

Lecture 11 - Chemical Reactions

①

Brief overview about chemical reactions in equilibrium systems.

We have discussed previously that the Gibbs free energy $G(T, P, N_1, N_2, \dots, N_r)$ of a system with r species should be a minimum in the thermodynamic equilibrium. More specifically, an infinitesimal variation of Gibbs free energy, dG , associated to an ^{infinitesimal} change of the particle number dN_j is given by

$$dG = -SdT + VdP + \sum_j \mu_j dN_j.$$

Typically, ^{chemical} reactions are performed at an open vessel, in which T and P are held fixed.

So that

$$dG = \sum_{j=1}^r \mu_j dN_j \quad (1)$$

giving a ^{generic} chemical reaction $A + B \rightleftharpoons C$,

we can also write it as

$$0 \rightleftharpoons -A - B + C \quad \text{or even}$$

$$0 \rightleftharpoons \sum_{j=1}^n \nu_j A_j \quad \text{where } \nu_j > 0, < 0 \quad \text{for}$$

products and reactants, respectively.

Typically, the changes in the number of moles are proportional to the stoichiometric coefficients, so that one can introduce the following quantity " $d\xi$ "

$$\frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \frac{dN_3}{\nu_3} = \dots \equiv d\xi$$

or equivalently,

$$dN_j = \nu_j d\xi$$

By inserting above expression in Eq. (1)

we have that

$$dG = d\xi \sum_j \mu_j \nu_j,$$

where $\sum_j \mu_j \nu_j$ can be defined as the affinity, $A \equiv - \sum_j \mu_j \nu_j$.

The equilibrium condition implies that

$dG = 0$ and hence the affinity vanishes,

$$A \equiv - \sum_j \mu_j \nu_j = 0. \quad (\text{at the thermodynamic equilibrium}).$$

(2)
If the initial quantities of each of the chemical components is N_j^0 , the chemical reaction proceeds to some extent and the mole numbers assume the new values

$$N_j = N_j^0 + \nu_j \xi^* \quad \left(\xi^* = \int d\xi \right)$$

Let us assume a dilute solution in which one can resort to the chemical reaction properties of ideal gases.

In particular, the chemical potential μ_j of the j -th component is given by

$$\mu_j = RT \left[\phi_j(T) + \ln P + \ln x_j \right],$$

where $\phi_j(T)$ solely depends on T , P

is the pressure and x_j is the mole

fraction $x_j = \frac{N_j}{N_1 + N_2 + \dots + N_M}$ of the j -th

component.

In the equilibrium

$$\sum_j \mu_j \nu_j = 0 \quad \text{or even} \quad \sum_j \nu_j \ln x_j = - \sum_j \nu_j \ln P + \sum_j \nu_j \phi_j(T)$$

Above equilibrium condition can alternatively

be rewritten as

$$\prod_j x_j^{\nu_j} = P^{-\sum_j \nu_j} \tilde{K}(T) \quad (2)$$

where $\tilde{K}(T) = e^{-\sum_j \nu_j \phi_j(T)}$ is the
equilibrium constant and (2) is
the mass action law.

Finally, the affinity can be written

(in terms of mass action law) as

$$A_{eq} = RT \ln \frac{K(T, P)}{\prod_j x_j^{(eq) \nu_j}} = 0$$

where $K(T, P) \equiv \tilde{K}(T) P^{-\sum_j \nu_j}$

(3)

For a set of distinct reactions and distinct constituents, some of previous expressions can be extended

$$dN_k = \sum_{j=1}^r \nu_{kj} d\xi_j,$$

where each one of r different chemical reactions, each of which has its own degree of ξ_j and ν_{kj} is the stoichiometric coefficient of substance k in the reaction j .

$j = 1, 2, \dots, r \rightarrow \underline{r}$ distinct chemical reactions

$k = 1, 2, \dots, n \rightarrow$ the number of species.

If the chemical potential μ_k fulfills

the relation $\sum_k \mu_k \nu_{kj} = 0$ for each

reaction $j = 1, 2, \dots, r$, then the system will reach an equilibrium steady state.

