C8863
Free Energy Calculations

2. Chemical Equilibrium

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Basic Overview

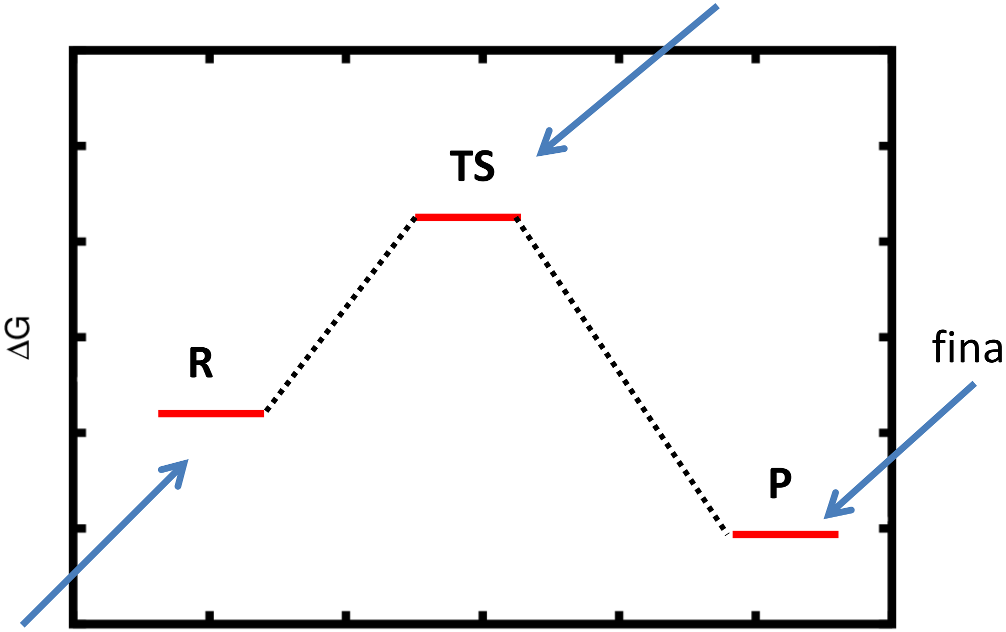
(repetition or what you already know)

Thermodynamics of Chemical Process

$$aA + bB \rightleftharpoons cC + dD$$

a, b, c, d – stochiometric coefficients

activated complex (transition state)



change of Gibbs (free) energy

final state (products)

initial state (reactants)

states (reaction coordinate)

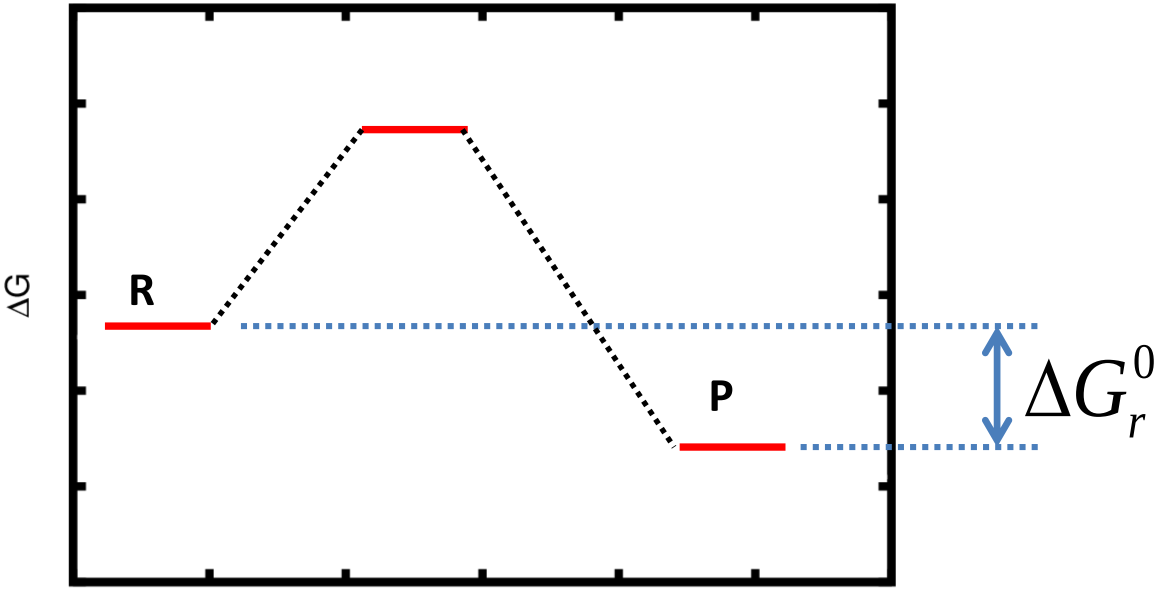
Equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

