

C8863 Free Energy Calculations

Lesson 3 Equilibrium

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Overview

macroworld

states

(thermodynamic properties, G, T,...)

phenomenological thermodynamics

equilibrium (equilibrium constant)

kinetics (rate constant)

free energy

(Gibbs/Heimholtz)

partition function

statistical thermodynamics

microstates

(mechanical properties, E)

microstate \neq microworld

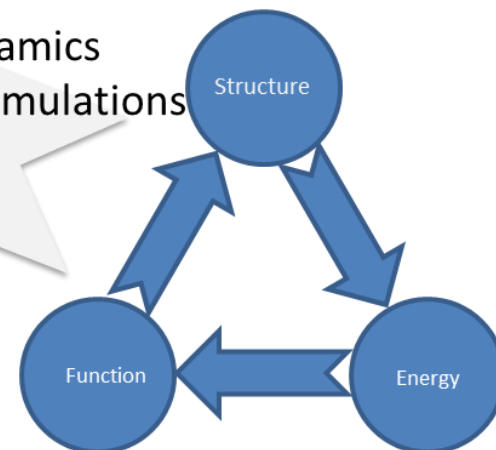
microworld

Description levels (model chemistry):

- quantum mechanics
 - semiempirical methods
 - ab initio methods
 - post-HF methods
 - DFT methods
- molecular mechanics
- coarse-grained mechanics

Simulations:

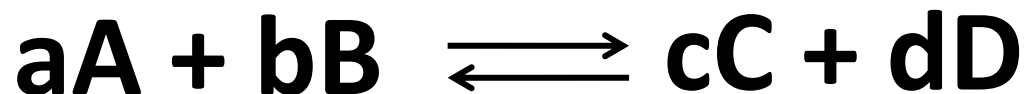
- molecular dynamics
- Monte Carlo simulations
- docking
- ...



Equilibrium

Or what you should already know....

Chemical transformation



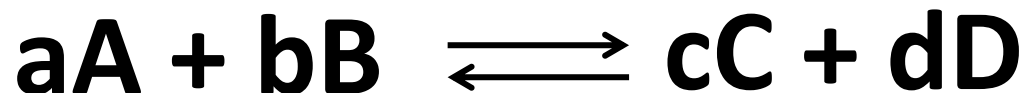
Reaction of A and B provides C and D and vice versa. Both processes continues until the rate of both forward and backward reactions is the same and equilibrium is established.

Principle questions:

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

Extent of reaction

The reaction progress can be described by **the extent of reaction**, which considers the stoichiometry of the transformation.



Extent of reaction ξ is defined as the molar change of a substance in relation to its stoichiometric coefficient:

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

Sign convention for ν_i

products (end state) - positive value
reactants (initial state) - negative value

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

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

Gibbs energy of reaction mixture

The **Gibbs energy of reaction mixture G** is a function of the composition of the reaction mixture.

At the **constant temperature and pressure**, it is possible to write the Gibbs energy as total differential in the following form:

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

N - number of reacting compounds, n_i is the molar amount of substance i

Employing **chemical potential μ** , the relation can be simplified:

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

Gibbs energy of reaction mixture

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

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

$$\xi = \frac{\Delta n_i}{\nu_i} \quad \longrightarrow \quad dn_i = \nu_i d\xi \quad \longrightarrow \quad dG = \sum_{i=1}^N \mu_i \nu_i d\xi$$

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

The chemical potential of the individual substances depends on their effective amount relative to the standard state, i.e., on the composition of the reaction mixture.

