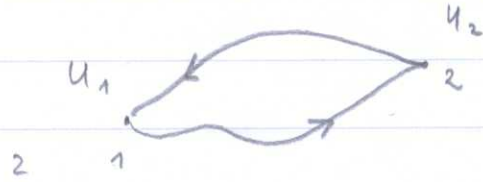


①

Thermodynamics

I law: $\Delta u = Q - w$



Work; $w = \int_1^2 p \cdot dV$, done by the system

Heat; Q , energy transfer to the system

Δu ; change in internal energy; $\Delta u = u_2 - u_1$

II law: $\Delta S = \frac{Q}{T}$, or $dS = \frac{dQ}{T}$ (dQ - reversible)

T ; absolute temperature

ΔS ; entropy change

Combination of law I and II.

$du = dQ - p \cdot dV = T \cdot dS - p \cdot dV$ (infinitesimal)

For closed systems: $u = u(S, v)$

Open systems: $u = u(S, v, n)$

n , particle number

(2)

The differential of u .

$$dU = \frac{\partial U}{\partial S} \cdot dS + \frac{\partial U}{\partial V} \cdot dV + \frac{\partial U}{\partial n} \cdot dn \quad \left. \vphantom{dU} \right\} \text{compare}$$

$$= T \cdot dS - p \cdot dV + \mu \cdot dn$$

Hence: $T = \frac{\partial U}{\partial S}$, $p = -\frac{\partial U}{\partial V}$, and $\mu = \frac{\partial U}{\partial n}$

μ : the chemical potential (definition)

$$dU = T \cdot dS - p \cdot dV + \mu \cdot dn; \quad \text{open systems}$$

$$dU = T \cdot dS - dW; \quad \text{closed systems}$$

$\mu \cdot dn$ can be considered to be a work

GIBBS FREE ENERGY, defined as:

$$G = U - T \cdot S + P \cdot V \quad (\text{why?})$$

If we make the differential of G

$$dG = dU - T \cdot dS - S \cdot dT + P \cdot dV + V \cdot dP$$

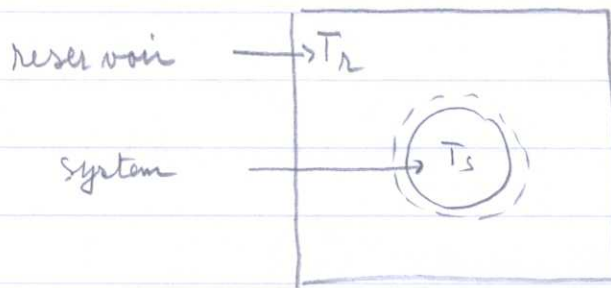
$$= (T \cdot dS - p \cdot dV + \mu \cdot dn) - T \cdot dS - S \cdot dT + p \cdot dV + V \cdot dP$$

$$= -S \cdot dT + V \cdot dP + \mu \cdot dn$$

the differentials are; dT , dP and dn ;
that is: at laboratory conditions ($p = \text{constant}$,
 $T = \text{constant}$)

$$dG = \mu \cdot dn = \left(\sum_i \mu_i \cdot dn_i \right)$$

(3)

ANOTHER INTRODUCTION OF G

the system undergoes a process.

Overall entropy change: $\Delta S = \Delta S_{\Delta} + \Delta S_R = \Delta S_{\Delta} + \frac{Q_R}{T_R}$

Q_R : heat exchange between system and reservoir

$$\Delta S = \Delta S_{\Delta} + \frac{\Delta U_R + W_R}{T_R} = \Delta S_{\Delta} + \frac{-\Delta U_S - P \cdot \Delta V}{T_R}$$

$$= \frac{(T_R \cdot \Delta S_{\Delta} - \Delta U_{\Delta} - P \cdot \Delta V)}{T_R} \equiv - \underline{\underline{\Delta G / T_R}}$$

, when ; $G = U - TS + P \cdot V \Rightarrow$

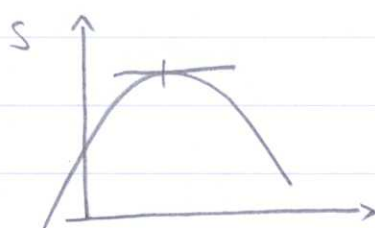
$$\Delta G = \Delta U - T \cdot \Delta S + P \cdot \Delta V \quad (T, P \text{ constant})$$

