System With Several Components

- Consider a system with mean energy E volume V and m different kinds of molecules.

- Let N_i be the number of molecules of type i.

- Entropy of the system is given by

$$S = S(E, V, N_1, \ldots, N_m)$$

- In a completely general infinitesimal quasistatic process

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \sum_{i=1}^{m}\left(\frac{\partial S}{\partial N_i}\right)_{\bar{N}_i, V, E} dN_i$$

$$\bar{N}_i = (N_1, \ldots N_{i-1}, N_{i+1}, \ldots, N_m)$$

- Suppose $dN_i \equiv 0$ for all $i = 1 \ldots m$

Then

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV$$

and in this situation we have already established that

$$dS = \frac{dQ}{T} = \frac{dE + p\,dV}{T}$$

Multiple components

$\therefore \quad T\,ds = dE + p\,dV$

$$ds = \frac{1}{T}\,dE + \frac{p}{T}\,dV$$

$$\therefore \left(\frac{\partial s}{\partial E}\right)_{V,N} = \frac{1}{T}\,; \quad \left(\frac{\partial s}{\partial V}\right)_{N,E} = \frac{p}{T}\,.$$

⊛ Lets define

$$\boxed{\frac{\mu_i}{T} \doteq -\left(\frac{\partial S}{\partial N_i}\right)_{E,V,\bar{N}_i}}$$

$$\therefore \boxed{T\,dS = dE + p\,dV - \sum_{i=1}^{m} \mu_i\,dN_i}$$

⊛ Note that

$$dE = T\,ds - p\,dV + \sum_{i=1}^{m} \mu_i\,dN_i$$

$$\therefore \left(\frac{\partial E}{\partial S}\right)_{V,N} = T\,; \left(\frac{\partial E}{\partial V}\right)_{T,N} = -p$$

$$\boxed{\left(\frac{\partial E}{\partial N_i}\right)_{\bar{N}_i,V,S} = \mu_i}$$

⊛ Note that

$$F = E - TS$$

$$\Rightarrow \quad dF = dE - T\,ds - S\,dT = dE - \left(dE + p\,dV - \sum \mu_i\,dN_i\right) - s\,dT$$

Multiple components

$$dF = -S\,dT - p\,dV + \sum_i \mu_i\, dN_i$$

$$\Rightarrow \left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

$$\left(\frac{\partial F}{\partial T}\right)_{T,N} = -p$$

$$\boxed{\left(\frac{\partial F}{\partial N_i}\right)_{\bar{N}_i, V, T} = \mu_i}$$

⊛ $G = E - TS + pV$

$$\Rightarrow dG = dF + p\,dV + V\,dp = -S\,dT + V\,dp + \sum_i \mu_i\, dN_i$$

$$\Rightarrow \left(\frac{\partial G}{\partial T}\right)_{p,N} = -S ; \left(\frac{\partial G}{\partial p}\right)_{T,N} = V$$

and

$$\boxed{\left(\frac{\partial G}{\partial N_i}\right)_{\bar{N}_i, p, T} = \mu_i}$$

⊛ μ_i is called the "chemical potential" per molecule of the i^{th} species

General Condition for chemical Equilibrium.

⊛ Suppose there are m different kinds of molecules $B_1, B_2, \cdots, B_m$.

⊛ Assume that there exists the possibility of transformation of molecules into each other where the total number of atoms of each kind are preserved.

⊛ A chemical reaction can be written in the form

$$\sum_{i=1}^{m} b_i B_i = 0 \quad --- \quad (*)$$

Example: $2H_2 + O_2 \rightleftarrows 2H_2O$

can be written as

$$-2H_2 - O_2 + 2H_2O \rightleftarrows 0$$

$$B_1 \equiv H_2 ; \quad B_2 \equiv O_2 ; \quad B_3 \equiv H_2O$$

and $b_1 = -2$; $b_2 = -1$; $b_3 = +2$

⊛ Note that b_i in $(*)$ are constrained in a manner such that the number of atoms in the chemical reaction are conserved.

Chemical Equilibrium.