The change is therefore proportional to the composition of the reaction mixture and the standard chemical potential of the individual reactants:

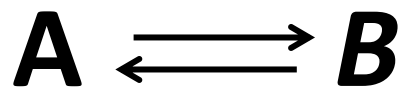
$$\frac{dG}{d\xi} = \sum_{i=1}^N \mu_i \nu_i = \sum_{i=1}^N \nu_i \mu_i^0 + RT \ln \prod_{i=1}^N a_i^{\nu_i}$$

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

reaction quotient

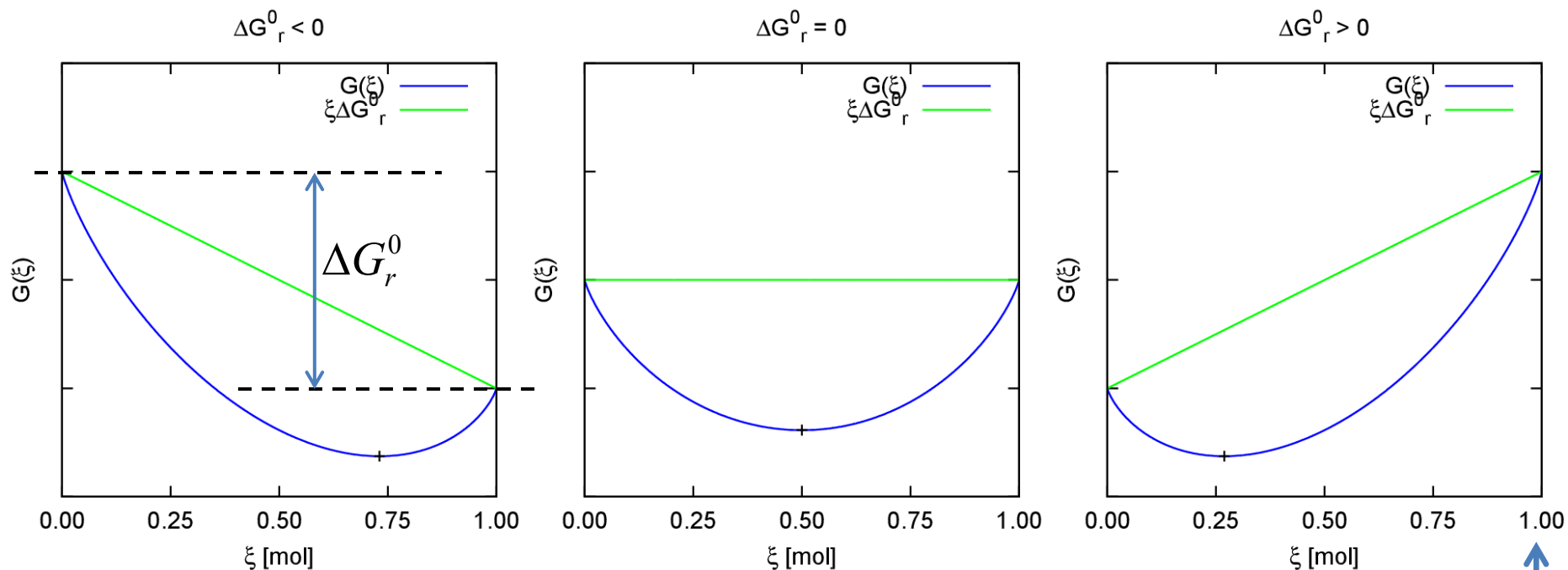
standard Gibbs reaction energy

