

# C8863 Free Energy Calculations

## Lesson 1 Phenomenological thermodynamics (Overview)

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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

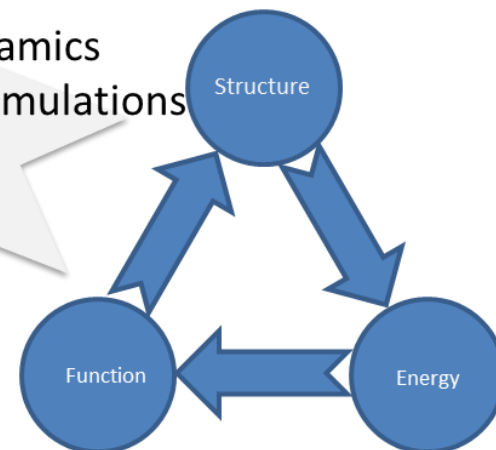
## microworld

### 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
- ...

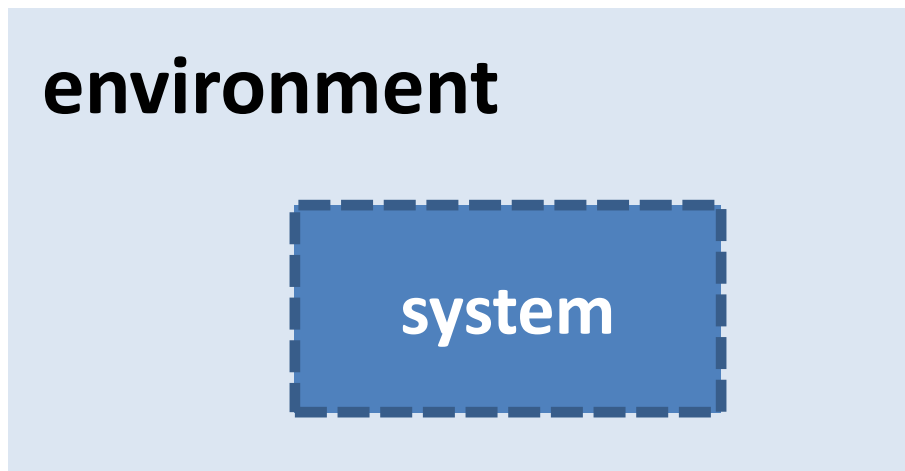


# Thermodynamics

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** (state variables or state quantities) are **state functions**. The state functions do not depend on the way how the system got into the given state.

## List of selected state functions:

- Mass ( $m$ )
- Energy ( $E$ )
  - Enthalpy ( $H$ )
  - Internal energy ( $U$ )
  - Gibbs free energy ( $G$ )
  - Helmholtz free energy ( $F$ )
  - Exergy ( $B$ )
- Entropy ( $S$ )
- Pressure ( $p$ )
- Temperature ( $T$ )
- Volume ( $V$ )
- Particle number ( $n_i$ )

**Heat and work are NOT state functions!**

# 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, phase separation, phase transition, etc.

**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:

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

[https://en.wikipedia.org/wiki/Laws\\_of\\_thermodynamics](https://en.wikipedia.org/wiki/Laws_of_thermodynamics)

# The first law

The first law postulates **internal energy** as a state variable.

For **closed systems with no change in chemical composition**, the change of internal energy is sum of exchanged heat and work done:

$$dU = dQ + dW$$

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**)

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

Since U and W are well defined, the first law can also be seen as a definition of heat.

# The first law - two notations

IUPAC (Chemists)

$$dU = dQ \oplus dW$$



W is the work done **on** the system

Physicists

$$dU = dQ \ominus dW$$



W is the work done **by** the system

see IUPAC Gold Book

<https://goldbook.iupac.org/terms/view/I03103>

In this course, we will use a sign notation recommended by IUPAC.



# Heat

In thermodynamics, **heat (Q)** is **energy in transfer to or from a thermodynamic system**, by mechanisms other than thermodynamic work or transfer of matter.

Amount of transferred heat can be **measured by calorimetry** or determined through **calculations based on other quantities**.

**Heat capacity or thermal capacity (C)** is a physical property of matter, defined as the amount of heat to be supplied to an object to produce a unit change in its temperature.

$$C = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T}$$

**At constant pressure (isobaric process):**

The heat supplied to the system contributes to **both the work done and the change in internal energy**.

**At constant volume (isochoric process,  $dV = 0$ ):**

The heat supplied contributes only to the change in internal energy.

$$dQ = dU + pdV = dH$$
$$C_p = \left( \frac{dQ}{dT} \right)_p = \frac{dH}{dT}$$

↔ enthalpy

at constant pressure

$$dQ = dU$$
$$C_V = \left( \frac{dQ}{dT} \right)_V = \frac{dU}{dT}$$

at constant volume

# The second law

It postulates the entropy as a state function:

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

reversible action

$$dS > \frac{dQ}{T}$$

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.**

# Reversible Process

In thermodynamics, a **reversible process** is a process, involving a system and its surroundings, whose **direction can be reversed by infinitesimal changes** in some properties of the surroundings, such as pressure or temperature.

