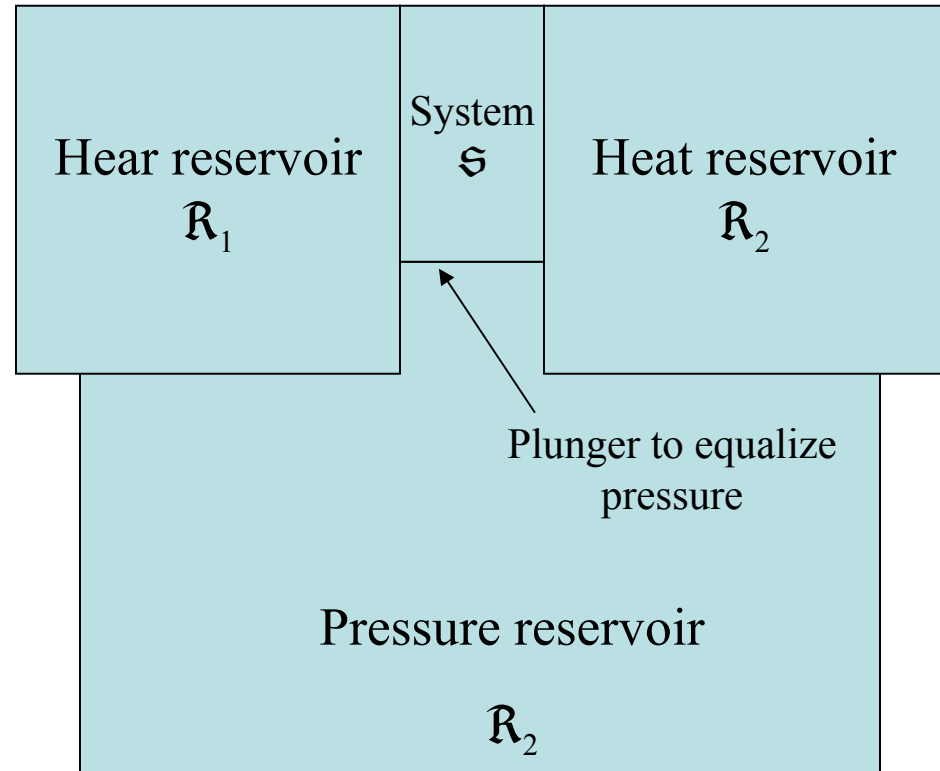


GIBBS FREE ENERGY AND CHEMICAL REACTIONS

GIBBS FREE ENERGY

The Helmholtz free energy F describes a system at constant volume and temperature. But in many experiments, and in particular chemical reactions, are performed at constant pressure. It is therefore useful to introduce a function to treat the equilibrium configuration at constant pressure and temperature.



A system in thermal equilibrium with a heat reservoir and in mechanical equilibrium with a pressure reservoir which maintains a constant pressure on the system. The pressure reservoir is thermally insulated.

Define the Gibbs free energy G as

$$G = F + pV$$

$$= U - \tau\sigma + pV$$

The differential of G is

$$dG = dU - \tau d\sigma - \sigma d\tau + p dV + V dp$$

$$\text{As } (dU = \tau d\sigma - p dV + \mu dN)$$

$$\Rightarrow dG = \tau d\sigma - p dV + \mu dN - \tau d\sigma - \sigma d\tau + p dV + V dp$$

$$= -\sigma d\tau + V dp + \mu dN$$

The differential may be written as

$$dG = \left(\frac{\partial G}{\partial \tau} \right)_{p, N} d\tau + \left(\frac{\partial G}{\partial p} \right)_{\tau, N} dp + \left(\frac{\partial G}{\partial N} \right)_{\tau, p} dN$$

Gibbs free energy is a minimum for a system \mathfrak{S} in equilibrium ($dG = 0$) at constant pressure when in thermal contact with a reservoir \mathfrak{R} .

The variables τ and p are **intensive quantities**: they do not change value when two identical systems are put together. But U, σ, V, N and G are **extensive quantities**: their value doubles when two identical systems are put together.

Since G is also extensive, if we have one specie then

$$G(\tau, p, N) = Ng(\tau, p)$$

$$\Rightarrow \mu = \frac{\partial G}{\partial N} = g(\tau, p) = \frac{G}{N}$$

Chemical potential = Gibbs free energy / particle

Natural variables for $\mu = \mu(\tau, p)$

If more chemical species are present

$$G = \sum_j N_j \mu_j$$

This ensemble is particularly well suited for chemical reactions.