Otherwise, if chemical potentials do not obey $\sum_k \mu_k \nu_k = 0$, the system will not reach equilibrium and will be found in a nonequilibrium stationary state.

at least one reaction is shifted either to the right or to the left, that is, either the products are being created and the reactants being annihilated (forward reaction) or the opposite case (backward reaction). In the stationary nonequilibrium state, entropy is continuously being produced and the rate of entropy production equals the flux of entropy. That is

$$\frac{dS}{dt} = \Pi(t) - \Phi(t) \quad (4)$$

Where when $\frac{dS}{dt} = 0 \Rightarrow \Pi_{N.E.S.S} = \Phi_{N.E.S.S}$

also $\frac{dU}{dt} = - \overbrace{\Phi_\mu}^{\text{energy flux.}}$ from/to the system to/from the reservoir.

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Let us focus our attention (for simplicity) in the one reaction case ($g=1$). So the first & law and second law of thermodynamics combined gives us $\left(\begin{array}{l} T \text{ is held} \\ \text{fixed} \end{array} \right)$

$$\frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} - \sum_{k=1}^n \frac{\mu_k}{T} \frac{dN_k}{dt}$$

$$\text{or } \frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} - \sum_{k=1}^n \frac{\mu_k}{T} \nu_k \frac{d\xi}{dt}$$

$$\text{Once again } A \equiv - \sum_{k=1}^n \mu_k \nu_k$$

$$\frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} + \frac{A}{T} \frac{d\xi}{dt}$$

or even

$$\frac{ds}{dt} = - \frac{1}{T} \phi_\mu + \frac{A}{T} \frac{d\xi}{dt}$$

By comparing with Eq. (4) one

has

$$\phi(t) = \frac{\phi_\mu}{T},$$

in accordance with our "intuitive"

relation between the entropy flux
as the "heat" over "the temperature",

and $\pi(t) = \frac{A}{T} \frac{d\xi}{dt}$ and the

"entropy production" is the
"affinity" (force) ^{thermodynamic} times "flux" $\frac{d\xi}{dt}$

In the NESS $\frac{d\xi}{dt} = W (Ch)$ and

the entropy production reads

$$\pi_{NESS} = \frac{A W}{T} > 0$$

$$A > 0 \Rightarrow W > 0$$

$$A < 0 \Rightarrow W < 0$$

as we shall
verify, if $\frac{W}{T}$
is small

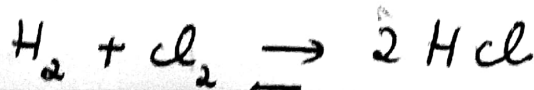
$$W \approx \frac{A}{T}$$

and $\pi = L \left(\frac{A}{T} \right)^2$
↑
Onsager

coefficient.

Example

Let us consider the chemical reaction



Where

(5)

$$\frac{dN_{H_2}}{-1} = \frac{dN_{Cl_2}}{-1} = \frac{dN_{HCl}}{2} \equiv d\xi$$

In the NESS $W = \frac{d\xi}{dt} = W_+ - W_- =$

$$= \underbrace{k_+ x_{H_2} x_{Cl_2}}_{W_+} - \underbrace{k_- x_{HCl}^2}_{W_-}$$

If $W > 0 \rightarrow$ forward reaction

$W < 0 \rightarrow$ backward reaction

$W = 0 \rightarrow$ equilibrium

$$k_+ x_{H_2}^{eq} x_{Cl_2}^{eq} = k_- x_{HCl}^{eq 2}$$

$$\frac{k_+}{k_-} = \frac{x_{HCl}^{eq 2}}{x_{H_2}^{eq} x_{Cl_2}^{eq}}$$

$$A = -\mu_{H_2} - \mu_{Cl_2} + 2\mu_{HCl} \quad \text{or}$$

even rewritten as

$$A = RT \ln \frac{k(T, p)}{\prod_k x_k^{\nu_k}} = RT \ln \frac{\prod_k x_k^{(eq) \nu_k}}{\prod_k x_k^{\nu_k}} =$$

$$= RT \ln \frac{x_{HCl}^{(eq)2} x_{H_2}^{(eq)-1} x_{Cl_2}^{(eq)-1}}{x_{HCl}^2 x_{H_2}^{-1} x_{Cl_2}^{-1}}$$

One can rewrite the w under a convenient way, in such a way one can relate with the affinity.