Throughout an entire reversible process, the system is in thermodynamic equilibrium, both physical and chemical, and nearly in pressure and temperature equilibrium with its surroundings. This prevents unbalanced forces and acceleration of moving system boundaries, which in turn **avoids friction and other dissipation**. To maintain equilibrium, reversible processes are extremely slow.

While processes in isolated systems are never reversible, cyclical processes can be reversible or irreversible. **Reversible processes are hypothetical or idealized but central to the second law of thermodynamics.**

Melting or freezing of ice in water is an example of a realistic process that is nearly reversible.

[https://en.wikipedia.org/wiki/Reversible\\_process\\_\(thermodynamics\)](https://en.wikipedia.org/wiki/Reversible_process_(thermodynamics))

# Combination of first and second laws

For closed system and reversible process without change in chemical composition, it is possible to combine the first and second laws:

$$\begin{array}{l} dU = \cancel{dQ} + \cancel{dW} \quad \text{first law} \\ \text{second law} \quad \cancel{dQ} = TdS \quad \cancel{dW} = -pdV \quad \text{pressure-volume work} \end{array}$$

Reorganization leads to the **fundamental thermodynamic relation**, which is also valid for irreversible processes because all variables are state functions:

$$dU = TdS - pdV$$

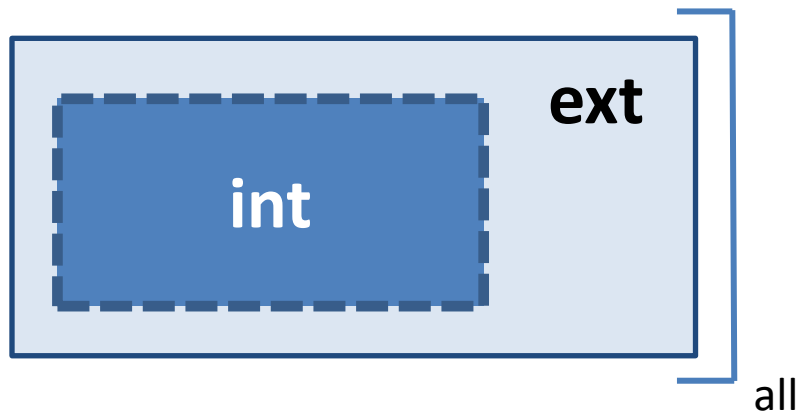
Internal energy is thus a state function  $U(S,V)$  depending on two state variables  $S$  and  $V$ .

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad \left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

reformulating as a total differential

[https://en.wikipedia.org/wiki/Thermodynamic\\_potential](https://en.wikipedia.org/wiki/Thermodynamic_potential)

# Spontaneity of Process



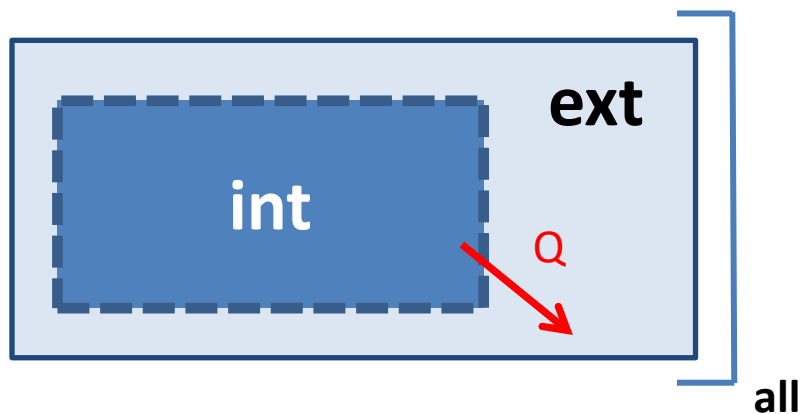
$$\Delta S_{\text{int}} + \Delta S_{\text{ext}} = \Delta S_{\text{all}}$$

In an isolated system, the **entropy increases** until equilibrium is reached.

$$dS_{\text{all}} > 0$$

irreversible action  
(spontaneous process)

# Spontaneity of Process



In an isolated system, the **entropy increases** until equilibrium is reached.