Change of G during reaction



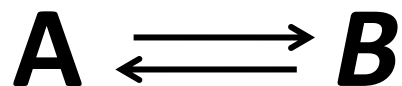
from integration $dG/d\xi$

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

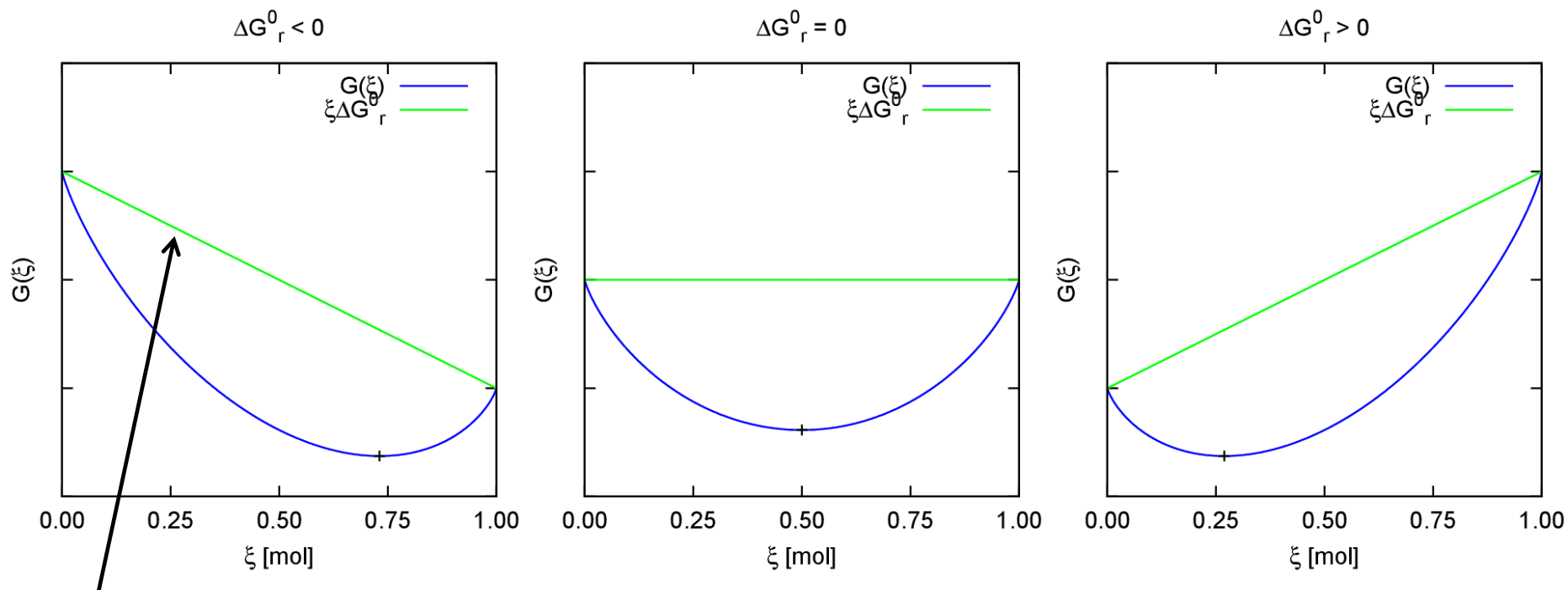


only for a given reaction and $n_{0,A} = 1.0$ mol

Change of G during reaction

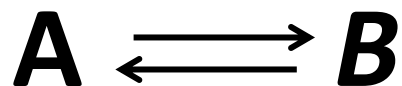


$$G(\xi) = \xi \Delta G_r^0 + RT \left\{ \xi \ln \xi - (\xi - n_{0,A}) \ln(n_{0,A} - \xi) - n_{0,A} \ln n_{0,A} \right\} + G_A^0$$