$$\begin{aligned} w &= k_+ x_{H_2} x_{Cl_2} - k_- x_{HCl}^2 \\ &= k_+ x_{H_2} x_{Cl_2} \left[1 - \frac{k_-}{k_+} \frac{x_{HCl}^2}{x_{H_2} x_{Cl_2}} \right] \\ &= k_+ x_{H_2} x_{Cl_2} \left[1 - \frac{x_{H_2}^{(eq)} x_{Cl_2}^{(eq)}}{x_{HCl}^{(eq)2}} \frac{x_{HCl}^2}{x_{H_2} x_{Cl_2}} \right] \\ &= k_+ x_{H_2} x_{Cl_2} \left[1 - e^{-A/RT} \right] \end{aligned}$$

$$\text{and } \pi_{NESS} = \frac{k_+ x_{H_2} x_{Cl_2}}{T} A (1 - e^{-A/RT}) > 0$$

close to the equilibrium regime, in which A is expected to be small, one has that

(6)

$$W \approx k_+ x_{H_2} x_{Cl_2} \frac{A}{RT} \quad \text{and then}$$

$$\pi = L \left(\frac{A}{T} \right)^2, \quad \text{where}$$

the Onsager coefficient $L = \frac{k_+ x_{H_2} x_{Cl_2}}{R} > 0$
(as expected).

Once again if

$$A = -\mu_{H_2} - \mu_{Cl_2} + 2\mu_{HCl} = 0,$$

the thermodynamic equilibrium is restored
and $\pi = 0$.

Coupled reactions

Now we shall extend the application
for a set of three coupled reactions.

In particular, we shall introduce distinct
concepts, such as Onsager reciprocal relations
and affinity be "adjusted" in order to

produce a "flux" against "it".

Let us consider for simplicity the reactions

$$A \xrightleftharpoons[k_{-1}]{k_1} B \xrightleftharpoons[k_{-2}]{k_2} C \xrightleftharpoons[k_{-3}]{k_3} A$$

(Stoichiometric coefficients reading ± 1).

the affinities associated to each reaction are given by

$$A_1 = -\mu_A + \mu_B$$

$$A_2 = -\mu_B + \mu_C$$

$$A_3 = -\mu_C + \mu_A$$

Note that $A_1 + A_2 + A_3 = 0$ revealing that only two reactions are independent, since the process is cyclic.

affinities can also be written as

$$-A_1 = RT \ln \frac{x_B^{eq} x_A}{x_A x_B^{eq}}$$

$$-A_2 = RT \ln \frac{x_C^{eq} x_A}{x_A^{eq} x_C}$$

$$-A_3 = RT \ln \frac{x_B^{eq} x_C}{x_B x_C^{eq}}$$

The entropy production (in the NESS) is

then given by

$$\dot{\Pi}_{NESS} = A_1 w_1 + A_2 w_2 + A_3 w_3 \quad \text{where}$$

$$w_1 = k_1 x_A - k_{-1} x_B$$

$[x_i] \rightarrow$ concentration
of species i.

$$w_2 = k_2 x_B - k_{-2} x_C$$

$$w_3 = k_3 x_C - k_{-3} x_A \quad \Rightarrow \text{since } A_3 = -A_1 - A_2$$

$$\dot{\Pi}_{NESS} = (w_1 - w_3) A_1 + (w_2 - w_3) A_2$$

A simpler analysis (but very remarkable)

can be carried out close to the equilibrium regime, where affinities are expected to

be small. By assuming that

$$x_A = x_A^{eq} + \Delta x_A$$

where $\Delta x_A \ll x_A^{eq}$

$$x_B = x_B^{eq} + \Delta x_B$$

$\Delta x_B \ll x_B^{eq}$

$$x_C = x_C^{eq} + \Delta x_C$$

$\Delta x_C \ll x_C^{eq}$

and

taking into account that

$$k_1 x_A^{eq} - k_{-1} x_B^{eq} = 0$$

$$K_3 x_C^{eq} = K_{-3} x_A^{eq} \quad (\text{equivalent to the detailed balance})$$

$$K_2 x_B^{eq} = K_{-2} x_C^{eq}$$

one can eliminate K_{-1}, K_{-2}, K_{-3} in the each term $(w_1 - w_3)$ and $(w_2 - w_3)$.

