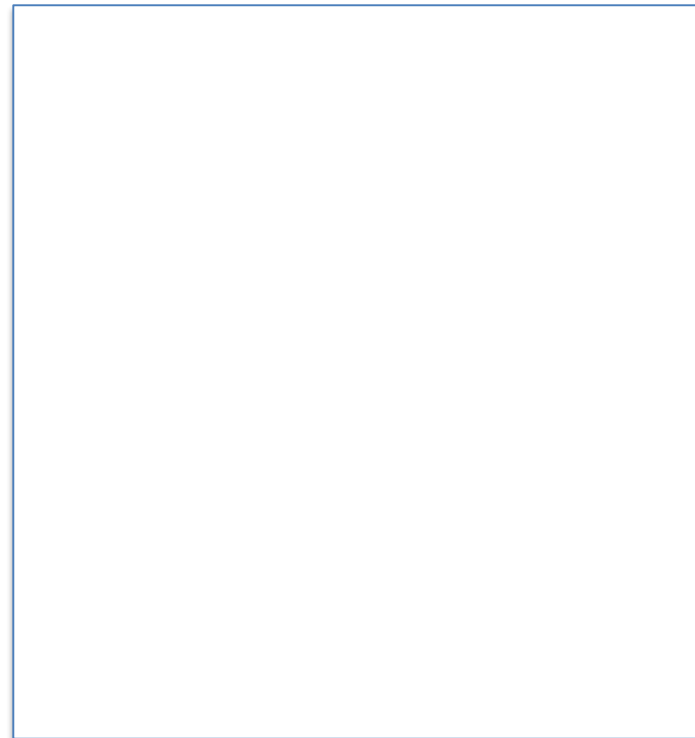
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (5.33)$$

$$S = S(T, V)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{(i)}$$

$$TdS = \delta q_v = dU = nc_v dT$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{nc_v}{T}$$



(ii)

(iii)

(iv)

(v)

5.9 Maxwell's Equations

For closed system of fixed composition,

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$
$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

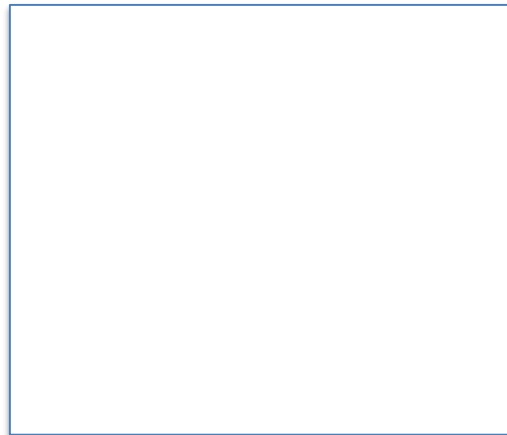
From (5.33)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Similarly, $dH = TdS + VdP$

From (5.34)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$



5.10 The Upstairs-Downstairs-Inside-Out Formula

For closed system of fixed composition, with 3 state properties, x , y , & z :

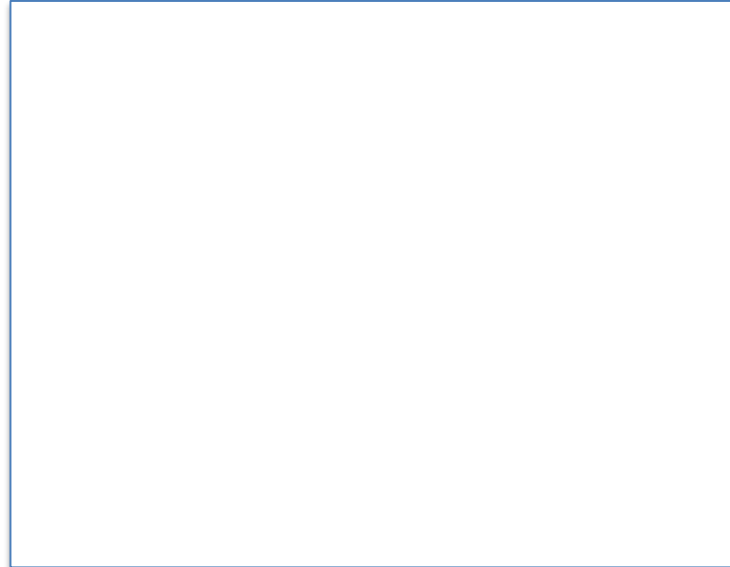
$$x = x(y,z)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

For an incremental change of state at const. x ,

then,

or,

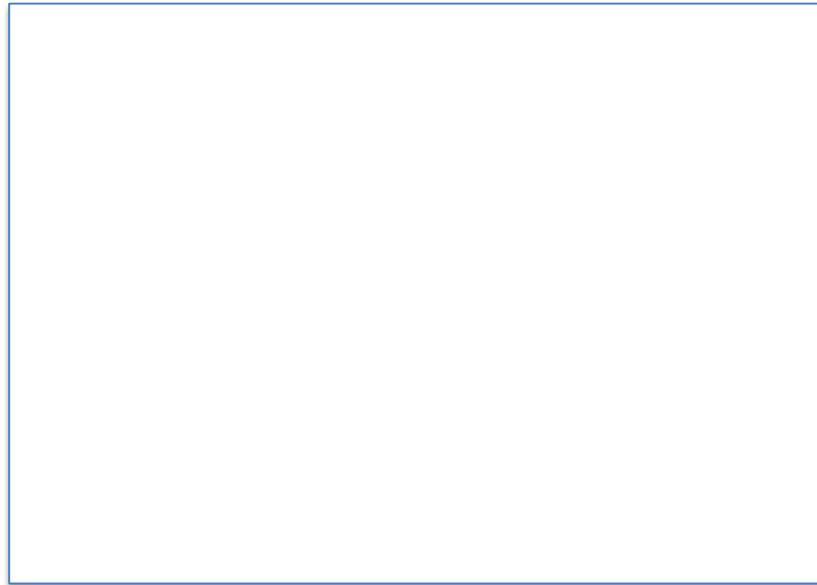


(5.35)

5.11 The Gibbs-Helmholtz Equation

$$G = H - TS$$

$$dG = -SdT + VdP \quad (5.12) \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$



5.11 The Gibbs-Helmholtz Equation



(5.36)

(5.36a)

ΔG can be determined from an experimentally measured ΔH ,

Similarly,

$$\begin{aligned} A &= U - TS \\ &= U + T \left(\frac{\partial A}{\partial T} \right)_V \end{aligned}$$

$$\frac{d(A/T)}{dT} = -\frac{U}{T^2} \quad \text{(5.37)}$$

$$\frac{d(\Delta A/T)}{dT} = -\frac{\Delta U}{T^2} \quad \text{(5.37a)}$$