* Now if dN_i denotes the change in the number of i^{th} molecule B_i then

$$dN_i = \lambda b_i \; ; \; i = 1 \cdots m, \text{ for some scalar } \lambda.$$

For the reaction

$$2H_2 + O_2 \rightleftarrows 2H_2O$$
$$2H_2O - 2H_2 - O_2 = 0$$
$$b_1 = -2 \; ; \; b_2 = -1 \; ; \; b_3 = 2$$

and $dN_{H_2O} : dN_{O_2} : dN_{H_2} = 2 : -1 : -2$

* Consider an equilibrium condition where constant temperature and pressure are maintained. Then as $dG = 0$ at eqlb^m. and

$$0 = dG = -SdT + Vdp + \sum_i \mu_i dN_i$$
$$= \sum_{i=1}^{m} \mu_i dN_i \qquad [\text{as } dT = dp = 0]$$
$$= \sum_{i=1}^{m} \mu_i \lambda b_i$$
$$\Rightarrow \sum_{i=1}^{m} \mu_i b_i = 0$$

Thus, the chemical potential of the various species at equilibrium needs to satisfy

Chemical Equilibrium

$$\boxed{\sum_{i=1}^{m} \mu_i b_i = 0}$$

(*) where μ_i is the chemical potential per mole of species i

and $\sum_{i=1}^{m} b_i B_i = 0$ defines the reaction

(*) Note that under constant temp. and volume

$dF = 0$ which again leads to

$$\sum_{i=1}^{m} \mu_i b_i = 0$$

Thus, the condition $\sum_{i=1}^{m} \mu_i b_i = 0$ can be shown to be a characteristic of equilibrium (maximum entropy of the isolated system) itself.

Calculation of chemical Potential

(α) Consider m molecular species in a volume V.

(γ) Suppose the state of the i^{th} molecular species is denoted by s_i which can belong to a set S_i. Let the energy of state s_i be $\varepsilon_i(s_i)$; $s_i \in S_i$

($\times$) The state of the mixture of m-molecular species is given by

$$s = (s_1, s_2, \dots s_m) \in S_1 \times S_2 \times S_3 \times \dots \times S_m$$

with energy $E(s) = \varepsilon_1(s_1) + \varepsilon_2(s_2) \dots + \varepsilon_m(s_m)$

(γ)

($+$) The partition function is given by

$$Z = \sum_{s_1 s_2 \dots s_m} e^{-\beta(\varepsilon_1(s_1) + \varepsilon_2(s_2) \dots + \varepsilon_m(s_m))}$$

$$= \Big[\sum_{s_1} e^{-\beta \varepsilon_1(s_1)}\Big] \Big[\sum_{s_2} e^{-\beta \varepsilon_2(s_2)}\Big] \dots$$

$$\dots \Big[\sum_{s_m} e^{-\beta \varepsilon_m(s_m)}\Big]$$

Let $\quad \xi_i := \sum_{s_i} e^{-\beta \varepsilon_i(s_i)}$

Chemical Potential of ideal gas mixture

® Now, if there are N_i molecules of i^{th} gas molecules that are indistinguishable then

let

$$Z_i = \frac{q_i^{N_i}}{N_i!}$$

and

$$Z = Z_1 Z_2 \cdots Z_m.$$

$$= \prod_{i=1}^{M} Z_i$$

clearly $\ln Z = \sum_{i=1}^{M} \ln Z_i$

and therefore

(a) $$\bar{E} = \tau^2 \frac{\partial \ln Z}{\partial \tau} = \sum_{i=1}^{M} \tau^2 \frac{\partial \ln Z_i}{\partial \tau} = \sum_{i=1}^{M} \bar{E}_i$$

where $\bar{E}_i = \tau^2 \frac{\partial \ln Z_i}{\partial \tau}$ the average energy of the i^{th} species

(b) $$\bar{P} = \tau \frac{\partial \ln Z}{\partial V} = \sum_{i=1}^{M} \tau \frac{\partial \ln Z_i}{\partial V} = \sum_{i=1}^{M} \bar{P}_i$$

chemical potential

where
$$\bar{p}_i = \tau \frac{\partial \ln z_i}{\partial V}$$
is the pressure of the i^{th} molecular species.