Hence

$$w_1 - w_3 = K_1 \Delta x_A - K_1 \frac{x_A^{eq}}{x_B^{eq}} \Delta x_B + K_3 \Delta x_A \frac{x_C^{eq}}{x_A^{eq}} - K_3 \Delta x_C$$

$$= K_1 x_A^{eq} \left(\frac{\Delta x_A}{x_A^{eq}} - \frac{\Delta x_B}{x_B^{eq}} \right) + K_3 x_C^{eq} \left(\frac{\Delta x_A}{x_A^{eq}} - \frac{\Delta x_C}{x_C^{eq}} \right) \quad (6)$$

analogously for $w_2 - w_3$ we have that

$$w_2 - w_3 = K_2 \Delta x_B - K_2 \frac{x_B^{eq}}{x_C^{eq}} \Delta x_C - K_3 \Delta x_C + K_3 \frac{x_C^{eq}}{x_A^{eq}} \Delta x_A$$

$$= K_2 x_B^{eq} \left(\frac{\Delta x_B}{x_B^{eq}} - \frac{\Delta x_C}{x_C^{eq}} \right) - K_3 x_C^{eq} \left(\frac{\Delta x_C}{x_C^{eq}} - \frac{\Delta x_A}{x_A^{eq}} \right) \quad (7)$$

Since we are dealing with the linear approach, we shall show that each term in the parenthesis is directly related to the affinity.

Given the affinity A_1

(8)

$$A_1 = RT \ln \frac{x_A x_B^{eq}}{x_B x_A^{eq}} \quad \text{where}$$

$$x_A = x_A^{eq} + \Delta x_A \quad \text{and}$$

$$x_B = x_B^{eq} + \Delta x_B$$

$$A_1 = RT \ln \left[\frac{x_A^{eq} (1 + \Delta x_A / x_A^{eq}) x_B^{eq}}{x_B^{eq} (1 + \Delta x_B / x_B^{eq}) x_A^{eq}} \right]$$

$$\approx RT \cdot \left(\frac{\Delta x_A}{x_A^{eq}} - \frac{\Delta x_B}{x_B^{eq}} \right) \quad \text{when } \frac{\Delta x_A}{x_A^{eq}} \ll 1$$

$$\frac{\Delta x_B}{x_B^{eq}} \ll 1$$

Analogously

$$A_3 = RT \left(\frac{\Delta x_C}{x_C^{eq}} - \frac{\Delta x_A}{x_A^{eq}} \right)$$

$$A_2 \approx RT \left(\frac{\Delta x_B}{x_B^{eq}} - \frac{\Delta x_C}{x_C^{eq}} \right) \quad \text{and}$$

then expressions for $w_1 - w_3$ and $w_2 - w_3$ in the

linear regime becomes

$$\omega_1 - \omega_3 = \frac{K_1 x_A^{eq}}{RT} A_1 - \frac{K_3 x_C^{eq}}{RT} A_3$$

$$\omega_2 - \omega_3 = \frac{K_2 x_B^{eq}}{RT} A_2 - K_3 x_C^{eq} \frac{A_3}{RT}$$

Taking into account that $A_3 = -A_1 - A_2$

we have that

$$\omega_1 - \omega_3 = L_{11} A_1 + L_{12} A_2$$

$$\omega_1 - \omega_3 = L_{21} A_1 + L_{22} A_2$$

where

$$L_{11} = \frac{1}{RT} (K_1 x_A^{eq} + K_3 x_C^{eq})$$

$$L_{12} = \frac{K_3 x_C^{eq}}{RT}$$

$$L_{21} = \frac{K_3 x_C^{eq}}{RT}$$

$$L_{22} = \frac{(K_2 x_B^{eq} + K_3 x_C^{eq})}{RT}$$

(9)

and finally $\Pi_{NESS} = (w_1 - w_3) A_1 + (w_2 - w_3) A_2$

$$\Pi_{NESS} = L_{11} A_1^2 + L_{12} A_2 A_1 + L_{21} A_1 A_2 + L_{22} A_2^2$$

Several lessons can be learned from:

1) The coupling between chemical reactions lead to a bilinear structure among fluxes and forces (affinities) in which a given flux $w_i' = (w_i - w_3)$ is not only due to the affinity A_i but also due to the other affinity A_j

2) In consistency with my first lecture $L_{11}, L_{22} \geq 0$ and $L_{12} = L_{21}$

(in the absence of time dependent drivings).