standard reaction Gibbs energy

$$\Delta G_r^0 = -RT \ln K$$

equilibrium constant



$$K = \frac{\{C\}_r^c \{D\}_r^d}{\{A\}_r^a \{B\}_r^b} \approx \frac{[C]_r^c [D]_r^d}{[A]_r^a [B]_r^b}$$

activities

concentrations

at equilibrium (r)

Chemical Equlibrium

Chemical Change

$$aA + bB \rightleftharpoons cC + dD$$

The reaction of substances A and B gives rise to substances C and D and vice versa, that is, the reaction of substances C and D produces substances A and B. Both processes (forward and reverse reactions) continue until the changes in both directions are balanced and equilibrium is reached .

Principal questions:

- **What is the composition of the reaction mixture in equilibrium and how it is determined?**
- How is it possible to influence the composition of the reaction mixture in equilibrium?

Progress of Reaction

Progress of reaction can be quantified by **extent of reaction**, which takes into account stoichiometry of the change.

$$aA + bB \rightleftharpoons cC + dD$$

Extent of reaction ξ is a quantity defined as ratio of molar amount change of a compound *i* to its stoichiometry coefficient:

$$\xi = \frac{\Delta n_i}{\upsilon_i}$$

Sign convention for ν_i

final state – positive value
initial state – negative value

Example: initial state: $n_{0,A}$; $n_{0,B}$

$$\xi = \frac{n_A - n_{0,A}}{-a} = \frac{n_B - n_{0,B}}{-b} = \frac{n_C}{c} = \frac{n_D}{d}$$

Gibbs Energy of Reaction Mixture

The Gibbs energy of the reaction mixture is a function of the composition of the reaction mixture. Under constant temperature and pressure, the total differential of the Gibbs energy of the reaction mixture can be written in the following form:

$$dG(n_1, n_2, \ldots, n_N) = \sum_{i=1}^{N} \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_j \neq n_i} dn_i$$

The derivation of the Gibbs energy according to the molar amount of a substance is a very useful quantity called **chemical potential μ_i** :

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_j \neq n_i}$$

n_i is molar amount of i

$$dG(n_1, n_2, \ldots, n_N) = \sum_{i=1}^{N} \mu_i dn_i$$

Chemical Potential

Chemical potential is a state function:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j \neq n_i}$$

Chemical potential expresses the ability of the substance to:

- react with another substance
- change its status
- change its spatial arrangement

Value of chemical potential:

- is related to the amount of the substance
- is related to the environment conditions (temperature, pressure, ...)
- however, it is not related to the nature of the substances with which it reacts or is transformed to

Relationship between chemical potential μ_i and activity of compound a_i:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

Dependence of μ_i on Activity a_i

For ideal gas (a system of non-interacting molecules), the change in Gibbs energy is equal to volume work when the pressure changes:

$$dG = Vdp = \frac{nRT}{p}dp \qquad G = \int_{p^0}^{p} \frac{nRT}{p}dp + G^0 = G^0 + nRT\ln\frac{p}{p^0}$$

The chemical potential can then be written as:

$$\mu = \mu^0 + RT\ln a$$

kde:

$$\mu = \frac{dG}{dn} \qquad a = \frac{p}{p^0}$$

The value of the chemical potential can only be expressed in relation to a precisely defined state.

The **activity of the substance** then expresses the effective amount of the substance **against the standard state**.

