C7790 Introduction to Molecular Modelling

TSM Modelling Molecular Structures

C9087 Computational Chemistry for Structural Biology

Lesson 4

Phenomenological thermodynamics (spontaneity of processes)

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Petr Kulhánek

kulhanek@chemi.muni.cz

National Centre for Biomolecular Research, Faculty of Science
Masaryk University, Kamenice 5, CZ-62500 Brno

Overview

macroworld | **microworld**

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

phenomenological thermodynamics

equilibrium (equilibrium constant)
kinetics (rate constant)

free energy
(Gibbs/Helmholtz)

partition function

statistical thermodynamics

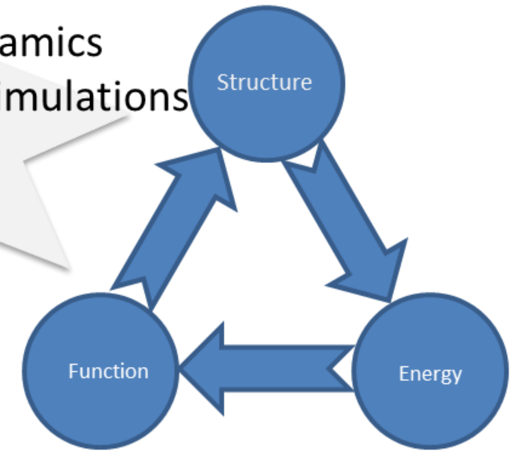
microstates
(mechanical properties, E)

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
- ...



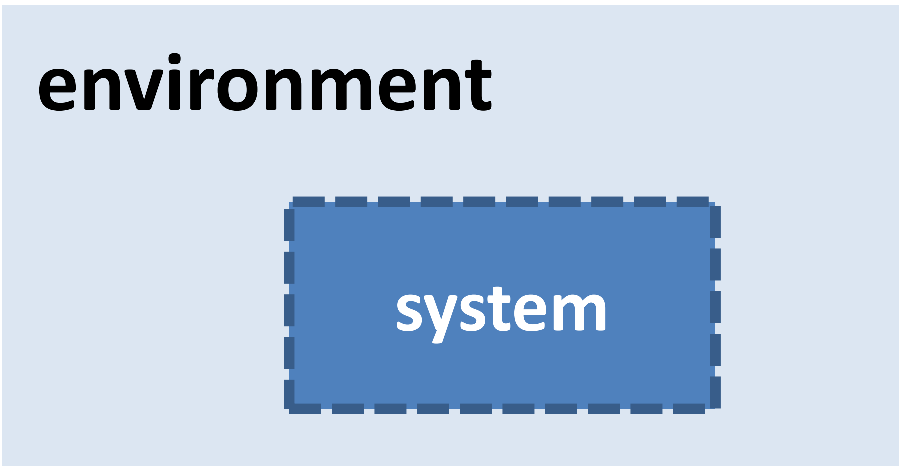
microstate ≠ microworld

Thermodynamics

Or what you should already know….

The system and its environment

system - the part of space and its material contents, which is the subject of thermodynamic consideration



the system is separated from the environment by **real** or **fictional** walls

System types	Description
isolated system	walls protects exchange of matter and energy with the environment
closed system	walls protects exchange of matter to the environment, but it can exchange energy with it
open system	it can exchange matter and energy with the environment

System state and its properties

System state can be described by properties (mass, volume, temperature, pressure, etc.), which are needed for the full state description.

Thermodynamic properties are **state functions**. The state functions do not depend on the way how the system got into the given state.

Heat and work are NOT state functions.

Thermodynamic properties can be divided into two groups:

Extensive properties: depend on the mass of the system and are additive. The value of the extensive property is equal to the sum of individual parts of which the system is composed. Examples are weight, energy, volume.

Intensive properties: do not depend on the size or mass of the system and are therefore non-additive. Examples are temperature, pressure, concentration.

Thermodynamic process and equilibrium

Thermodynamic process corresponds to system state change. It can represent a change in volume, temperature, pressure, or change in composition as a result of chemical reaction.

Thermodynamic equilibrium is a state in which no state function changes over time. (Chemical or other transformations may still take place in the system. However, these must take place in conjunction so that they do not affect the state of the system as a result.)

Thermodynamic laws:

- **0th law** about thermodynamic equilibrium of multiple systems
- **1st law** energy conservation law
- **2nd law** about the spontaneity of events
- **3rd law** about absolute entropy

The first law

It postulates internal energy as a state variable, which is sum of other energy forms:

$$dU = đQ + đW$$

change of internal energy of the system

heat exchanged with the environment (form of energy)

work done (form of energy)

It is a generalization of the energy conservation law to dissipative systems, i.e., such systems that exchange heat and work with their surroundings.

