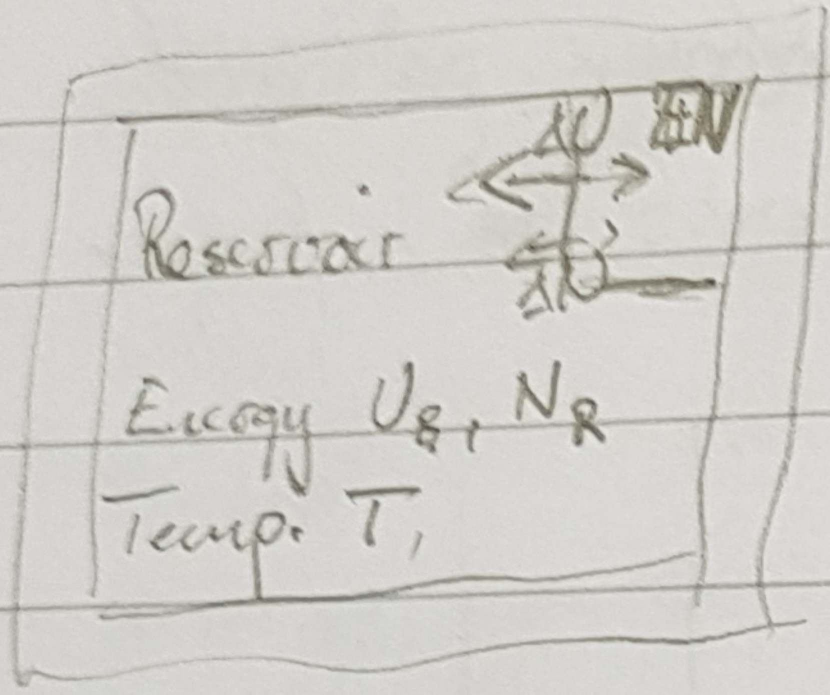
20.10.19

② The Gibbs factor



For an isolated system
- All accessible microstates are equally probable
- Reservoir + System = isolated system
- Microstates s_1 & s_2

$$\Omega_S(s_1) = \Omega_S(s_2) = 1$$

$$P(s_i) = \frac{\Omega_S(s_i)\,\Omega_R(s_i)}{\sum \Omega_S(s_i)\,\Omega_R(s_i)}$$

Ratio of probabilities of 2 microstates:

$$\frac{P(s_1)}{P(s_2)} = \frac{\Omega(s_1)}{\Omega(s_2)} \qquad S = k \ln \Omega$$

$$\Rightarrow \quad = e^{[S_R(s_1) - S_R(s_2)]/k}$$

$R \gg S \Rightarrow$ change $dS_R = S_R(s_1) - S_R(s_2)$ infinitesimal

TDI

$$T\,dS_R = dU_R + P\,dV_R - \mu\,dN_R$$

$$dU_R = -dU_S = -[E(s_1) - E(s_2)]$$

$$dN_R = -dN_S = N(s_1) - N(s_2)$$

$$\Rightarrow \quad dS_R = S_R(s_1) - S_R(s_2) = \frac{-1}{T}\Big(-[E(s_1) - E(s_2)] + \mu\,(N(s_1) - N(s_2))\Big)$$

$$\frac{P(s_1)}{P(s_2)} = \frac{e^{-(E(s_1) - \mu N(s_1))/kT}}{e^{-(E(s_2) - \mu N(s_2))/kT}}$$

$$\Rightarrow \quad P(s) = \frac{1}{Z_G}\, \overbrace{e^{-(E(s) - \mu N(s))/kT}}^{\text{Gibbs factor}}$$

$$Z_G = \sum_s e^{-(E(s) - \mu N(s))/kT}$$

Grand Canonical partition function

$$\bar{N} = \sum_s N(s) P(s) = \frac{1}{Z_G} \sum N(s)\, e^{-(E(s) - \mu N(s))/kT}$$

$$\frac{\partial e^{-\beta(E - \mu N)}}{\partial \mu} = \beta N\, e^{-\beta(E - \mu N)}$$

$$\Rightarrow \quad \bar{N} = \frac{1}{Z_G} \sum_s \frac{1}{\beta} \frac{\partial e^{-\beta(E - \mu N)}}{\partial \mu}$$

$$= \frac{kT}{Z_G} \frac{\partial Z_G}{\partial \mu} = kT\, \frac{\partial \ln Z_G}{\partial \mu}$$

1

Equilibrium between two systems

- $N=N_A+N_B$, $V=V_A+V_B$, $U=U_A+U_B$, all (N,V,U) constant
- Can vary one of the three $\alpha \in (N,V,U)$,
  - keeping the other 2 constant
  - keep total constant: $\alpha = \alpha_A + \alpha_B =$ const.
- $S_{tot} = S_A + S_B$ is maximum in equilibrium

(Multiplicity $\Omega_{tot} = \Omega_A \Omega_B$ is max in eq.)