If each of the m molecular species is an ideal gas then

$$\bar{p}_i = n_i \tau \quad ; \quad n_i = \frac{N_i}{V}$$

and therefore

$$\bar{p} = \sum_i \bar{p}_i = \sum_i n_i \tau = n\tau$$

where $n = \sum_i n_i$

$\therefore \quad \bar{p} = n k_B T$ [Also $\frac{\bar{p}_i}{\bar{p}} = \frac{n_i}{n} = c_i$ is the fractional concent.]

Also,
$$F = -\tau \ln Z = \sum_{i=1}^{m} -\tau \ln Z_i = \sum_{i=1}^{m} F_i$$

Now as
$$Z = \prod_{i=1}^{m} (Z_i) = \prod_{i=1}^{m} \frac{(\varsigma_i)^{N_i}}{N_i!}$$

For an ideal gas $\varsigma_i = \left(\frac{M_i \tau}{2\pi\hbar^2}\right)^{3/2} V$

Chemical Potential

$$\therefore \quad Z_i = \frac{(\xi_i)^{N_i}}{N_i!}$$

$$\ln Z_i = N_i \ln \xi_i - \ln N_i!$$

$$\approx N_i \ln \xi_i - N_i \ln N_i + N_i$$

Now we have shown that

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{\overline{N_i}, \tau, V} =$$

$$= -\tau[\ln \xi_i - 1 - \ln N_i + 1]$$

$$= -\tau(\ln \xi_i - \ln N_i)$$

$$\therefore \quad \mu_i = -\tau \ln \frac{\xi_i}{N_i}$$

$$\boxed{\mu_i = -k_B T \ln \frac{\xi_i}{N_i}}$$

Chemical Reaction

⊛ For an ideal gas we have

$$\xi_i = \left(\frac{M_i \tau}{2\pi\hbar^2}\right)^{3/2} V$$

and

$$\mu_i = -\tau \ln\left(\frac{\xi_i}{N_i}\right) \qquad n_i = \frac{N_i}{V}$$

$$= \tau \ln\left(\frac{N_i}{\xi_i}\right)$$

$$= \tau \ln\left[\frac{N_i}{(M_i\tau)^{3/2} V}(2\pi\hbar^2)^{3/2}\right]$$

$$= \tau \ln\left[\frac{N_i}{V}\tau \frac{(2\pi\hbar^2)^{3/2}}{(M_i\tau)^{3/2}\tau}\right]$$

$$= \tau \ln\left(\frac{N_i \tau}{V}\right) + \tau \ln \frac{(2\pi\hbar^2)^{3/2}}{(M_i\tau)^{3/2}\tau}$$

$$= \tau \ln p_i + f_i(\tau) \,; \quad p_i = n_i \tau = \frac{N_i}{V}\tau$$

where $f_i(\tau) \doteq \tau \ln \frac{(2\pi\hbar^2)^{3/2}}{(M_i\tau)^{3/2}\tau}$.

Chemical Reaction: Equilibrium Conditions

$$\therefore \quad \mu_i = \tau \ln p_i + f_i(\tau).$$

Under thermal Equilibrium

$$\sum_{i=1}^{m} \mu_i \, dN_i = 0 \qquad ; \qquad dN_i = -\lambda b_i$$

$$\Rightarrow \quad \sum_{i=1}^{m} \mu_i b_i = 0 \longrightarrow \text{Reaction } \sum b_i B_i = 0$$

$$\Rightarrow \quad \sum_{i=1}^{m} \left(\tau \ln p_i + f_i(\tau)\right) b_i = 0$$

$$\Rightarrow \quad \sum_{i=1}^{m} b_i \tau \ln p_i = -\sum_{i=1}^{m} f_i(\tau) b_i$$

$$\Rightarrow \quad \sum_{i=1}^{m} b_i \ln p_i = -\left(\sum_{i=1}^{m} f_i(\tau) b_i\right)/\tau$$

$$\Rightarrow \quad \ln\left(\prod_{i=1}^{m} p_i^{b_i}\right) = -\left(\sum_{i=1}^{m} f_i(\tau) b_i\right)/\tau$$

$$\Rightarrow \quad \ln \prod_{i=1}^{m} p_i^{b_i} = e^{-\left(\sum_{i=1}^{m} f_i(\tau) b_i\right)/\tau}$$

$$A(\tau) := \exp\left[-\frac{\sum_{i=1}^{m} f_i(\tau) b_i}{\tau}\right]$$

$$p_1^{b_1} \, p_2^{b_2} \cdots p_m^{b_m} = A(\tau)$$

Law of Mass Action

Thus, 'Law of mass action follows.