Sign convention for energy change:

+ (positive) - the system receives energy

- (negative) - the system releases energy

d complete differential (U is a function of system properties, a **state function**)

$đ$ incomplete differential (Q and W are not state functions)

The second law

It postulates the entropy as a state function:

$$dS = \frac{dQ_{rev}}{T}$$

reversible action

$$dS > \frac{đQ}{T}$$

irreversible action (spontaneous)

The most important postulate of thermodynamics. It speaks about time flow direction (time arrow). The direction of time is determined by the irreversible events.

For an isolated system, the direction of time is the same as the increase in entropy.

Spontaneous events are accompanied by an increase in entropy.

In an isolated system, the entropy increases until equilibrium is reached. At equilibrium, the value of entropy is maximal and constant in time.

Spontaneous process

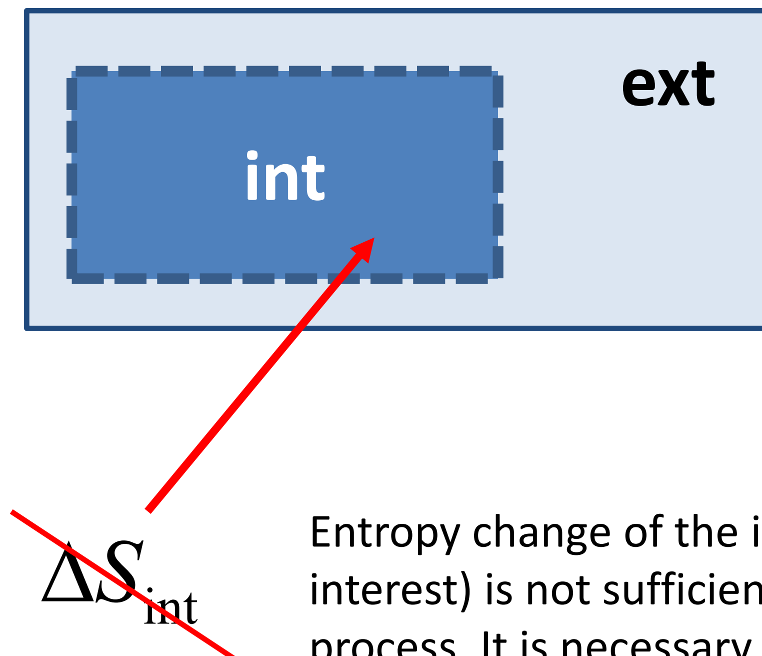
Or what you should already know….

Entropy and spontaneity

$$dS > 0$$

irreversible action
(spontaneous process)

In an isolated system, the **entropy increases** until equilibrium is reached. At equilibrium, the value of entropy is maximal and constant in time.



Entropy change of the internal system (int, system of interest) is not sufficient to assess spontaneity of the process. It is necessary to assess the entropy change of the **system including with its surroundings**.

Free energy and spontaneity

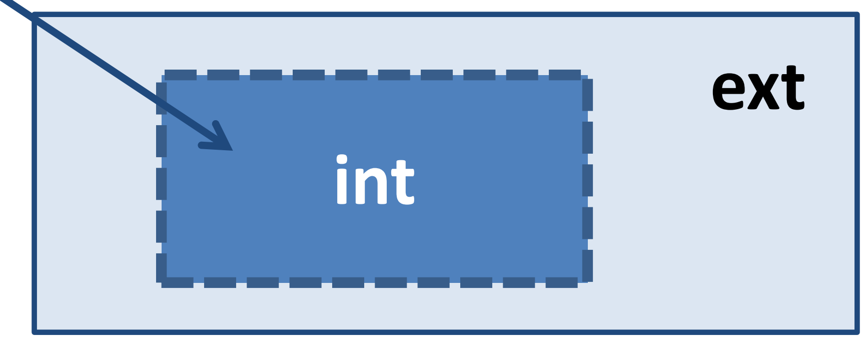
Is there a property of the internal system, which can describe the entropy change of the entire system (int+ext)?

