

$$dS = \underbrace{\delta S^{(r)}}_{\text{entropy supply}} + \underbrace{\delta S^{(i)}}_{\text{entropy production}} \quad (3)$$

where $\delta S^{(i)} = \begin{cases} 0 & \text{reversible process} \\ \text{non zero} & \text{irreversible process} \end{cases}$

$$\delta S^{(r)} = \frac{\delta q}{T}$$

Overall entropy change of system is a state function $\Rightarrow dS$
Entropy supply/production are not; depend on particular processes that the state has changed $\Rightarrow \delta S^{(r)}, \delta S^{(i)}$

For an isolated system, $\delta q = 0$, thus Eq. (2) becomes

$$dS \geq 0 \quad (4)$$

ie. entropy ~~change~~ of an isolated system remains the same or increases.

3. First and Second Law combined

Since $T > 0$, Eq. (2) gives $\delta q \leq T dS$

Write Eq. (1) as $dU = \delta q + \delta W_p + \delta W_e$
 $= \delta q - p dV + \delta W_e \leq T dS - p dV + \delta W_e$

$$dU \leq T dS - p dV + \delta W_e \quad (5)$$

where equality holds at equilibrium.

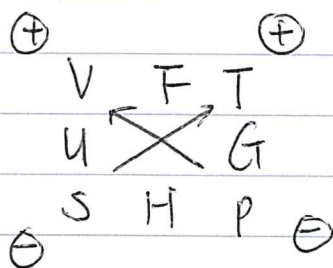
3.1 ^{energy} other state function

$$H = U + pV = A + TS$$

$$A = U - TS = G - pV$$

$$G = H - TS = U + pV - TS = A + pV$$

3.2 Fundamental Relations other than Eq. (5) can be obtained from a thermodynamic square or from ~~the~~ Section 3.1 definition of energy state functions.



3.3 Maxwell Equations follow from the fact that all the energy state functions are path independent and that their differentials are exact

• if $df = udx + vdy$ is an exact differential, then

$$\left(\frac{\partial u}{\partial y}\right)_x = \left(\frac{\partial v}{\partial x}\right)_y$$

so, given $dU = Tds - pdV$, we have

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

since dU is an exact differential. Same things apply to dA , dG , dH .

3.4 Any energy state function can be regarded as a function of any pair of variables from p, V, S, T

eg. given $dU = Tds - pdV \Rightarrow U = U(S, V)$

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

Now, only need to find $\left(\frac{\partial U}{\partial T}\right)_V$ and $\left(\frac{\partial U}{\partial V}\right)_T$.

$$dU = Tds - pdV$$

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

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

$$\Rightarrow dU = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right]dV$$

4. Heat Capacities.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{and} \quad C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

From T.S.,

$$dH = Vdp + Tds$$

$$dU = Tds - pdV$$

At constant pressure, $dp=0$,

At constant volume, $dV=0$

$$dH = Tds$$

$$dU = Tds$$

$$C_p dT = Tds$$

$$C_v dT = Tds$$

$$ds = \frac{C_p}{T} dT$$

$$ds = \frac{C_v}{T} dT$$

$$\int_{T_1}^{T_2} ds = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

$$\int_{T_1}^{T_2} ds = \int_{T_1}^{T_2} \frac{C_v}{T} dT$$

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT$$

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_v(T)}{T} dT$$

If $T_1 \rightarrow T_2$ includes T_{pc} at which phase transition occurs, then,

at T_{pc} ,

$$\Delta S_{pc} = \frac{\Delta H_{pc}}{T_{pc}}$$

$$\Rightarrow S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT + \sum_{pc} \frac{\Delta H_{pc}}{T_{pc}}$$