Activity

Activity expresses the effective amount of a substance against a standard state. It is a **dimensionless quantity**.

f – fugacity
p – partial pressure
c – molar concentrations
γ – activity coefficient

gaseous mixtures $a_i = \frac{f_i}{p^0} \approx \frac{p_i}{p^0}$

mixture of gasees
solution

mixture of ideal gases
ideal solution (diluted solution)

solutions $a_i = \gamma_i \frac{c_i}{c^0} \approx \frac{c_i}{c^0}$

solid a liquid substances at the standard state: $a_i = 1$

Standard state conditions (IUPAC):

p^0 = 100 kPa
c^0 = 1 mol dm^{-3} = 1 M

The reason for introducing of an activity coefficient (or fugacity) is to maintain a simple relationship between activity and chemical potential. Therefore, a relationship can be taken as definition of activity:

$$a_i = e^{\frac{\mu_i - \mu_i^0}{RT}}$$

Standard Chemical Potential

The standard chemical potential is a change in the Gibbs energy, which is associated with the formation of one mole of the substance in the standard state. The change of Gibbs energy is most often expressed in the form of standard formation Gibbs energy.

$$\mu_i^0 = \Delta G_{f,i}^0$$

The standard Gibbs formation energy is a change in the Gibbs energy, which corresponds to the formation of one mole of substance from the individual chemical elements in the standard state. Chemical elements in the standard state have a zero Gibbs energy (this is definition of the reference state).

Standard state conditions (IUPAC):

p^0 = 100 kPa

c^0 = 1 mol dm^{-3} = 1 M

Gibbs Energy of Reaction Mixture

$$dG(n_1, n_2, \ldots, n_N) = \sum_{i=1}^{N} \mu_i dn_i$$

It is suitable to express Gibbs energy using the extent of reaction:

$$\xi = \frac{\Delta n_i}{\upsilon_i} \longrightarrow dn_i = \upsilon_i d\xi$$

$$dG = \sum_{i=1}^{N} \mu_i \upsilon_i d\xi$$

Derivation of the Gibbs energy according to the extent of the reaction can be used to quantify the change in the Gibbs energy that occurs during the reaction:

$$\frac{dG}{d\xi} = \sum_{i=1}^{N} \mu_i \upsilon_i \xrightarrow{\text{integration}} \Delta G = G(\xi) - G(0) = \int_0^{\xi} \frac{dG}{d\xi} d\xi$$

Gibbs Energy of Reaction Mixture

$$\frac{dG}{d\xi} = \sum_{i=1}^{N} \mu_i \upsilon_i \xrightarrow{\text{integration}} \Delta G = G(\xi) - G(0) = \int_0^{\xi} \frac{dG}{d\xi} d\xi$$

What is the function of ΔG?

It is necessary to take into account the fact that the chemical potential of the individual substances depends on their effective amount relative to the standard state, i.e., the composition of the reaction mixture.

$$\frac{dG}{d\xi} = \sum_{i=1}^{N} \mu_i \upsilon_i = \sum_{i=1}^{N} \upsilon_i \mu_i^0 + RT \ln \prod_{i=1}^{N} a_i^{\upsilon_i}$$

standard Gibbs reaction energy

reaction quotient

$$\frac{dG}{d\xi} = \Delta G_r^0 + RT \ln Q$$

Change of G During Reaction

Example:

$$\mathbf{A} \rightleftharpoons \boldsymbol{B}$$

$$\xi = \frac{n_A - n_{0,A}}{-1} = \frac{n_B}{1} \qquad Q = \frac{[B]}{[A]} = \frac{\xi}{n_{0,A} - \xi}$$

- constant volume
- activity coefficients are 1 (ideal solution)

$$\frac{dG}{d\xi} = \Delta G_r^0 + RT\ln Q = \Delta G_r^0 + RT\ln\frac{\xi}{n_{0,A} - \xi}$$

