Reactions - Macroscopic Treatment

Example reaction $A + 2B \rightleftharpoons C$ $\quad K_{eq} = \dfrac{[C]}{[A][B]^2}$ why?

At const T, P $\quad G(T, P, N_A, N_B, N_C)$ is min

But - N_A, N_B, N_C are no longer independent!

In general, can write any reaction as

$$\nu_1 M_1 + \nu_2 M_2 + \cdots + \nu_n M_n = 0$$

ν_i: stoichiometric coefficients + for prod. − for react.

reaction extent ξ : $dN_i = \nu_i d\xi$

$$N_i = N_{i,0} + \nu_i \xi$$

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

at const. T, P $\quad dG = \sum_i \mu_i dN_i = \left(\sum_i \nu_i \mu_i\right) d\xi$

at equilibrium $\dfrac{dG}{d\xi} = 0 \Rightarrow \boxed{\sum_i^n \nu_i \mu_i = 0}$ (1)

For independent reactions, each has its own extent ξ_j, min G w.r.t all ξ's

For ideal gases. $\mu_i = \mu_i^\circ(T) + k_B T \ln P_i$

(1) $\Rightarrow \sum_i \nu_i (\mu_i^\circ + k_B T \ln P_i) = 0 \rightarrow$

$$-\frac{1}{k_B T} \sum_i \nu_i \mu_i^\circ = \sum_i \nu_i \ln P_i = \ln\left(\prod_i P_i^{\nu_i}\right)$$

$$\Rightarrow \prod_i P_i^{\nu_i} = \exp\left(-\frac{\sum_i \nu_i \mu_i^\circ}{k_B T}\right) = \underbrace{K(T)}$$

equilibrium "constant"

The standard free energy change of reaction is

$$\boxed{\Delta g^\circ(T) = \sum_i \nu_i \mu_i^\circ(T)} \quad ②$$

In general, non-ideal systems

$$\mu_i(T, P, \{x_i\}) = RT \ln f_i + \mu_i^\circ(T, P^\circ, \text{pure } i)$$

$$① \Rightarrow \prod_i f_i^{\nu_i} = f_1^{\nu_1} f_2^{\nu_2} \cdots f_n^{\nu_n} = K(T)$$

Recall that the convenient, dimensionally inconsistent form of f_i is used – this results in a dimensionally inconsistent expression for $K(T)$

Strictly speaking we should write

$$\left(\frac{f_1}{f_1^\circ}\right)^{\nu_1}\left(\frac{f_2}{f_2^\circ}\right)^{\nu_2} \cdots \left(\frac{f_n}{f_n^\circ}\right)^{\nu_n} = K(T)$$

$$f_1^\circ = f_2^\circ = \cdots f_n^\circ = 1 \text{ bar}$$

Δg° for reactions are usually obtained from thermochemical tables that list Δg°_{form} of chemical species from the elements.

E.g. for the "reaction" $H_2O(\ell) \rightleftharpoons H_2O(g)$ $\Delta g^\circ = 8.55$ kJ/mol @ 298 K

Which one is true at equilibrium for H_2O @ 298 K?

(A) $f(\text{liquid } H_2O) = f(\text{vapor } H_2O)$

(B) $\frac{f(\text{vapor})}{f(\text{liquid})} = \exp\left(-\frac{\Delta g^\circ}{RT}\right) = 0.0317$

} — inconsistent

The apparent discrepancy is resolved when one considers the reference state at which $f_i^\circ = 1$ bar in the expression $\mu_i = RT \ln f_i + \mu_i^\circ(T, P^\circ, \text{pure } i)$

For (A), and phase equil. calculations w/o reactions more generally, we use a common reference state for both phases, namely the gas at P = 1 bar.