① for a chemical reaction

$$\sum_{i=1}^{m} b_i B_i = 0$$

assuming all molecules B_i can be considered as a mixture of ideal gases with no interaction potential energy the equilibrium condition satisfies

$$p_1^{b_1} p_2^{b_2} \cdots p_m^{b_m} = A(\tau)$$

where $p_i = \frac{N_i}{V}\tau$ with p_i being the pressure due to the i^{th} species
$= n_i \tau$

- Note that the pressure p of the mixture is
$$p = \sum_{i=1}^{m} p_i \,;$$

Let $N = \sum_{i=1}^{m} N_i$ and $c_i = \frac{N_i}{N}$ denote the number concentration of the species i. Then

Law of mass action

$$\frac{p_i}{p} = \frac{n_i z}{p} = \frac{\frac{N_i}{V} z}{\sum_{i=1}^{m} \frac{N_i}{V} z} = \frac{N_i}{\sum N_i} = c_i$$

$$\therefore \boxed{p_i = c_i p},$$

where c_i is the concentration of species i.

Therefore as

$$p_1^{b_1} p_2^{b_2} \cdots p_m^{b_m} = A(\tau) \text{ we have}$$

$$\Rightarrow (c_1 p)^{b_1} (c_2 p)^{b_2} \cdots (c_m p)^{b_m} = A(\tau)$$

$$\Rightarrow c_1^{b_1} c_2^{b_2} \cdots c_m^{b_m} = p^{-\sum b_i} A(\tau)$$

$\therefore$ The concentration at equilibrium satisfies

$$\boxed{\begin{aligned} \prod_{i=1}^{m} c_i^{b_i} &= p^{-\sum b_i} A(\tau) \\ &=: K(p,\tau) \end{aligned}}$$

where the reaction is $\sum_{i=1}^{m} b_i B_i = 0$.

Chemical Reaction

Suppose the reaction occurs at constant temperature and pressure

Then the minimum amount of work required to change the configuration of the system is governed by Gibbs free Energy. Indeed in the case of constant temperature and pressure

$$dG = \sum_i \mu_i dN_i$$

$$= \sum_i \mu_i \lambda b_i$$

$$= \lambda \sum_i \mu_i b_i$$

Now, $\mu_i = \tau \ln p_i + f_i(\tau)$

$$\therefore dG = \lambda \sum_i [\tau \ln p_i + f_i(\tau)] b_i$$

$$= \lambda \tau \sum_i \left[(\ln p_i) b_i + \frac{f_i(\tau) b_i}{\tau}\right]$$

$$= \lambda \tau \sum_i \left(\ln p_i^{b_i} - \ln[A(\tau)]\right)$$

Chemical reaction

Thus,

$$\Delta G = \lambda\tau\left[\sum_{i=1}^{n} \ln p_i^{b_i} - \ln A(\tau)\right]$$

$$= \lambda\tau \sum_{i=1}^{n}\left[\ln p_i^{b_i} - \ln(p_{i,eq})^{b_i}\right]$$

$$\left[\text{at eqlb}^{m} \text{ conditions } A(\tau) = \prod_{i=1}^{m} (p_{i,eq})^{b_i}\right.$$

$$\therefore \Delta G = \lambda\tau \sum_{i=1}^{m} \ln\left[\frac{p_i}{(p_i)_{eq}}\right]^{b_i}$$

$$= \lambda\tau \sum_{i=1}^{m} \ln \frac{p_1^{b_1} p_2^{b_2} \cdots p_m^{b_m}}{(p_{1,eq})^{b_1} \cdots p_{m,eq}}$$