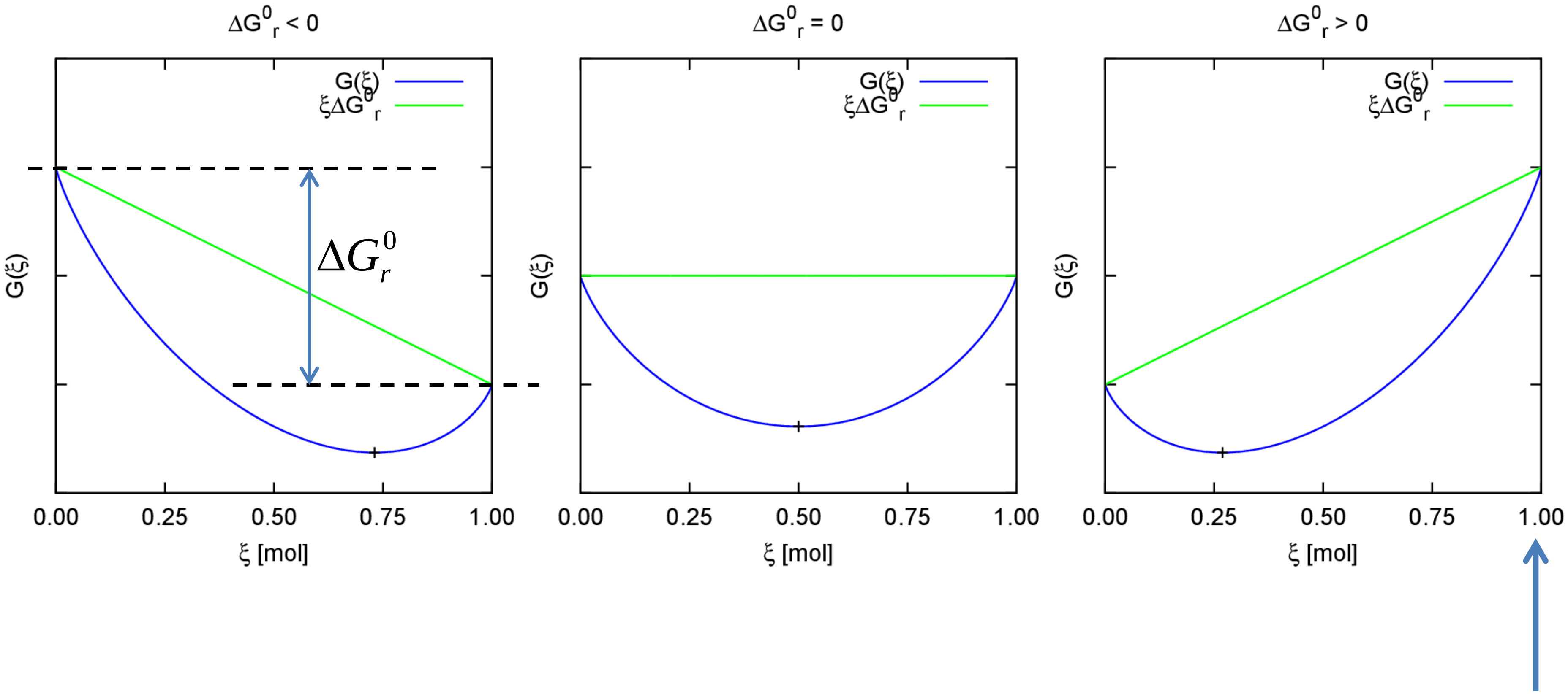
Result:

$$G(\xi) = \int_0^{\xi}\frac{dG}{d\xi}d\xi + G(0) = \Delta G_r^0\xi + RT\left\{\xi\ln\xi - \left(\xi - n_{0,A}\right)\ln\left(n_{0,A} - \xi\right) - n_{0,A}\ln n_{0,A}\right\} + G_A^0$$

Change of G During Reaction

$$A \rightleftharpoons B$$

$$G(\xi) = \xi \Delta G_r^0 + RT\left\{\xi \ln \xi - \left(\xi - n_{0,A}\right)\ln\left(n_{0,A} - \xi\right) - n_{0,A} \ln n_{0,A}\right\} + G_A^0$$