The thermodynamic identity is

$$dG = \sum_j \mu_j dN_j - \sigma d\tau + V dp.$$

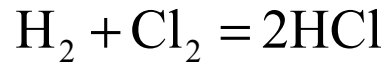
Equilibrium in Reactions

A chemical reaction may be written as

$$\nu_1 A_1 + \nu_2 A_2 + \dots + \nu_l A_l = 0$$

$$\sum_j \nu_j A_j = 0.$$

Example:



We have

$$A_1 = \text{H}_2 \quad \nu_1 = 1$$

$$A_2 = \text{Cl}_2 \quad \nu_2 = 1$$

$$A_3 = \text{HCl} \quad \nu_3 = -2$$

Since reactions proceed at $\tau = \text{constant}$, $p = \text{constant}$.

$$dG = \sum_i \mu_i dN_i - \sigma d\tau + V dp = 0$$

In equilibrium $dG = 0$,

Since dN_j is proportional to v_j in $\sum v_j A_j = 0$

$$dN_j = v_j \cdot \underbrace{d\hat{N}}_{\text{how often reaction takes place}}$$

$$\Rightarrow dG = \left(\sum_j v_j \mu_j \right) d\hat{N} = 0$$

$$\Rightarrow \boxed{\sum_j v_j \mu_j = 0}$$

Condition for equilibrium for transformation of matter at constant τ and p .

Equilibrium For Ideal Gases

A simple form of the general equilibrium condition ($\sum_j \nu_j \mu_j = 0$) can be obtained by assuming that each constituent acts as an ideal gas.

$$\mu_j = \tau (\log n_j - \log c_j)$$

where n_j is the concentration of the species j and

$$c_j \equiv n_Q Z_j \text{ (internal partition function)}$$

which depends on the temperature but not on the concentration.

Then,

$$\sum_j \nu_j \mu_j = 0$$

$$\Rightarrow \sum_j \nu_j \log n_j = \sum_j \nu_j \log c_j$$

$$\Rightarrow \sum_j \log n_j^{\nu_j} = \sum_j \log c_j^{\nu_j}$$

$$\Rightarrow \log \prod_j n_j^{\nu_j} = \log \prod_j c_j^{\nu_j} = \log K(\tau)$$

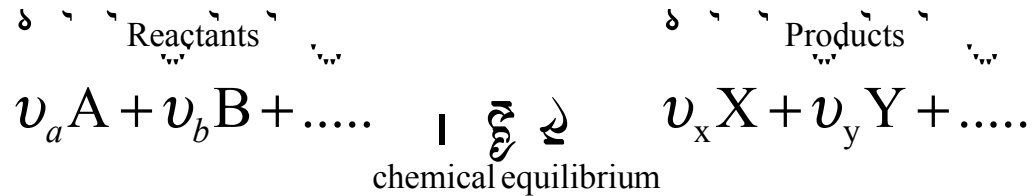
equilibrium constant depends on τ

$$\Rightarrow \prod_j n_j^{\nu_j} = K(\tau)$$

Which is known as **law of mass action**.

Energies of Chemical Reaction

A typical chemical reaction is written like this



The Gibbs free energy for the system ($\tau, P = \text{constant}$)

$$G = \sum_i \mu_i N_i \quad (\text{equilibrium iff } dG = 0)$$

$$0 = dG = \sum_i \mu_i dN_i = \mu_a dN_a + \mu_b dN_b + \dots + \mu_x dN_x + \mu_y dN_y + \dots$$

$$dN_a = -v_a d\xi, \quad dN_b = -v_b d\xi, \quad dN_x = v_x d\xi, \quad dN_y = v_y d\xi$$

$$0 = \left(-\nu_a \mu_a - \nu_b \mu_b - \dots - \underbrace{\sum_i \nu_i \mu_i}_{\text{must be zero}} + \nu_x \mu_x + \nu_y \mu_y + \dots \right) d\xi$$

$$\nu_a \mu_a + \nu_b \mu_b + \dots = \nu_x \mu_x + \nu_y \mu_y + \dots \quad (\text{Chemical Equilibrium})$$

In order to proceed further one often assumes “ideal gas behavior”.

