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Inovace bakalářského studijního oboru Aplikovaná chemie

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Introduction to Physical Chemistry

Lecture 7

- Thermodynamics
  - Entropy
  - Third law of thermodynamics
  - Gibbs energy
- Chemical equilibrium
  - Guldberg-Waage law
  - Temperature dependence

Lecture vocabulary:

melt	tát
freeze	tuhnout, mrznout
spontaneously	spontánně, samovolně
hot body	horké těleso
unlikely	nepravděpodobný
convince	přesvědčit
significance	význam
heat delivered	dodané teplo
Carnot engine working medium	náplň Carnotova stroje
remain	zůstávat
store	skladovat
disorder	nepořádek, neuspořádanost
notion	vjem, pojem
doubtless	bezpochyby
far-fetched	za vlasy přitažený
comprehension	pochopitelnost
concern	mít starost s nějakým problémem
overly used	nadužívaný
reason	důvod
uncertainty	neurčitost
motion	pohyb
envision, envisage	zaobírat se
snapshot	snímek
sampling	vzorkování
approach	blížit se
finite	určitý, konečný, ohraničený
direction	směr
reversing	obrácení
case	případ
attain	dosáhnout
equilibrium	rovnováha
reversible	zvratný, reversibilní
forward	dopředný
reverse	zpětný
counteract	čelit, působit proti
relate	vztahovat

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Entropy

At room temperature:

- **Ice melts but water does not freeze spontaneously**
- **Heat spontaneously flows from hot body but never from cold body**

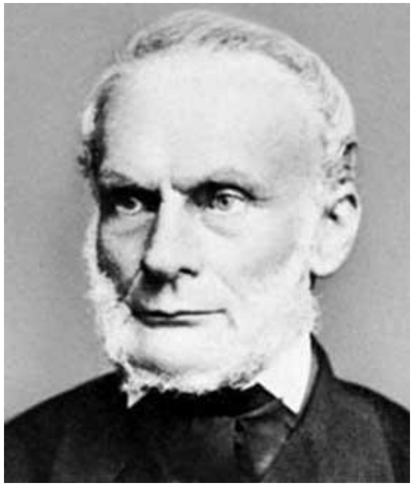
↓

Not all processes are allowed by nature

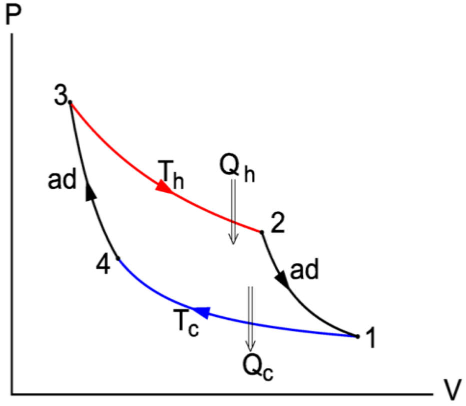
We need a concept which makes non-spontaneous processes highly unlikely

Entropy

Entropy (S) is a term introduced by Rudolph Clausius. (greek word = turning into)



Clausius was convinced of the significance of the ratio of heat delivered and the temperature at which it is delivered



In Carnot cycle, the first process is reversible isothermal expansion. To keep the temperature of the working medium constant, heat is transferred from the reservoir into the medium.

Something has to change in the Carnot engine working medium if we pump (heat) energy into it and the temperature remains constant. That something is entropy – the energy is “stored” in the form of “disorder”.

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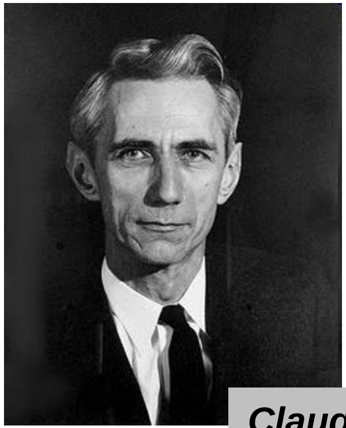
Entropy

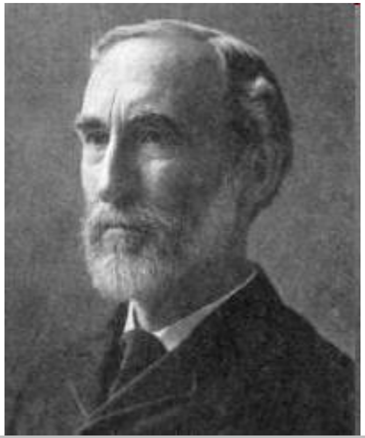
„Any method involving the notion of entropy, the very existence of which depends on the second law of thermodynamics, will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension.“

Josiah Willard Gibbs, Graphical Methods in the Thermodynamics of Fluids (1873)



Claude Shannon
1916-2001

John Von Neumann
1903-1957



Josiah Willard Gibbs
1839-1903

My greatest concern was what to call it. I thought of calling it ‘information’, but the word was overly used, so I decided to call it ‘uncertainty’. When I discussed it with John von Neumann, he had a better idea. Von Neumann told me, ‘You should call it entropy, for two reasons. In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important, *nobody knows what entropy really is*, so in a debate you will always have the advantage.