Now; $p = c_i p_i$ and $p_{eq} = c_{i,eq}\, p_{i,eq}$

$$\therefore \Delta G = \lambda\tau \sum \ln \frac{c_1^{b_1} c_2^{b_2} \cdots c_m^{b_m}}{c_{1,eq}, \cdots c_{m,eq}}$$

as $p_{eq} = p$ [constant pressure operation]

$$\therefore \Delta G = \lambda\tau\left[\ln c_1^{b_1} c_2^{b_2} \cdots c_m^{b_m}\right] + \Delta G^0$$

Chemical reaction

$$\therefore \quad \Delta G = \Delta G^0 + \lambda\tau \ln\left(c_1^{b_1} c_2^{b_2} \ldots c_m^{b_m}\right)$$

where $\Delta G^0 = -\lambda\tau \ln (c_1)_{eq}^{b_1} (c_2)_{eq}^{b_2} \ldots (c_m)_{eq}^{b_m}$

$$= -\lambda\tau \ln \left[K_{eq}(p, \tau)\right]$$

$$\boxed{\Delta G = \Delta G^0 + RT \ln \frac{c_1^{b_1} \ldots c_m^{b_m}}{(c_1)_{eq}^{b_1} \ldots (c_m)_{eq}^{b_m}}}$$

Gibbs Factor and the Grand Canonical Ensemble.

(a) Consider a very large body, $A^{(0)}$ with constant energy $E^{(0)}$ and constant number of particles $N^{(0)}$

(i) $A^{(0)}$ is composed of two parts
  (a) a large reservoir R
  (b) The System S.

R and S can exchange particles as well as energy

Probabilities

Question: What is the probability of finding the system A with N particles and to be in a state s with energy ε_s?

Answer: All accessible states of $A^{(0)}$ are equally likely.

① The number of ways in which $A^{(0)}$ can be in a state where A has N particles, in a state s with energy ε_s is proportional to

$$\Omega^{(0)}(\varepsilon_s, N) = \Omega_R(E^{(0)} - \varepsilon_s, N^{(0)} - N)$$

Probability

Thus

$$P(N, \varepsilon_s) \propto \Omega_R(E^{(0)} - \varepsilon_s, N^{(0)} - N)$$

and let $\sigma_R := \ln \Omega_R$

$$\ln P(N, \varepsilon_s) \propto \ln \Omega_R(\varepsilon^{(0)} - \varepsilon_s, N^{(0)} - N)$$

$$= \Omega_R(\varepsilon^{(0)}, N^{(0)}) - \varepsilon_s \overbrace{\left(\frac{\partial \sigma_R}{\partial \varepsilon} \Big|_{\varepsilon = \varepsilon^{(0)}} \right)_{N_0}}^{\text{"} \frac{1}{\tau} = \beta}$$

$$- \left(N \frac{\partial \sigma_R}{\partial N} \Big|_{N = N^{(0)}} \right)_{E} + \cdots$$

$$= \Omega_R(\varepsilon^{(0)}, N^{(0)}) - \varepsilon_s \beta + \mu \beta N$$

where $\mu := -1/\beta \left(\frac{\partial \sigma}{\partial N} \right)_E \Big|_{N' = N^{(0)}}.$

Probability

Thus

$$\ln P(N, \varepsilon_s) = \ln C\, e^{-\beta \varepsilon_s + \mu \beta N}.$$

$$\Rightarrow \quad P(N, \varepsilon_s) = C\, e^{+\beta[\mu N - \varepsilon_s]}$$

and $\quad C = \mathcal{Z}^{-1}$

$$\mathcal{Z} = \sum_N \sum_{s(N)} e^{-\beta[\varepsilon_s - \mu N]}$$

Note that the possible states depend on the Number of particles N

Grand Canonical Ensemble.

$$\mathcal{Z} = \sum_{N_1} \sum_{N_2} \cdots \sum_{N_M} \sum_{s_M(N_M)} \cdots \sum_{s_1(N_1)} e^{-\beta[\varepsilon_i(s_i) - \mu_i N_i]}$$

is called the grand canonical ensemble.