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[120BM0014]

①

# THERMODYNAMICS

## MID-SEM

Q1) We know two eqn's:

$$G = H - TS$$

$$dG = VdP - SdT$$

So if we do,

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT} dG - \frac{G}{R} \frac{1}{T^2} dT$$

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT} (VdP - SdT) - \left(\frac{H - TS}{RT^2}\right) dT$$

$$= \frac{1}{RT} (VdP - \cancel{SdT} - \frac{HdT}{T} + \cancel{SdT})$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT$$

So,

$$\left. \frac{d\left(\frac{G}{RT}\right)}{dP} \right|_{T=\text{const}} = \frac{V}{RT} \quad \left[ \begin{array}{l} \text{So, if we differentiate} \\ \text{wrt. } P \text{ we get } V \end{array} \right]$$

$$\left. \frac{d\left(\frac{G}{RT}\right)}{dT} \right|_{P=\text{const}} = \frac{-H}{RT^2} \quad \left[ \begin{array}{l} \text{So, if we differentiate} \\ \text{wrt. } T, \text{ we get } H \end{array} \right]$$

hence,  $G = H - TS$

$$\Rightarrow S = -\frac{G}{T} + \frac{H}{T}$$

$$\& U = H - PV$$

Hence, if we know  $G/RT$ , we can get  $V, U, H, S$ .

23) a) So, we have to assume an open system of  $i$  constituents like  $n_1, n_2, n_3, \dots$ .  
Let  $G$  be the free energy.

$G$  is the func<sup>n</sup> of temp, pressure & amount of other components.

$$G = f(T, P, n_1, n_2, n_3, \dots, n_i)$$

Now, a small change occurs in  $G$  as  $dG$  due to change in other factors.

$$dG = \left( \frac{\partial G}{\partial T} \right)_{P, n_1, n_2, n_3, \dots} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_1, n_2, n_3, \dots} dP + \left( \frac{\partial G}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{T, P, n_1, n_3, \dots} dn_2 + \dots$$

We can also write

$$\left( \frac{\partial G}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} \equiv \boxed{\bar{G}_1 dn_1}$$

$\bar{G}_1$  is the partial molar free energy.

Now, this  $\bar{G}_1$  is identical to chemical potential  $\mu$ .  
So, constant  $T$  &  $P$   $dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \dots + \bar{G}_i dn_i$   
 $\therefore dG = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots + \mu_i dn_i \quad \text{--- (2)}$

However, we know that system has definite composition.

$$\text{So, } (G)_{T, P, n} = \mu_1 n_1 + \mu_2 n_2 + \dots + \mu_i n_i$$

No definite composition.

(3)

So, differentiating it we get.

$$dG = (n_1 dn_1 + n_1 d\mu_1) + (n_2 dn_2 + n_2 d\mu_2) + \dots + (n_i dn_i + n_i d\mu_i)$$

$$\Rightarrow dG = (n_1 dn_1 + n_2 dn_2 + \dots + n_i dn_i) + (n_1 d\mu_1 + \dots + n_i d\mu_i)$$

So, at constant T & P, which give eqn (2)

$$dG = dG + [n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_i d\mu_i]$$

$$\text{So } \left[ \sum_{i=1}^i n_i d\mu_i = 0 \right] \quad \text{Gibbs-Duhem equation.}$$

b) Partial molar property is a thermodynamic quantity and tells us how an extensive property of a solution changes if a mixture's molar composition, while the temp & Pressure are constant. Eg- Like adding Ethanol of one mole to a large sample of ethanol & water soln.

Q4) Entropy is the randomness and disorder of the system.

a) ~~Entropy~~ Energy always flows downhill and makes entropy even increasing. Like energy spontaneously flows from hot to cold region (more energy to less energy). Energy tends to spread as much as it can and entropy defines the spread of energy.

$$\Delta S = q \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{as, } T_2 < T_1 \Rightarrow \frac{1}{T_2} > \frac{1}{T_1}$$

So  $\Delta S$  is always positive and even increasing.



(4)

$$\text{Also, } Q - W = m \Delta H$$

$$W_s = Q - m \Delta H$$

$$\boxed{\frac{Q_{rev}}{m} = T_{sur} \Delta S}$$

$$W_{rev} = m(T_{sur} \Delta S - \Delta H) \quad (\text{Reversible})$$

$$W_{actual} = Q_{actual} - m \Delta H \quad (\text{Actual})$$

$$W_{lost} = (m T_{sur} \Delta S - m \Delta H) - (Q_{actual} - m \Delta H)$$

$$\boxed{W_{lost} = W_{rev} - W_{actual}}$$

$$\text{also, } W_{lost} = m T_{sur} \Delta S - Q_{actual}$$

2) Compressibility - can be defined as fractional differential change in volume due to ~~differential~~ change in pressure.

$$K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (\text{-ve sign as volume decreases})$$

Expansivity - can be defined as fractional differential change in volume due to change in temperature.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad (\text{+ve sign as volume expands})$$

(5)

- 6) a) Living entities are considered to feed on negative entropy as the entropy of the body remains constant. "Negative entropy" means becoming less disordered or using up the energy. The entropy that is produced in the body through metabolism is used up or dissipated, hence "life feeds on negative entropy".

