Chemical Reactions

* statistical mechanical description of chemical reactions uses the chemical potential
* here we consider gas phase reactions
  - for example: $2H_2 + O_2 \rightleftharpoons 2H_2O$

"symbolic" equation: $\boxed{-2H_2 - O_2 + 2H_2O = 0}$

  - can write in general

$$\boxed{\sum_{i=1}^{m} b_i B_i = 0} \longrightarrow b_i \text{ - stoichiometric coefficients}$$

B_i – chemical species (H_2, O_2, etc)

  - assuming $dE = dV = 0$

maximum entropy condition

$$TdS = 0 \Rightarrow \sum_i \mu_i dN_i = 0$$

in a chemical reaction $dN_i \to$ same proportions as the stoichiometric coefficients $\Rightarrow$ $\boxed{\sum_i \mu_i b_i = 0}$

  - can also obtain by using $dG = 0$ (T,P) or $dF = 0$ (T,V)

can derive the "law of mass action":

partition function: $Z = \prod_{i=1}^{m} \frac{(VQ_i)^{N_i}}{N_i!}$

$$Q_i = \frac{1}{\lambda_i^3} \underbrace{\sum_s \exp[-\beta \varepsilon_s]}$$

partition function associated with a particular species

energy levels (internal) of a particular species (rotation/vibration/electronic)

λ_i = thermal wavelength

$$\mu_i := \left.\frac{\partial F}{\partial N_i}\right)_{T,V,N_j \neq N_i} = -kT \ln \frac{VQ_i}{N_i}$$

$$\sum_i b_i \mu_i = 0 \Rightarrow \sum_i b_i \left(-kT \ln \frac{VQ_i}{N_i}\right) = 0$$

$$\Rightarrow \sum_i \ln \frac{V^{b_i} Q_i^{b_i}}{N_i^{b_i}} = \sum_i \ln \frac{Q_i^{b_i}}{n_i^{b_i}} = 0$$

$$\boxed{\prod_{i=1}^{m} Q_i^{b_i} = \prod_{i=1}^{m} n_i^{b_i}}$$

$$\boxed{K(T) = \prod_{i=1}^{m} n_i^{b_i} = \prod_{i=1}^{m} Q_i^{b_i}}$$

$K(T) \rightarrow$ equilibrium constant

Grand canonical ensemble

- describes a system which can exchange both energy and particles with a reservoir

$\Rightarrow$ fixed $\bar{E} = \langle E \rangle$ and $\bar{N} = \langle N \rangle$

in this case: $\hat{D} = \dfrac{\exp[-\beta \hat{H} + \alpha \hat{N}]}{Q}$

$$Q = \mathrm{Tr} \exp[-\beta \hat{H} + \alpha \hat{N}]$$

Q - grand partition function

- space in which $\hat{D}$ acts in a Hilbert space which is a <u>direct sum</u> of sub-Hilbert spaces

$\rightarrow$ direct sum of spaces with $N = 0$, $N = 1$, $N = 2$, ... $N = \infty$

for direct sum: $\mathcal{H} = \bigoplus_N \mathcal{H}^{(N)} \Rightarrow$

$$\mathrm{Tr}[A_1 \oplus A_2] = \mathrm{Tr} A_1 + \mathrm{Tr} A_2$$

(direct product: $\mathrm{Tr}[A_1 \otimes A_2] = \mathrm{Tr} A_1 A_2$

$$\Rightarrow \quad Q = \sum_{N=0}^{\infty} \exp[-\beta \mathcal{H}_N] \exp(\alpha \hat{N})$$

(assuming $\mathcal{H}_N$ commutes with N)

(most often the case)

1

- since $[H, N] = 0$

$$\Rightarrow \hat{H}|N,r\rangle = E_r(N, x_i)|N,r\rangle$$

x_i - external parameters

$$\hat{N}|N,r\rangle = N|N,r\rangle$$

$$\langle N,r| e^{-\beta \hat{H} + \alpha \hat{N}} |N,r\rangle = e^{-\beta E(N, x_i)} e^{\alpha N}$$

$$\mathrm{Tr}_N\, e^{-\beta \hat{H}} e^{\alpha \hat{N}} = e^{\alpha N} \sum_r e^{-\beta E_r(N, x_i)}$$

grand partition function:

$$Q(\alpha, \beta, x_i) = \sum_{N=0}^{\infty} e^{\alpha N} \underbrace{\sum_r e^{-\beta E_r(N, x_i)}}_{\substack{\text{canonical partition function} \\ Z_N(\beta)}}$$

$$\boxed{Q(\alpha, \beta, x_i) = \sum_{N=0}^{\infty} e^{\alpha N} Z_N(\beta)}$$

determine β, α $\quad (\beta = 1/k_B T)$

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta} \qquad \bar{N} = \frac{\partial \ln Q}{\partial \alpha} \qquad \underbrace{X_i = -\frac{1}{\beta}\frac{\partial \ln Q}{\partial x_i}}_{}$$

for example

if $x_i = -V \Rightarrow X_i = p$

$$p = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V}\Big|_{\alpha\beta}$$