Ideal gas approximation, species 1, 2, 3,.....

$$Z = \left(\frac{Z_1^{N_1}}{N_1!} \right) \left(\frac{Z_2^{N_2}}{N_2!} \right) \dots$$

Gas 1

$$\mu_i = \left(\frac{\partial F}{\partial N_i} \right)^{-\tau \ln Z} = -\tau \frac{\partial}{\partial N_i} \left(\ln \frac{Z_1^{N_1}}{N_1!} + \ln \frac{Z_2^{N_2}}{N_2!} + \dots \right)$$

$$= -\tau \frac{\partial}{\partial N_i} \ln \frac{Z_i^{N_i}}{N_i!} \underset{\text{stirling}}{\approx} \tau \ln \frac{N_i}{Z_i} = \tau \ln \frac{N_i/V}{Z_i/V} = \tau \ln \frac{n_i}{Z_i/V}$$

$\frac{p_i/\tau}{\tau}$

$$= \tau \ln \frac{P_i}{\tau(Z_i/V)} = \tau \ln \frac{P_i/P^\phi}{\tau(Z_i/V)/P^\phi} = \tau \ln \frac{P_i}{P^\phi} + \mu_i^\phi$$

$$\text{where } \mu_i^\phi = -\tau \ln \frac{\tau(Z_i/V)}{P^\phi}$$

$P^\phi \leftrightarrow$ "standard pressure" = 1 atm = 101.325 kPa

$\mu_i^\phi \leftrightarrow$ "standard chemical potential"

Remember: $Z = \underbrace{Z_{\text{tran}}}_{\text{proportional to } V} \cdot \underbrace{Z_{\text{rot}} \cdot Z_{\text{vib}} \cdot Z_{\text{el}}}_{\text{does not depend on } V} \propto V$



Z/V does not depend on volume and can only depend on τ

μ_i^ϕ depends only on τ .

Chemical Equilibrium:

As

$$v_a \mu_a + v_b \mu_b + \dots = v_x \mu_x + v_y \mu_y + \dots$$

$$\Rightarrow v_a \tau \ln \frac{n_a}{Z_a/V} + v_b \tau \ln \frac{n_b}{Z_b/V} + \dots = v_x \tau \ln \frac{n_x}{Z_x/V} + v_y \tau \ln \frac{n_y}{Z_y/V} + \dots$$

$$\Rightarrow \ln \frac{n_x^{v_x} \cdot n_y^{v_y} \dots}{n_a^{v_a} \cdot n_b^{v_b} \dots} = \ln \frac{(Z_x/V)^{v_x} \cdot (Z_y/V)^{v_y} \dots}{(Z_a/V)^{v_a} \cdot (Z_b/V)^{v_b} \dots} = \ln K(\tau)$$

By exponentiation

$$\frac{n_x^{v_x} \cdot n_y^{v_y} \dots}{n_a^{v_a} \cdot n_b^{v_b} \dots} = \frac{(Z_x/V)^{v_x} \cdot (Z_y/V)^{v_y} \dots}{(Z_a/V)^{v_a} \cdot (Z_b/V)^{v_b} \dots} = \ln K(\tau)$$

Which is Law of mass action.

A change in the concentration of one specie will force the change in the concentration of the other specie.

Chemist write:

$$\frac{[\text{X}]^{v_x} [\text{Y}]^{v_y} \dots}{[\text{A}]^{v_a} [\text{B}]^{v_b} \dots} = K(\tau)$$

Warning! When calculating the various partition function, we need to agree on a unique energy scale! This is conveniently done as follows:

Assume that the point of lowest energy of species i is ε_i , when to from some agreed energy scale. Then:

$$\begin{aligned}
 Z_i &= \sum \exp(-H/\tau) = \sum \exp\left(-\left(\overset{\text{lowest energy}}{\overset{\circ}{H}} + \varepsilon_i\right)/\tau\right) \\
 &= \exp\left(-\varepsilon_i/\tau\right) \sum \exp\left(-\overset{\circ}{H}/\tau\right) = \exp\left(-\varepsilon_i/\tau\right) \overset{\circ}{Z}_i \\
 \Rightarrow K &= \frac{(Z_x/V)^{v_x} \dots}{(Z_a/V)^{v_a} \dots} = \frac{\left(\overset{\circ}{Z}_x/V\right)^{v_x} \dots}{\left(\overset{\circ}{Z}_a/V\right)^{v_a} \dots} \exp\left(\frac{(\varepsilon_x + \varepsilon_y + \dots - \varepsilon_a - \varepsilon_b \dots)}{\tau}\right)
 \end{aligned}$$

This is basically ΔU
This is usually the most important contribution to K.