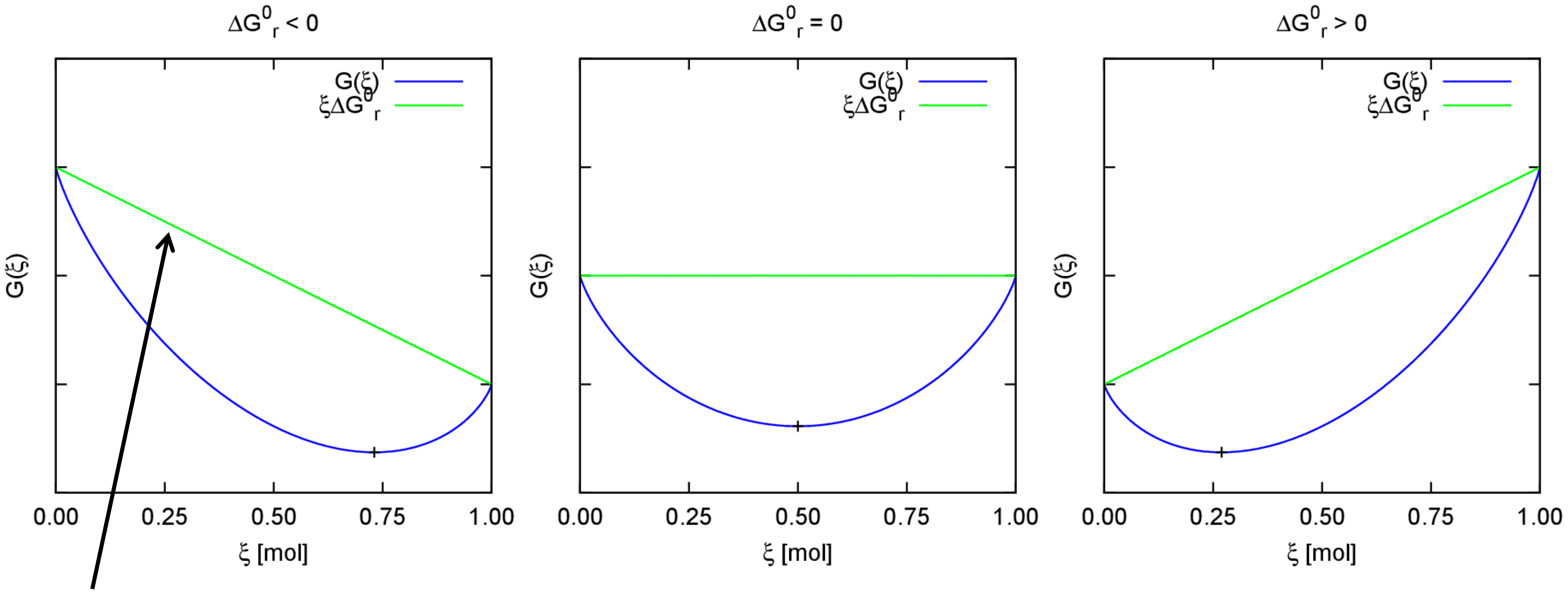


only for given reaction and $n_{0,A}$ = 1.0 mol

Change of G During Reaction

$$\mathbf{A} \rightleftarrows \mathbf{B}$$

$$G(\xi) = \xi\Delta G_r^0 + RT\left\{\xi\ln\xi - \left(\xi - n_{0,A}\right)\ln\left(n_{0,A} - \xi\right) - n_{0,A}\ln n_{0,A}\right\} + G_A^0$$