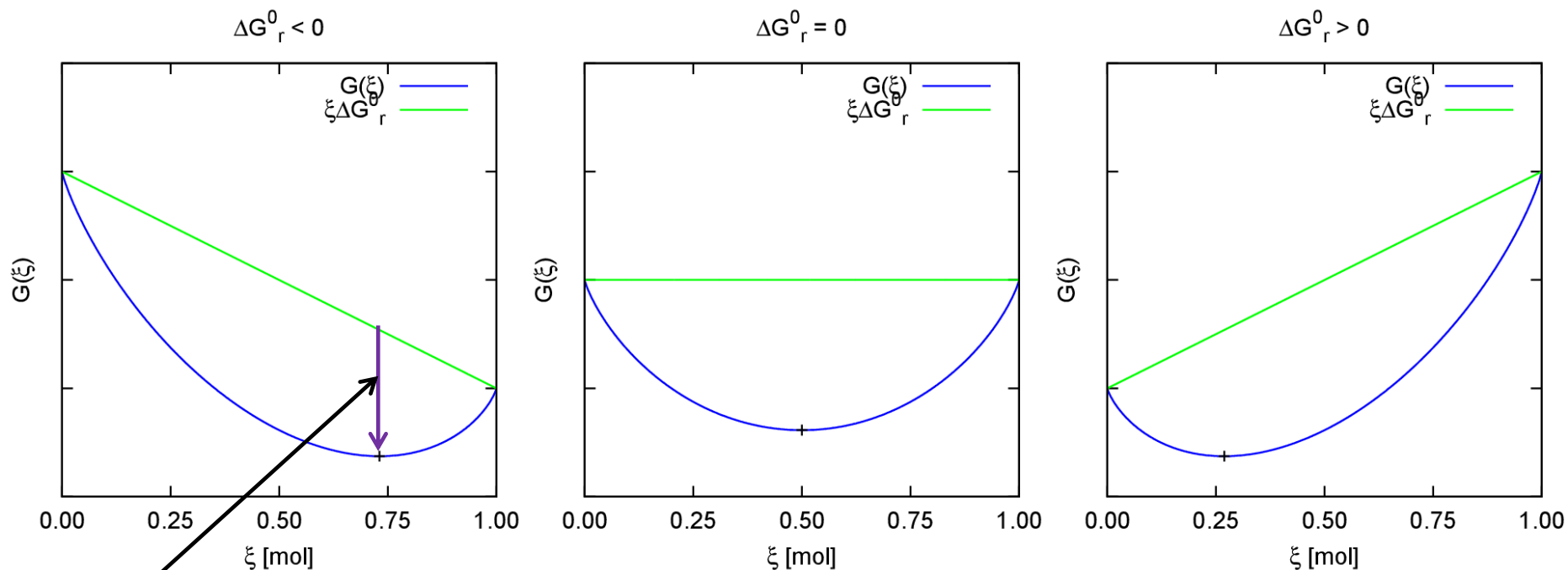


change of Gibbs energy due to the reaction (this is the Gibbs energy of individual substances in the standard state in the amount determined by the extent of the reaction)

Change of G during reaction

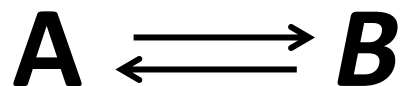


$$G(\xi) = \xi \Delta G_r^0 + RT \left\{ \xi \ln \xi - (\xi - n_{0,A}) \ln (n_{0,A} - \xi) - n_{0,A} \ln n_{0,A} \right\} + G_A^0$$