Equilibrium criterium:

$$\frac{\partial S_B}{\partial \alpha_B} = \frac{\partial S_A}{\partial \alpha_A}$$

Entropy: $S = k \ln \Omega(N,V,U)$

Thermal equilibrium: $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$, $\quad \frac{1}{T} \equiv (\frac{\partial S}{\partial U})_{N,V}$, $\quad \frac{[S]}{[U]} = \frac{J\,K^{-1}}{J}$

Mechanical equilibrium: $\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$, $\quad P \equiv T(\frac{\partial S}{\partial V})_{N,U}$, $\quad \frac{[P]}{[T]} = \frac{J}{m^3 K}$

Chemical equilibrium: $\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$, $\quad \mu \equiv -T(\frac{\partial S}{\partial N})_{U,V}$, $\quad \frac{[\mu]}{[T]} = \frac{J}{K}$

$\mu_A = \mu_B$

impractical

Use G (T, P)

Need the TDI: $dU = TdS - PdV + \sum_i \mu_i dN_i$

$G \equiv U + PV - TS$

$dG = dU + PdV + VdP - TdS - SdT$

$= \cancel{TdS} - \cancel{PdV} + \sum_i \mu_i dN_i + \cancel{PdV} + VdP - \cancel{TdS} - SdT$

$= \sum_i \mu_i dN_i + VdP - SdT$

$= \sum \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_{j\neq i}} dN_i + \left(\frac{\partial G}{\partial P}\right)_{T,N_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P,N_i} dT$

$\left(\frac{\partial G}{\partial P}\right)_{T,N_i} = V$, $\quad \left(\frac{\partial G}{\partial T}\right)_{P,N_i} = -S$

$\Rightarrow \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_{j\neq i}}$

At T, P const : * $dG = \sum_i \mu_i dN_i$

* equilibrium G is minimum

$dG = 0$ $\quad \mu_1 dN_1 + \mu_2 dN_2 = 0$

Ideal gas & ideal mixtures (No volume change on mixing $\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V}$)

$\mu_i = \mu_i^0 + kT \ln x_i$ $\quad x_i = \frac{c_i}{\sum_i c_i}$

Non-ideal $\mu_i = \mu_i^0 + kT \ln(\gamma_i x_i)$ $\quad \gamma_i$ - activity coeff.

reference conc: $\mu(c, T) = \mu(c_0, T) + kT \ln \frac{c}{c_0}$

$c_0 = 1M = 1 \frac{mole}{l}$

$$\mu_{tot} = \mu_{internal} + \mu_{external}$$

Sentrifuge $\quad U(z) = maz$

Electric field $\quad U(z) = qV(z)$, $\quad V$: el. field

$$\mu = \mu^0(T) + U(z) + k_B T \ln \frac{c}{c_0}$$

3

Chemical reactions $\quad$ i: $1 \rightarrow 2$

$\mu_1 \rightarrow \mu_2$: equilibrium $\quad dG = 0$

$$O_2 + 2H_2 \rightleftharpoons 2H_2O$$

$$\Delta G = 2\mu_{H_2O} - 2\mu_{H_2} - \mu_{O_2}$$

Equil.: $\quad 0 = \frac{\Delta G}{kT} = \underbrace{\frac{2\mu^0_{H_2O} - 2\mu^0_{H_2} - \mu^0_{O_2}}{kT}}_{= \frac{\Delta G_0}{kT}} + \ln\left[\left(\frac{c_{H_2O}}{c_0}\right)^2\left(\frac{c_{H_2}}{c_0}\right)^{-2}\left(\frac{c_{O_2}}{c_0}\right)^{-1}\right]$

$\boxed{K_{eq} \equiv e^{-\frac{\Delta G_0}{kT}}}$ can be calculated from tables

$$\frac{\Delta G}{kT} = 0 \Rightarrow K_{eq} = \frac{c_{H_2O}^2 \cdot c_0}{c_{H_2}^2 c_{O_2}} \quad \text{Equilibrium constant}$$

$$= e^{\frac{457\,kJ}{mol}/kT}$$

21.10.19

Oblig 06 - FYS2160 - 2015

Ex 08

a)
$$\mu = \mu_{int} + \mu_{ext} = \mu_0 + kT\ln\left(\frac{c_+(x)}{c_{+,0}}\right) + q\phi(x)$$

$n(x)$

b) Equil. $\quad \mu = \text{const} \quad \mu(0) = \mu(L)$

c) $\quad kT\ln\left(\frac{n(0)}{n_0}\right) = kT\ln\left(\frac{n(L)}{n_0}\right) + q\phi_L$

$$n(0) = n(L)\, e^{\frac{q\phi_L}{kT}}$$

n_0 on average. Assume $n(\frac{L}{2}) = n_0$

$$\Rightarrow \frac{n(0) + n(L)}{2} = n_0 \Rightarrow n(0) = 2n_0 - n(L)$$

$$\Rightarrow 2n_0 - n(L) = n(L)\, e^{\frac{q\phi_L}{kT}}$$

$$n(L) = \frac{2n_0}{1 + e^{q\phi_L/kT}}$$

$$n(0) = \frac{2n_0}{1 + e^{-q\phi_L/kT}}$$