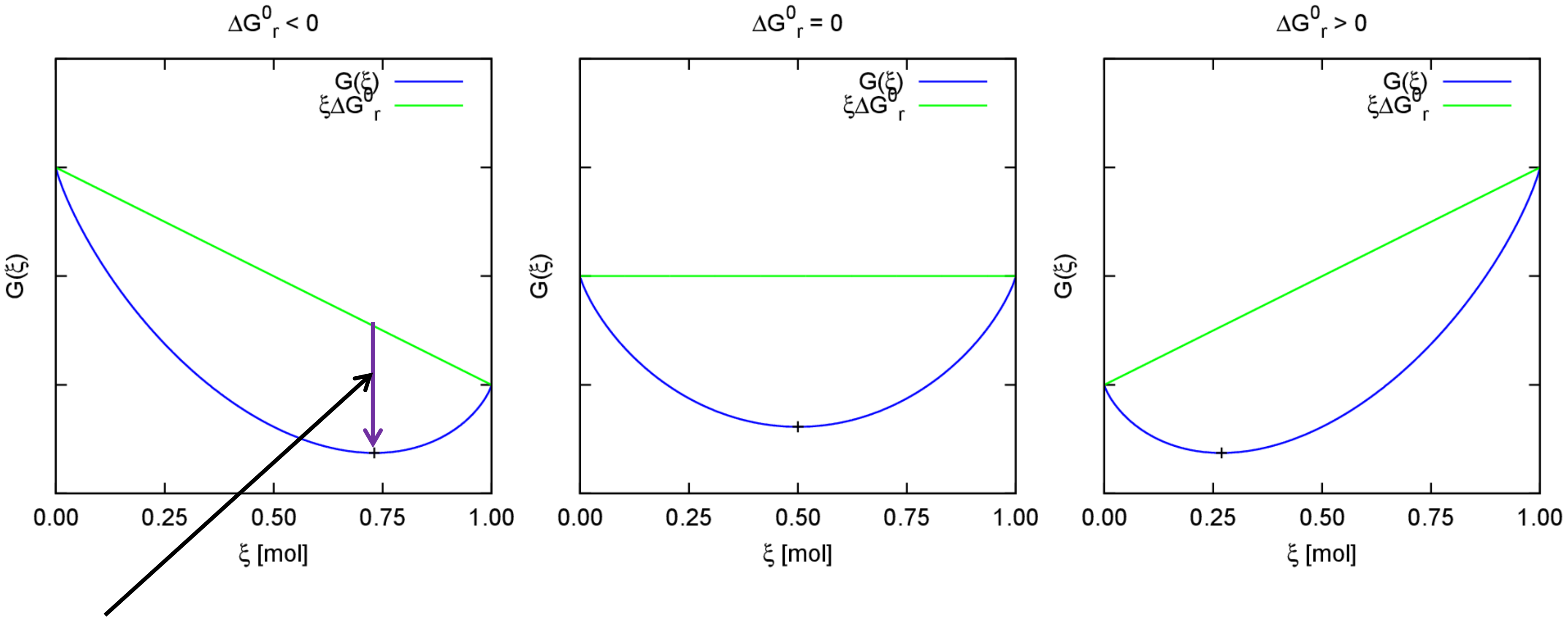


change of Gibbs energy as a result of reaction, i.e., response to change of reaction mixture composition (sum of G of individual substances in the standard state in the amount determined by the extent of reaction)

Change of G During Reaction

$$A \rightleftarrows B$$

$$G(\xi) = \xi\Delta G_r^0 + RT\left\{\xi\ln\xi - \left(\xi - n_{0,A}\right)\ln\left(n_{0,A} - \xi\right) - n_{0,A}\ln n_{0,A}\right\} + G_A^0$$