5. Variation of G .

$$dG = -SdT + Vdp$$

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

• At constant T , $dT=0$, $V = \left(\frac{\partial G}{\partial P}\right)_T$

$$\int_{P_1}^{P_2} dG = \int_{P_1}^{P_2} V dp$$

$$G(P_2, T) - G(P_1, T) = \int_{P_1}^{P_2} V(P, T) dp$$

For ideal gas, $V = \frac{RT}{P}$ per mole,

$$G(P_2, T) - G(P_1, T) = \int_{P_1}^{P_2} \frac{RT}{P} dp$$

$$= RT \ln \frac{P_2}{P_1}$$

↳ isothermal

Set $P_1 = P^\circ$, then,

$$G_m(P_2, T) = G_m^\circ(P^\circ, T) + RT \ln \left(\frac{P}{P^\circ}\right)$$

Since, for ideal gas, $P \propto \frac{1}{V}$ at constant pressure

$$G(P_2, T) - G(P_1, T) = RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_1}{V_2}$$

• At constant P

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

Consider

$$\left(\frac{\partial \left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{T \left(\frac{\partial G}{\partial T}\right)_P - G \left(\frac{\partial T}{\partial T}\right)}{T^2}$$

$$= \frac{-ST - G}{T^2} = -\frac{(G + TS)}{T^2} = -\frac{H}{T^2}$$

(Gibbs Helmholtz eqn)

$$\left(\frac{\partial (\Delta_r G^\circ / T)}{\partial T} \right)_P = - \frac{\Delta_r H^\circ}{T^2}$$

At equilibrium $\Delta_r G^\circ = -RT \ln K$

$$\Rightarrow \left(\frac{\partial (-RT \ln K)}{\partial T} \right)_P = - \frac{\Delta_r H^\circ}{T^2}$$

$$\left(\frac{\partial \ln K}{\partial T} \right)_P = \frac{\Delta_r H^\circ}{RT^2}$$

$$\int_{T_1}^{T_2} d \ln K = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ}{RT^2} dT \quad \text{at constant } P$$

$$\ln K(T_2) = \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)}{RT^2} dT$$

If assume $\Delta_r H^\circ$ does not change over $T_1 \rightarrow T_2$, then,

$$\begin{aligned} \ln K(T_2) &= \ln K(T_1) + \frac{\Delta_r H^\circ}{R} \left[-\frac{1}{T} \right]_{T_1}^{T_2} \\ &= \ln K(T_1) - \frac{\Delta_r H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \end{aligned}$$

or do indefinite integral, then,

$$\int d \ln K = \int \frac{\Delta_r H^\circ}{RT^2} dT$$

$$\ln K(T) = - \frac{\Delta_r H^\circ}{RT} + \text{constant} \quad \text{same assumption as above.}$$

\therefore plot $\ln K(T)$ against $\frac{1}{T}$ allows $\Delta_r H$ to be determined.

Alt: Set $\Delta_r G^\circ = -RT \ln K = \Delta_r H^\circ - T \Delta_r S^\circ$

$$\ln K = - \frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$

plot $\ln K(T)$ against $\frac{1}{T}$

6. Phase equilibria

For 2 phases at equilibrium,

$$G_{m,1} = G_{m,2}$$

Since $dG = Vdp - SdT$, we have,

$$dG_{m,1} = dG_{m,2}$$

$$V_{m,1} dp - S_{m,1} dT = V_{m,2} dp - S_{m,2} dT$$

$$(V_{m,1} - V_{m,2}) dp = (S_{m,1} - S_{m,2}) dT$$

Clapeyron Eqn: $\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$

slope of ~~p-T~~ p-T
phase boundary

At phase equilibrium, $\Delta G = \Delta H - T\Delta S = 0$

$$\Rightarrow \Delta S = \frac{\Delta H}{T}$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$

(P_2, T_2) For sublimation and vapourization, assume $\Delta V \approx V_g = \frac{RT}{P}$
(i.e. negligible condensed phase volume), then,

$$\frac{dp}{dT} = \frac{\Delta H}{TV} = \frac{P\Delta H}{RT^2}$$

$$\int_{P_1}^{P_2} \frac{1}{P} dp = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT$$

$$\ln\left(\frac{P_2}{P_1}\right) = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT \approx \frac{\Delta H}{R} \left[-\frac{1}{T}\right]_{T_1}^{T_2} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

assume
ac to L.

(P_1, T_1)