CRITERIA FOR EQUILIBRIUM

1) IN ISOLATED SYSTEMS , $\Delta S = p \Delta S$, $dS = 0$, $S \text{ max}$

2) AT LABORATORY CONDITIONS

$$\Delta G = \text{neg} , dG = 0 , G \text{ min}$$



reaction coordinate



ANOTHER EXPRESSION FOR μ

We know now; $G = G(T, P, m)$

the differential:

compare $\left\{ \begin{aligned} dG &= \frac{\partial G}{\partial T} \cdot dT + \frac{\partial G}{\partial P} \cdot dP + \frac{\partial G}{\partial m} \cdot dm \\ &= -S \cdot dT + V \cdot dP + \mu \cdot dm \end{aligned} \right.$

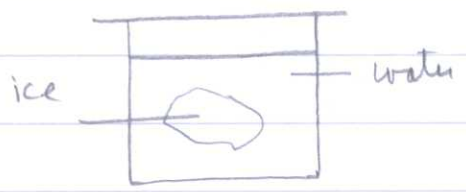
$\frac{\partial G}{\partial T} = -S$, $\frac{\partial G}{\partial P} = V$, $\mu = \frac{\partial G}{\partial m}$

EQUILIBRIUM; OPEN SYSTEMS; an example

$dG = -S \cdot dT + V \cdot dP + \sum \mu_i \cdot dm_i = \sum \mu_i \cdot dm_i$,
when T and P is constant

example; two phases in equilibrium (e.g. water/ice)

$dG = \mu_1 \cdot dm_1 + \mu_2 \cdot dm_2 = (\mu_1 - \mu_2) \cdot dm_1$



$m_0 = m_1 + m_2 \Rightarrow$
 $0 = dm_1 + dm_2 \Rightarrow$
 $dm_1 = -dm_2$

at equilibrium: $dG = 0 \Rightarrow \underline{\mu_1 = \mu_2}$

Then: $\mu_i = \mu_i(T, P, c_i)$, for the i-th component

$\frac{\partial \mu_i}{\partial T} = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial m_i} \right) = \frac{\partial}{\partial m_i} \left(\frac{\partial G}{\partial T} \right) = - \frac{\partial S}{\partial m_i} \equiv -\bar{S}_i$

$\frac{\partial \mu_i}{\partial P} = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial m_i} \right) = \frac{\partial}{\partial m_i} \left(\frac{\partial G}{\partial P} \right) = \frac{\partial V}{\partial m_i} \equiv \bar{V}_i$

\bar{s}_i and \bar{v}_i ; partial molar entropy and volume of component i . (5)

Make use of the gas law: $P_i = \frac{n_i R T}{V} = c_i R T$

$$\frac{\partial \mu_i}{\partial c_i} = \left(\frac{\partial \mu_i}{\partial P_i} \right) \cdot \left(\frac{\partial P_i}{\partial c_i} \right) = R T \cdot \frac{\partial \mu_i}{\partial P_i}$$

Henry's law (law of partial pressure); $P = \sum_{i=1}^n P_i$

$$\frac{\partial \mu_i}{\partial P_i} = \frac{\partial \mu_i}{\partial P} \cdot \frac{\partial P}{\partial P_i} = \frac{\partial \mu_i}{\partial P} \cdot 1 = \bar{v}_i \quad (\text{see above})$$

$$\bar{v}_i = \frac{\partial V}{\partial n_i} = \frac{R T}{P_i} = \frac{R T}{c_i R T} = \frac{1}{c_i}$$

Hence: $\frac{\partial \mu_i}{\partial c_i} = \frac{R T}{c_i} = R T \frac{d(\ln c_i)}{d c_i}$, and

finally: $d\mu_i = -\bar{s}_i \cdot dT + \bar{v}_i \cdot dP + R T d(\ln c_i)$

Integration from; $T=0$ to $T=T$, $P=0$ to $P=P$
and $c_i=1$ to c_i

$$\mu_i = \mu_i^0 - \bar{s}_i \cdot T + \bar{v}_i \cdot P + R T \ln \left(\frac{c_i}{1} \right)$$

at laboratory conditions; $dP = dT = 0$

$$\mu_i = \mu_i^0 + R T \ln \left(\frac{c_i}{1} \right)$$