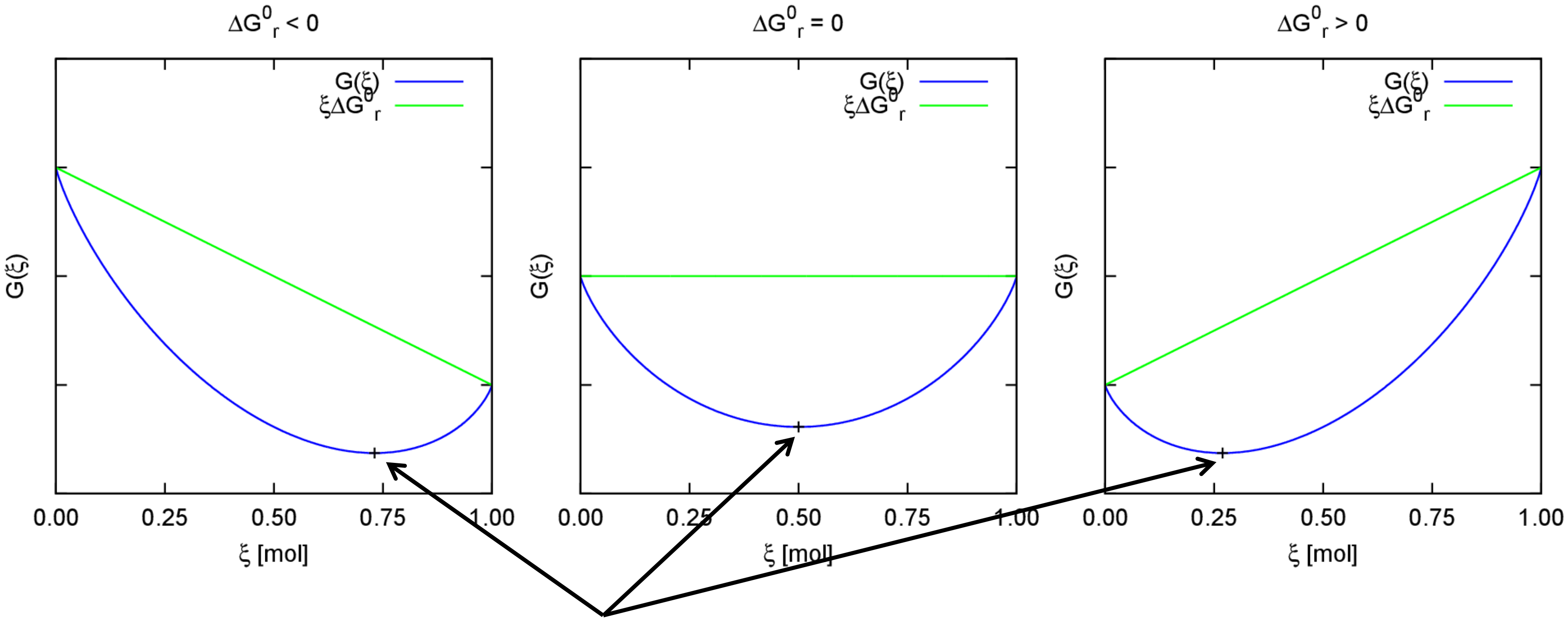


mixing Gibbs energy (The Gibbs energy released as a result of mixing the substances in the standard state in the amount determined by the extent of reaction)

Change of G During Reaction

$$A \rightleftharpoons B$$

$$\boxed{G(\xi)} = \boxed{\xi\Delta G_r^0} + \boxed{RT\left\{\xi\ln\xi - \left(\xi - n_{0,A}\right)\ln\left(n_{0,A} - \xi\right) - n_{0,A}\ln n_{0,A}\right\}} + G_A^0$$



local extreme (minimum) – it determines the composition of the reaction at the equilibrium

Qualitative Conclusions

- Change of the Gibbs energy is result of two contributions:
    - a) “reaction"
    - b) “mixing"
- Changing the Gibbs energy from the initial or final state to the equilibrium is always negative. Even if the standard Gibbs reaction energy is zero or positive.
- There is only one local extreme (minimum) of the Gibbs energy function to the extent of the reaction that corresponds to the state of equilibrium.

Finding the Extreme

In the local extreme, the derivative takes on a zero value:

$$\frac{dG}{d\xi} = \Delta G_r^0 + RT \ln Q_r = 0$$

$$\boxed{\Delta G_r^0 = -RT \ln Q_r = -RT \ln K}$$

The equilibrium constant K is a dimensionless quantity that corresponds to the reaction quotient in the equilibrium. The value of the equilibrium constant depends only on the nature of the reaction, the temperature and the definition of the standard state, but does not depend on the starting composition of the reaction mixture

$$K = \prod_{i=1}^{N} a_{r,i}^{\upsilon_i}$$

Sign convention for ν_i

final state	– positive value
initial state	– negative value

at equilibrium (r)

Example

$$K = \prod_{i=1}^{N} a_{r,i}^{\upsilon_i}$$

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

$$\underbrace{K = a_{r,A}^{-a} a_{r,B}^{-b} a_{r,C}^{c} a_{r,D}^{d} = \frac{a_{r,C}^{c} a_{r,D}^{d}}{a_{r,A}^{a} a_{r,B}^{b}} = \frac{\{C\}_r^c \{D\}_r^d}{\{A\}_r^a \{B\}_r^b}}_{\text{unitless}} \approx \frac{[C]_r^c [D]_r^d}{[A]_r^a [B]_r^b}$$

!!! it has a unit !!!

only the values given in (mol dm^{-3})^{n}, where n is the sum of the stoichiometric coefficients (the sign convention) are compatible with unitless version of K

at equilibrium (r)

Summary

Conclusions

- The equilibrium constant at a given temperature and definition of the standard state is determined only by the standard Gibbs reaction energy:

$$\Delta G_r^0 = -RT \ln K$$

- The standard reaction Gibbs energy corresponds to the conversion of the initial state to the final, which is a hypothetical event that does not actually occur.
- When establishing the equilibrium from the initial or final state, the change in Gibbs energy is always negative regardless of the standard Gibbs energy is zero or positive.
- Thus, the reactions always proceed spontaneously to the equilibrium from the initial or final state.