Consider:

$$\frac{S}{k} = ?$$

$$\frac{S}{k} = -\mathrm{Tr}\, D \ln D = -\mathrm{Tr}\, D\left[-\beta\hat{H} + \alpha\hat{N}\right] + \ln Q$$

$$= \beta\bar{E} - \alpha\bar{N} + \ln Q$$

$$\frac{dS}{k} = \beta\, d\bar{E} + \bar{E}\, d\beta - \alpha\, d\bar{N} - \bar{N}\, d\alpha + \underline{d\ln Q}$$

$$d\ln Q = \frac{\partial \ln Q}{\partial \beta} d\beta + \frac{\partial \ln Q}{\partial \alpha} d\alpha + \frac{\partial \ln Q}{\partial x_i} dx_i$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$= -\bar{E}\, d\beta + \bar{N}\, d\alpha - \beta X_i\, dx_i$$

$$\frac{dS}{k} = \beta\, d\bar{E} - \alpha\, d\bar{N} - \beta X_i\, dx_i$$

$$T\, dS = d\bar{E} - \frac{\alpha}{\beta} d\bar{N} - X_i\, dx_i$$

$$\Rightarrow d\bar{E} = T\, dS + \underbrace{X_i\, dx_i}_{-p\,dV} + \underbrace{\frac{\alpha}{\beta} d\bar{N}}_{\mu = \frac{\alpha}{\beta}} \Rightarrow \boxed{\alpha = \frac{\mu}{kT}}$$

Mono-atomic gas

$$Q = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta)$$

$$Z_N(\beta) = \frac{V^N}{N!} \frac{1}{\lambda^{3N}} = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

$$Q = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{e^{\beta\mu} V}{\lambda^3}\right)^N \qquad \exp x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$$

$$\Downarrow$$

$$Q = \exp\left[\frac{e^{\beta\mu} V}{\lambda^3}\right]$$

$$\Downarrow$$

$$\bar{N} = \frac{1}{\beta}\frac{\partial \ln Q}{\partial \mu} \Rightarrow \frac{1}{\beta}\frac{\partial}{\partial \mu}\left[e^{\beta\mu}\frac{V}{\lambda^3}\right] = \frac{1}{\cancel{\beta}}\cancel{\beta} e^{\beta\mu}\frac{V}{\lambda^3} = e^{\beta\mu}\frac{V}{\lambda^3}$$

$$p = \frac{1}{\beta}\frac{\partial \ln Q}{\partial V}\bigg|_{\mu,\beta} = \frac{1}{\beta}\frac{e^{\beta\mu}}{\lambda^3}$$

$$\Rightarrow \boxed{pV = \bar{N} kT}$$

Thermodynamics and Fluctuations

$$Q = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta)$$

$$\bar{N} = \frac{1}{\beta}\frac{\partial \ln Q}{\partial \mu} = \frac{\cancel{1}}{\cancel{\beta}} \frac{1}{\sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta)} \sum_{N=0}^{\infty} e^{\beta\mu N} \cancel{\beta} N Z_N(\beta)$$

$$\frac{\partial \bar{N}}{\partial \mu} = \frac{1}{\beta^2}\frac{\partial^2 \ln Q}{\partial \mu^2} = \frac{1}{\beta^2}\left[\frac{1}{Q}\frac{\partial^2 Q}{\partial \mu^2} - \left(\frac{1}{Q}\frac{\partial Q}{\partial \mu}\right)^2\right]$$

$$= \frac{1}{\beta^2}\left[\langle N^2\rangle - \langle N\rangle^2\right]$$

$\Rightarrow$ fluctuations in N (i.e. σ_N^2) are proportional to $\bar{N}$

$$\sigma_N^2 \sim \frac{\partial \bar{N}}{\partial \mu} \sim N$$

relative fluctuations: $\quad \frac{\sigma_N}{N} \sim \frac{1}{\sqrt{N}}$

$$N \to \infty \qquad \frac{\sigma_N}{\bar{N}} \to 0$$

$\Rightarrow$ at least away from phase transitions (where there are non-analyticities) the canonical and grand canonical ensembles are equivalent as $N \to \infty$

* can also consider N which has the maximum probability

$$\Rightarrow \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta) \sim e^{\beta\mu N_*} Z_{N_*}(\beta)$$

maximize $e^{\beta\mu N} Z_N(\beta)$

$$\frac{\partial}{\partial N} e^{\beta\mu N} Z_N(\beta) = \beta\mu e^{\beta\mu N} + e^{\beta\mu N} \frac{\partial Z_N(\beta)}{\partial N} = 0$$

$$\Rightarrow \beta[\mu - \mu_{can}] = 0 \Rightarrow \underline{\mu = \mu_{can}}$$

$$\ln Q = \beta\mu N_* + \ln Z_{N_*}(\beta)$$

$$= \beta(\mu N_* - F_{N_*})$$

$$= \beta(G - F) = \beta PV$$

---

since $G = \mu N$

$$\boxed{\Omega = -\frac{\ln Q}{\beta} = -PV}$$