For (B), and in thermochemical tables, the standard states of liquids + solids are the condensed phases at 1 bar, $f_i^\circ(T, 1 \text{ bar}, \text{liq. } H_2O) = 1$ bar

The two reference states lead to the same result, $P^{sat} = 0.0317$ bar at equilibrium

Temperature Dependence of K(T)

$K(T) = \exp(-\Delta g^\circ / k_B T)$

Recall that $\frac{\partial (G/T)}{\partial T} = \frac{1}{T}\frac{\partial G}{\partial T} - \frac{G}{T^2} = \frac{S}{T} - \frac{G}{T^2} = \frac{-H}{T^2}$

$$\therefore \quad \frac{d \ln K(T)}{dT} = \frac{d}{dT}\left[-\frac{\Delta g^\circ}{k_B T}\right] = +\frac{\Delta h^\circ}{k_B T^2}$$

$$\text{or} \quad \frac{d \ln K(T)}{d(1/T)} = -\frac{\Delta h^\circ}{k_B}$$

van't Hoff relation

$\Delta h^\circ > 0$ endothermic, $K \uparrow$ as $T \uparrow$

$\Delta h^\circ < 0$ exothermic, $K \downarrow$ as $T \uparrow$

One could also express $K(T)$ in terms of activities (in solution), for which

$$\mu_i(T, P, \{x_i\}) = RT \ln a_i + \mu_i^\circ(T, P, \text{pure } i)$$

($a_i = \gamma_i x_i$)

$$\Rightarrow K_p(T) = \prod_i a_i^{\nu_i}, \quad K_p = \exp\left(-\frac{\sum_i \nu_i \mu_i^\circ}{k_B T}\right)$$

Note that this is at P, not P°

In this case, the equilibrium "constant" is also a function of pressure, through the dependence of μ_i° on P.

Reactions at microscopic level – fluctuations

One could consider a system at const. T and V

A is min $\Rightarrow$ $dA = -SdT - PdV + \sum_i \mu_i dN_i = 0$

$$\Rightarrow \sum_{i=1}^{n} \nu_i \mu_i = 0$$ same as before

Consider a simple isomerization reaction:

$$A \overset{k}{\rightleftharpoons} B \qquad N = N_A + N_B = \text{const.}$$

$$Q(T,V,N) = \sum_{N_A=0}^{N} \sum_{\substack{\text{all states} \\ m \text{ @ } N_A, N_B, V}} e^{-\beta E_m} = \sum_{N_A=0}^{N} Q(T,V,N_A,N_B)$$

For independent (ideal-gas) particles,

$$Q(T,V,N_A,N_B) = \frac{q_A^{N_A} q_B^{N_B}}{N_A!\, N_B!}$$

$$Q(T,V,N) = \sum_{N_A=0}^{N} Q(T,V,N_A,N_B) = \frac{(q_A+q_B)^N}{N!}$$

[Recall $(x+y)^n = \sum_{i=0}^{n} \binom{n}{i} x^i y^{n-i}$]

$$\mathcal{P}(N_A) = \frac{Q(T,V,N_A,N_B)}{Q(T,V,N)} = \frac{1}{Q(T,V,N)} \frac{q_A^{N_A} q_B^{N_B}}{N_A!\, N_B!}$$

$$\langle N_A \rangle = \sum_{N_A=0}^{N} \mathcal{P}(N_A) N_A = \frac{1}{Q(T,V,N)} \sum_{N_A=0}^{N} N_A \frac{q_A^{N_A} q_B^{N_B}}{N_A! N_B!}$$

$$= q_A \left(\frac{\partial \ln Q(T,V,N)}{\partial q_A} \right)_{T,V,N,q_B} = N \frac{q_A}{q_A+q_B}$$

$$\therefore \frac{\langle N_B \rangle}{\langle N_A \rangle} = \frac{q_B}{q_A}$$ microscopic analog of equilibrium constant

By analogy, $\sigma_{N_A}^2 = \langle N_A^2 \rangle - \langle N_A \rangle^2 = \left. \frac{\partial \ln Q}{\partial (1/q_A)^2} \right)_{T,V,q_B}$

$$= q_A \left. \frac{\partial \langle N_A \rangle}{\partial q_A} \right)_{T,V,N,q_B} = \frac{\langle N_A \rangle \langle N_B \rangle}{N}$$

Since $N_A + N_B = N = \text{const.}$, $\sigma_{N_B}^2 = \sigma_{N_A}^2$

Relative fluctuations $\frac{\sqrt{\sigma_{N_A}^2}}{\langle N_A \rangle} = \left(\frac{\langle N_B \rangle}{\langle N_A \rangle N} \right)^{1/2}$

[10% for $\langle N_A \rangle = \langle N_B \rangle$, $N = 100$]