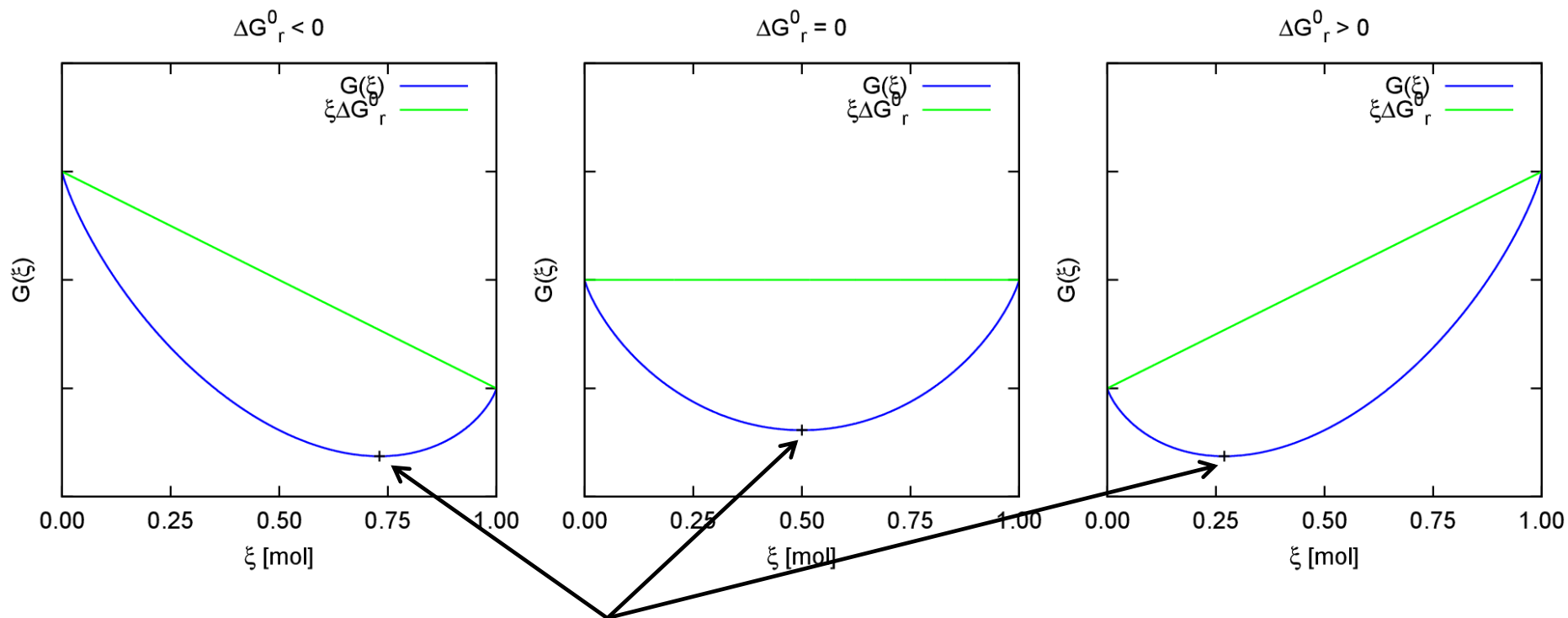


mixing Gibbs energy (Gibbs energy that is released as a result of mixing substances in the standard state in an amount determined by the extent of the reaction)

Change of G during reaction



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



local extreme (minimum) determines the composition of the reaction mixture in equilibrium

Qualitative conclusions

- The change in Gibbs energy consists of **two contributions** due to:
 - a) reaction
 - b) mixing (entropy)
- The change of Gibbs energy from the initial or final state to equilibrium is always negative, so it is a spontaneous process. Even if the standard Gibbs reaction energy is zero or positive.
- **There is only one local extreme** (minimum) of reaction Gibbs energy and it corresponds to the equilibrium state.

Finding the extreme

At the local extreme, the derivative of the function takes zero value:

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

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

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

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

Sign convention for ν_{and}

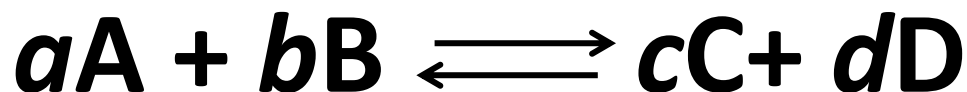
end state - positive value

default state - negative value

at equilibrium (r)

Example

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



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

dimensionless

!!! it has a dimension !!!

the dimension is $(\text{mol dm}^{-3})^n$ (or M^n), where n is the sum of stoichiometric coefficients

This follows from the definition of the standard state for solution.

at equilibrium (r)

Conclusion

- At the given temperature and definition of the standard state, the **equilibrium constant** is determined only by the **standard reaction Gibbs energy**:

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

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

$$\Delta G_r^0 \langle \rangle \Delta G(\xi)$$

it determines composition of the reaction mixture, but it does not say anything about spontaneity of the reaction

it determines spontaneity of the process
 ξ is the extent of reaction (\neq reaction coordinate)

Recommended Literature

- Atkins, P. W. *Physical Chemistry*, 5. ed., repr. (with correct.); Oxford Univ. Press: Oxford, 1994.
- Dill, K. A.; Bromberg, S. *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*, 2nd ed.; Garland Science: London ; New York, 2011.