3) Since $\Pi_{NESS} \geq 0$ (always) we have the following constraint among Onsager coefficients

$$A_1 = - \frac{L_{12} A_2 \pm \sqrt{L_{12}^2 - L_{11} L_{22}}}{L_{11}} \quad \text{and} \quad L_{12}^2 - L_{11} L_{22} \leq 0$$

4) Above coupling between reactions can be used to determine the efficiency in which the "free energy" is exchanged reactions.

In many biological situations, the transfer of free energy is important, in which it can be used from the conversion into work. However, it can not be studied from the classical perspective of thermal engines, because biological systems are often at homogeneous temperature, so that the Carnot efficiency would be zero. But these concepts can be interpreted in the framework of nonequilibrium thermodynamics. This will be done next.

Efficiency

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A particularly appealing problem in nonequilibrium thermodynamics is to determine the efficiency which the free energy is exchanged between coupled chemical reactions.

Indeed, in many biological situations, the transfer of free energy is of decisive importance but sometimes this subject can not be studied from the perspective of classical thermal engines, since the temperature is constant. However, the present approach, based on the ideas of linear "stochastic" / irreversible thermodynamics is suited.

Let us consider the above expression for the entropy production

$$\sigma = w_1 A_1 + w_2 A_2 \text{ or even.}$$
$$\sigma = L_{11} A_1^2 + 2L_{12} A_1 A_2 + L_{22} A_2^2$$

and distinct works have considered another definition of efficiency, given by the ratio between the two above terms of the entropy production:

$$\eta = \frac{-w_1 A_1}{w_2 A_2}$$

above relation can be understood as follows:

The conversion of a given type of energy into another one requires the existence of a generic affinity A_1 operating against its flux $\omega_1, A_1 \leq 0$ counterbalancing with the "driving force" A_2 in which $\omega_2 A_2 \geq 0$.

The force " A_1 " is commonly referred as "loading" force. Note that when $\omega_1, A_1 \leq 0$

the above efficiency will be positive.

Conversely, when both $\omega_1, A_1 \geq 0$ and $\omega_2, A_2 > 0$ the efficiency is negative, meaning that
 ~~or~~ there is not "conversion" of a force 2 into the "force" 1. (actually conversion of energy from the reaction 2 to the 1st reaction)

In the case of chemical reactions, the reaction 2 is supplying some free energy, a part of which is taken up by reaction 1 to proceed against its usual direction, whereas the remaining part is lost under the form of heat. In terms of Onsager coefficients, above definition of η reads

$$\eta = - \frac{L_{11} A_1^2 + L_{12} A_1 A_2}{L_{12} A_2 A_1 + L_{22} A_2^2}$$

For simplicity we shall introduce

(11)

the reduced quantities:

$$z^2 = \frac{L_{22}}{L_{11}}, \quad q = \frac{L_{12}}{\sqrt{L_{11} L_{22}}}$$

whose efficiency then reads:

$$\eta = - \frac{A_1^2 + qz A_1 A_2}{qz A_1 A_2 + z^2 A_2^2}$$

$$\text{and } \frac{\pi}{L_{11}} = A_1^2 + 2qz A_1 A_2 + z^2 A_2^2$$

It is worth mentioning that η and π are not independent. In particular by minimizing π with respect to A_1 , we have

$$\left(\frac{\partial \pi}{\partial A_1} \right) \bigg|_{A_1 = A_{MS}^*} = 0 \Leftrightarrow 2 A_{MS}^* + 2qz A_2 = 0$$

$$A_{MS}^* = -qz A_2$$

$$\text{and then } \eta(A_{MS}^*) = - \frac{q^2 z^2 A_2^2 - q^2 z^2 A_2^2}{-q^2 z^2 A_2^2 + z^2 A_2^2} = 0,$$

meaning that the reaction 1 will proceed against the usual direction when $0 \leq A_1 \leq A_{MS}^*$

and in such case $0 \leq \eta \leq 1$.

In particular the value A_{mE} in which η is maximum is given by

$$A_{mE} = \frac{-A_2 Z + \sqrt{+(1-q^2)A_2^2 Z^2}}{q} = \frac{A_2 Z}{q} \left[-1 + \sqrt{1-q^2} \right]$$

$$\text{and } \eta_{mE} = \frac{1}{q^2} \left[2 - q^2 - 2\sqrt{1-q^2} \right],$$

Which is independent on Z .

Above figure illustrate above behaviors for some values of q and Z .