Decay means disintegration in general and breaking away of radio-active material if specific.

So, naturally decay in thermodynamic terms would be increase in the entropy of the living thing as randomness increases during disintegration.

$$S = \int \frac{dQ}{T}$$

- b) Elevation in boiling point and depression in freezing point and colligative properties all depend on the number of particles i.e. on ions & molecules, is a fixed amount of solvent irrespective of the nature of the solute.

Q5) i) Entropy

Heat energy flows from a hotter object to colder object always.

$$\text{So, } ds = \frac{dq_{rev}}{T}$$

$$\Delta S = \int_i^f ds = \int_i^f \frac{dq_{rev}}{T} \quad \Rightarrow \quad \Delta S = \frac{q_{rev}}{T}$$

$$\text{Also, } \boxed{ds = \frac{dU + PdV}{T}} \quad (\text{pressure-volume work})$$

ii) Enthalpy - total heat content of system.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots$$

$$\Delta H_{\text{reacn}} = \sum_{\text{prod}} Mh - \sum_{\text{reactant}} Mh$$

$$\Delta H = M \Delta h_v$$

$$\boxed{\Delta H = MC_p \Delta T = MC_p (T_2 - T_1)}$$

$$\boxed{H = E + PV}$$

iii) Gibbs Free Energy

$$\text{So, } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surround}}$$

GFE - maximum work that can be done by a process going from non-equilibrium to equilibrium (at  $T=P=\text{const}$ )

$$\text{So, } G = H - TS$$

$$\boxed{\Delta G = \Delta H - \underbrace{T \Delta S}_{\text{unavailable}} - \underbrace{S \Delta T}_{\text{possible}}}$$

$$\text{So, } \Delta U = T \Delta S - P \Delta V$$

$$\boxed{\Delta G = V \Delta P - S \Delta T}$$

$$\text{So, } \Delta G = \underbrace{\Delta H}_{\substack{\downarrow \\ \text{enthalpy}}} - \underbrace{T \Delta S}_{\substack{\downarrow \text{Temp} \quad \swarrow \text{entropy}}}$$

GFE



Helmholtz Free Energy - it is a system in equilibrium with environment having  $S$  &  $U$  with fixed temp. ⑦

$$H = U + PV$$

Helmholtz -  $\boxed{F = U - TS}$

So, isothermal process

$$\Delta F = \Delta U - T \Delta S$$

$$\boxed{dF = -SdT - PdV}$$

or, Quasi static,

$$\Delta F = W$$

Q2

a)  $V_m = \frac{RT}{P} + B$

$$\boxed{\left( \frac{PV}{RT} = 1 + \frac{BP}{RT} \right)}$$

$$B(T) = b - \frac{a}{RT}$$

So,  $\alpha = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_P = \frac{1}{V_m} \left( \frac{R}{P} + \frac{dB}{dT} \right)$

$$K_1 = -\frac{1}{V_m} \left( \frac{\partial V_m}{\partial P} \right)_T = -\frac{1}{V_m} \left( -\frac{RT}{P^2} \right)$$

b)  $C_v = 200 \text{ J K}^{-1}$

$$T_i = 400 \text{ K} \text{ \& } 420 \text{ K}$$

So, the copper are  $C_1$  &  $C_2$

$$\text{So, } m C_v (T_f - T_{i1}) + m C_v (T_f - T_{i2}) = 0$$

$$\Rightarrow T_f - T_{i1} = T_{i2} - T_f$$

$$\Rightarrow 2T_f = 420 + 400$$

$$= 20 \text{ K}$$

$$T_f = 400 \text{ K} + 10 \text{ K} = 410 \text{ K}$$

(8)

Change in entropy

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= m \times 200 \left( \ln \left( \frac{410}{400} \right) + \ln \left( \frac{410}{420} \right) \right)$$

$$= 200m \left( 0.025 + (-2.33) \right)$$

$$= 200m \left( -2.305 \right)$$

$$\Rightarrow = -200 \times m (2.305)$$

No, the sign of  $\Delta S$  is inconsistent with 2<sup>nd</sup> law.