Spontaneous process:

$$\Delta S_{ext} + \Delta S_{\mathrm{int}} > 0$$

?

we can measure for given process (int change)



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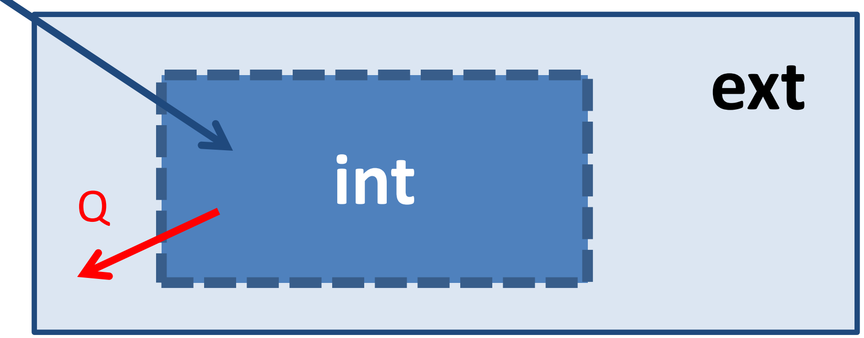

we can estimate from heat exchange between int and ext

$$\Delta S_{ext} = \frac{Q_{rev}}{T}$$

for the isothermal process

What is Q equal to?

Free energy and spontaneity

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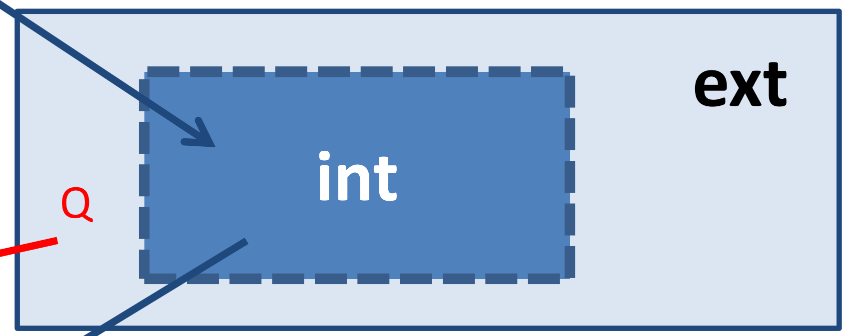
we can measure for given process (int change)

int and ext are in thermal equilibrium



$$\Delta S_{ext} = \frac{Q_{rev}}{T} = \frac{-\Delta H_{\text{int}}}{T}$$

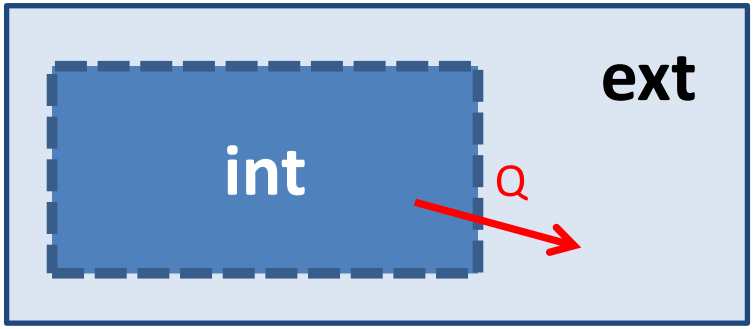
for the isothermal and isobaric process

- for reversible process, it is the lowest estimate
- for irreversible process, the change will be higher

Free energy and spontaneity

For an isolated system (second law):

$$\Delta S_{all} = \Delta S_{ext} + \Delta S_{\mathrm{int}} > 0$$



int and ext are in thermal equilibrium

$$-\frac{\Delta H_{int}}{T} + \Delta S_{int} > 0$$

reorganization

$$\Delta G_{int} = \Delta H_{int} - T\Delta S_{int} = -T\Delta S_{all} < 0$$

Summary

Free energy and spontaneity

for process at constant temperature and pressure

$$\Delta G = \Delta H - T\Delta S < 0$$

spontaneous process

$$\Delta G = \Delta H - T\Delta S = 0$$

the system is in equilibrium

$$\Delta G = \Delta H - T\Delta S > 0$$

non-spontaneous process

The change in Gibbs free energy indicates whether the process can occur spontaneously. However, it does not determine in what time the actual transformation will take place.

Recommended Literature

- Atkins, P. W. *Physical Chemistry*, 5. ed., repr. (with correct.).; Oxford Univ. Press: Oxford, 1994.
- Bokshteĭn, B. S.; Mendelev, M. I.; Srolovitz, D. J. *Thermodynamics and Kinetics in Materials Science: A Short Course*; Oxford University Press: New York, 2005.
- Dill, K. A.; Bromberg, S. *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*, 2nd ed.; Garland Science: London ; New York, 2011.