Alternatively,

$$n_i = \frac{p_i}{\tau} = \frac{p_i}{p^\phi} \cdot \frac{p^\phi}{\tau}$$

Law of mass action :

$$\frac{(p_x/p^\phi)^{v_x} (p_y/p^\phi)^{v_y} \dots}{(p_a/p^\phi)^{v_a} (p_b/p^\phi)^{v_b} \dots} = \frac{\left(\frac{(Z_x/V)\tau}{p^\phi}\right)^{v_x} \left(\frac{(Z_y/V)\tau}{p^\phi}\right)^{v_y}}{\left(\frac{(Z_a/V)\tau}{p^\phi}\right)^{v_a} \dots} = K_p(\tau)$$

$K_p(\tau)$ is a dimension less quantity!

$$-\tau \ln K_p = -\tau v_x \ln \frac{(Z_x/V)\tau}{p^\phi} + (-\tau) v_y \ln \frac{(Z_y/V)\tau}{p^\phi} \dots + \tau v_a \ln \frac{(Z_a/V)\tau}{p^\phi} \dots$$

$$= v_x \mu_x^\phi + v_y \mu_y^\phi - v_a \mu_a^\phi - v_b \mu_b^\phi$$

$$= \Delta G^\phi \quad \Rightarrow$$

$$K_p = \exp(-\Delta G^\phi / \tau)$$

Example

pH and ionization of water:



At room temperature

$$[\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ l}^{-2}$$

In pure water

$$[\text{H}^+][\text{OH}^-] = 10^{-7} \text{ mol l}^{-1}$$

pH is defined as:

$$\text{pH} := -\log_{10}[\text{H}^+]$$

If a solution has $\text{pH} < 7$ then solution is acidic (apple ~ pH3) and

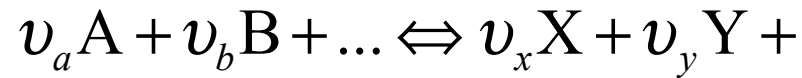
If a solution has $\text{pH} > 7$ then solution would be basic (Human blood plasma 7.3 – 7.5)

Acid: proton donor

Base: $[\text{OH}^-]$ donor

The concentration of H^+ ions is increased by adding an acid to the water and the concentration of OH^- ions will decrease as required to maintain the product $[\text{H}^+][\text{OH}^-]$ constant.

if $\Delta G^\phi < 0$, $K_p \gg 1$



if $\Delta G^\phi > 0$, $K_p \ll 1$

Example

Dissociation of a weak acid:



$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K$$

Let

$$[\text{H}^+] = x \Rightarrow [\text{A}^-] = x \quad (\text{Neglect } \text{H}^+ \text{ in water})$$

$$[\text{HA}] = [\text{HA}]_{\text{initial}} - x = a - x$$

$$\Rightarrow \frac{x^2}{a-x} = K$$

Assumption of weak acid means

$$x \ll a \Rightarrow a-x \approx a$$

$$\Rightarrow \frac{x^2}{a} = K \Rightarrow x = \sqrt{a \cdot K}$$

Taking log of both sides

$$\log_{10} x = \frac{1}{2} \log_{10} a + \frac{1}{2} \log_{10} K \quad (\text{Note: } \log_{10} x = \log_{10} [\text{H}^+] = -\text{pH})$$

$$\Rightarrow -\text{pH} = -\frac{1}{2} \text{p}K + \frac{1}{2} \log_{10} [\text{HA}]_{\text{initial}} \quad \text{Define: } \text{p}K = -\log_{10} K$$

$$\text{if } \text{pH} = \text{p}K$$

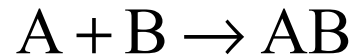
$$\text{then } -\text{pH} = \log_{10} [\text{HA}]_{\text{initial}}$$

$$\Rightarrow [\text{H}^+] = [\text{HA}]_{\text{initial}} \quad \text{It means half of the acid is dissociated.}$$

Example

Kinetic model of mass action:

Suppose that atoms A and B combine to form a molecule AB. We suppose that AB is formed in a biatomic collision of A and B.



Let n_A , n_B , n_{AB} denote the concentration of A, B, and AB respectively.

$$\frac{d}{dt} n_{AB} = \underbrace{C}_{\substack{\text{rate constant} \\ \text{for formation}}} n_A n_B - \underbrace{D}_{\substack{\text{disintegration} \\ \text{constant}}} n_{AB}$$

In thermal equilibrium the concentrations of all constituents are constant so that

$$\frac{d}{dt} n_{AB} = 0$$

$$\Rightarrow C n_A n_B = D n_{AB}$$

$$\Rightarrow \frac{n_A n_B}{n_{AB}} = \frac{D}{C}, \text{ Function of temperature only, consistent with the law of mass action.}$$

Suppose AB needs some catalytic process:



At the end E is returned to its initial state.