$$dS_{all} > 0$$

irreversible action  
(spontaneous process)

it is a property of the system

$$\Delta S_{int} + \Delta S_{ext} = \Delta S_{all}$$

it can be estimated from heat exchange with surroundings

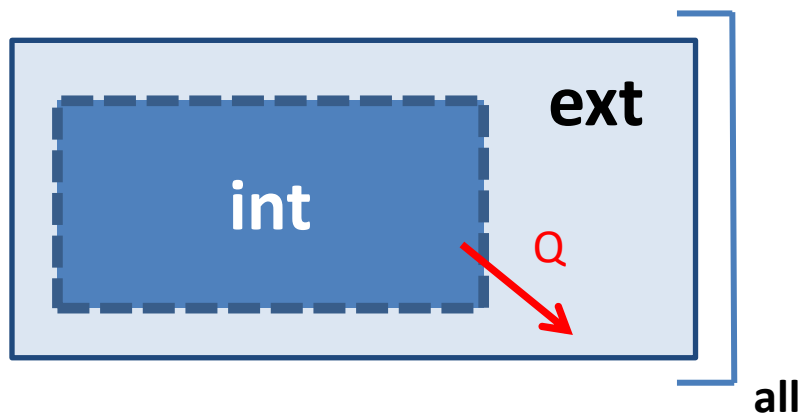
$$\Delta S_{ext} = \frac{\Delta Q_{rev,ext}}{T} = \frac{-\Delta H_{int}}{T}$$

for reversible process  
at constant temperature and pressure

$$\Delta S_{ext} = \frac{\Delta Q_{rev,ext}}{T} = \frac{-\Delta U_{int}}{T}$$

for reversible process  
at constant temperature and volume

# Spontaneity of Process



In an isolated system, the **entropy increases** until equilibrium is reached.

$$dS_{all} > 0$$

irreversible action  
(spontaneous process)

$$\Delta S_{int} + \frac{-\Delta H_{int}}{T} = \Delta S_{all}$$

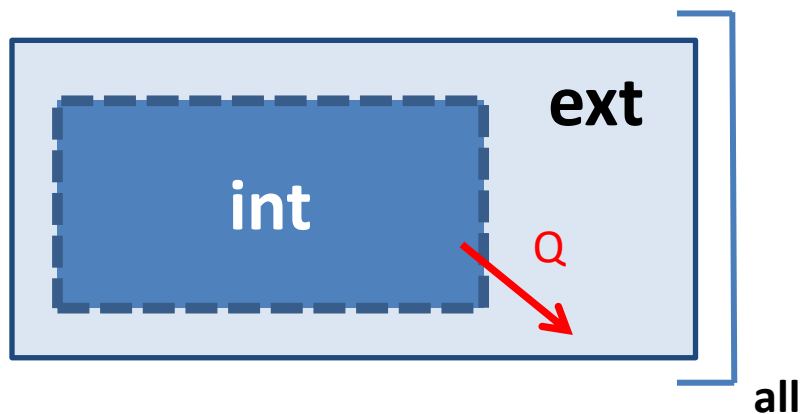
Reorganization:

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

↑ Gibbs energy (free energy)

for reversible process  
at constant temperature and  
pressure

# Spontaneity of Process



In an isolated system, the **entropy increases** until equilibrium is reached.

$$dS_{all} > 0$$

irreversible action  
(spontaneous process)

$$\Delta S_{int} + \frac{-\Delta H_{int}}{T} = \Delta S_{all}$$

Reorganization:

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

for reversible process  
at constant temperature and  
pressure

$$\Delta A_{int} = \Delta U_{int} - T\Delta S_{int} = -T\Delta S_{all}$$

for reversible process  
at constant temperature and  
volume

 Helmholtz energy (free energy)



# 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.**

Similar relations are valid for Helmholtz energy.

# Ideal Gas

Or what you should already know....

# Ideal Gas

An **ideal gas** is a theoretical gas composed of many randomly moving **point particles that are not subject to interparticle interactions**.

The ideal gas obeys the following **equation of state**:

The diagram shows the equation of state for an ideal gas:  $pV = nRT = nN_A k_B T$ . The first part,  $pV = nRT$ , is enclosed in a red box. Blue arrows point from labels below to each variable in the equation: 'pressure' to  $p$ , 'volume' to  $V$ , 'molar amount' to  $n$ , 'the ideal gas constant' to  $R$ , 'Avogadro constant' to  $N_A$ , 'Boltzmann constant' to  $k_B$ , and 'thermodynamic temperature' to  $T$ .

The empirical form of the equation of state was derived by combining four laws (Benoît Paul Émile Clapeyron, 1834) :

- Boyle's law (1662)
- Charles's law (1801)
- Avogadro's law (1812)
- Gay-Lussac's law (1809)

Other derivations are possible employing, for example, statistical thermodynamics.

[https://en.wikipedia.org/wiki/Ideal\\_gas](https://en.wikipedia.org/wiki/Ideal_gas)

# Ideal Gas - Internal Energy

Internal energy of the ideal gas is (see later statistical thermodynamics for derivation):

$$U = \frac{3}{2}nRT$$

Then the following statement is true:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

This is consequence of the fact that there is no interaction between particles.

# Recommended Literature

- Atkins, P. W. *Physical Chemistry*, 5. ed., repr. (with correct.); Oxford Univ. Press: Oxford, 1994.
- Bokshteĭn, B. S.; Mendeleev, 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.