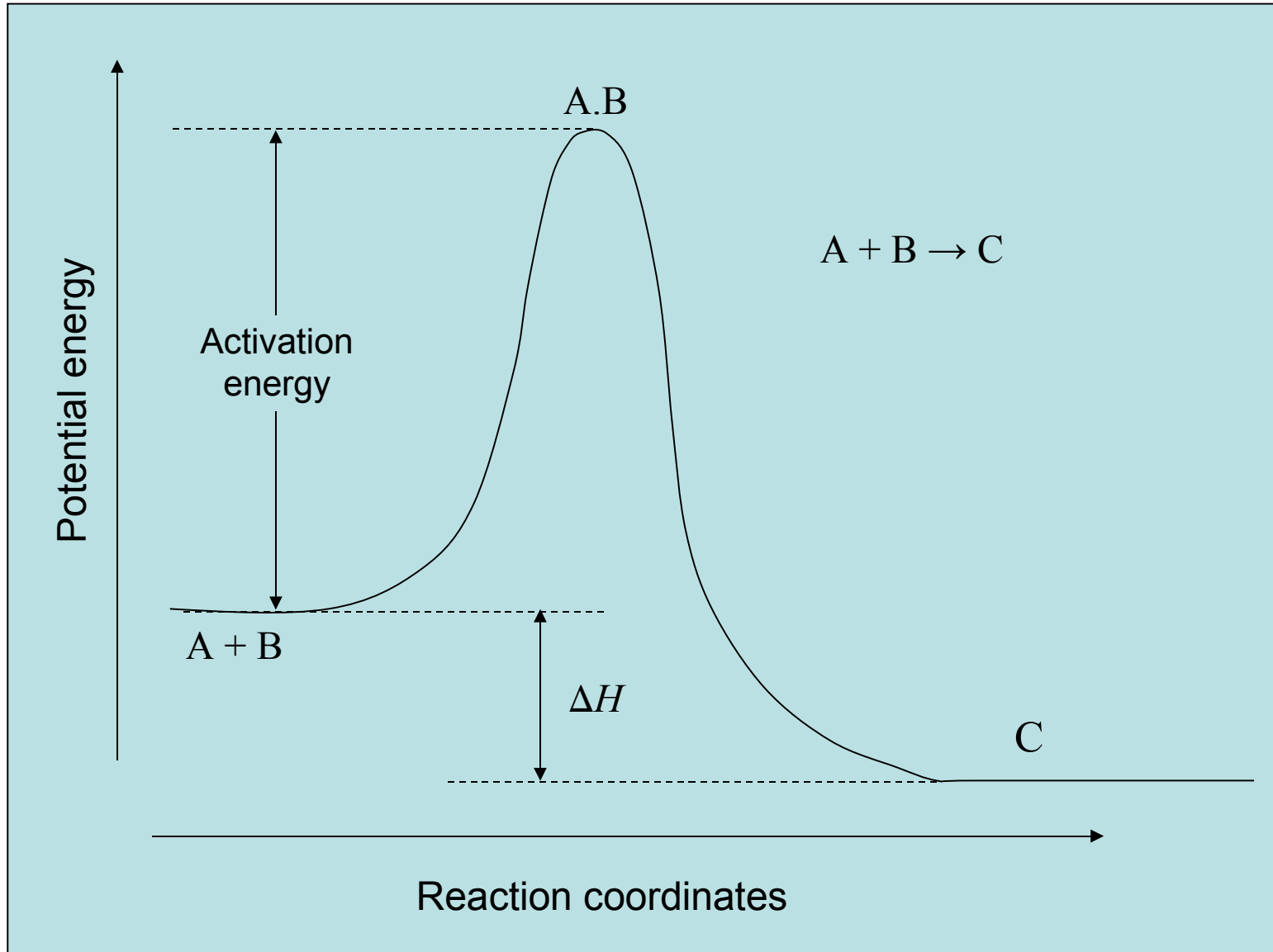
If the intermediate state AE is very short lived (no A is tied up as AE), the ratio $n_A n_B / n_{AB}$ in equilibrium must be the same as in the direct process $A + B \leftrightarrow AB$. The rates, however, may differ.

The equality in equilibrium of the direct and indirect reaction rate is called the **principle of detailed balance**.

$$\frac{n_A n_B}{n_{AB}} = \frac{D}{C} = \text{constant.}$$

Comments: Reaction rates.

The law of mass action does not tell us about the speed of the reaction $A + B = C$.



The quantity ΔH measures the energy evolved in the reaction and determine the equilibrium concentration ratio $[A][B] / [C]$.

A and B may have to negotiate a potential barrier (activation energy) before the reaction can occur to produce C.

Only molecules on the high energy end of their energy distribution will be able to react; others will not be able to get over the potential hill.

A catalyst speeds up a reaction by offering an alternate reaction path with a lower energy of activation, but it does not change the equilibrium concentrations.