—Conversation between Claude Shannon and John von Neumann regarding what name to give to the “measure of uncertainty” or attenuation in phone-line signals

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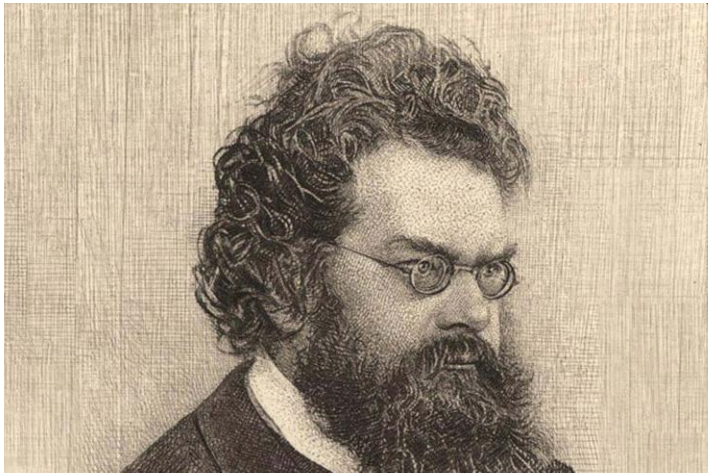
Entropy – statistical interpretation

Ludwig Boltzmann described the concept of entropy on the molecular level. The interpretation of entropy in statistical mechanics is the measure of uncertainty, or *mixedupness* in the phrase of Gibbs

Molecules exhibit several types of motion:
Translational: **Movement of the entire molecule**
Vibrational: **Periodic motion of atoms within a molecule**
Rotational: **Rotation of the molecule on about an axis or rotation about bond**

The energy of a molecule depends on these modes of motion



Boltzmann envisioned the motions of a sample of molecules at a particular instant in time. This is like taking a snapshot of all the molecules. He referred to this sampling as a microstate of the thermodynamic system.

Each thermodynamic state has a specific number of microstates, *W*, associated with it. Entropy is $S = k \ln W$, where k is the Boltzmann constant, 1.38×10^{-23} J/K.

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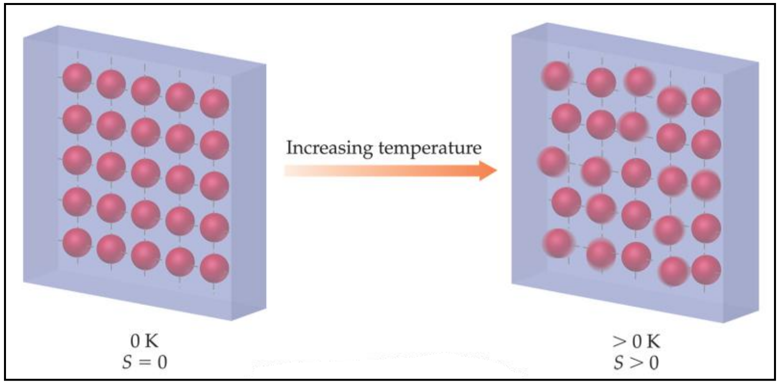
The third law of thermodynamics

The third law of thermodynamics is a statistical law of nature regarding entropy:
The change of entropy of a perfect crystal approaches zero as temperature approaches absolute zero.



$$\Delta S = -k \ln W = k \ln 1 = 0$$

This version states not only ΔS will reach zero at 0 K, but S itself will also reach zero as long as the crystal has a ground state with only one configuration.

An alternative version of the third law of thermodynamics as stated by Gilbert N. Lewis and Merle Randall in 1923:
If the entropy of each element in some (perfect) crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.

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Entropy – processes and arrow of time

Spontaneous processes are those that once started can proceed without any outside intervention.

Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.

Above 0 C it is spontaneous for ice to melt
Below 0 C the reverse process is spontaneous

In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

Irreversible processes cannot be undone by exactly reversing the change to the system.

All spontaneous processes are irreversible.
All real processes are irreversible
The direction of real processes indicates the direction of time

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The case of ice melting

System:
Ice and whisky: 0 C

Surroundings:
Air in the room: 25 C

If the system absorbs some heat from the surroundings, its entropy *increases* by:

$$\Delta S_{system} = \frac{\delta Q}{273.15}$$

At the same time the entropy of surroundings *decreases* by:

$$\Delta S_{surroundings} = \frac{-\delta Q}{298.15}$$

Note, that the increase in entropy of the system is greater than the decrease of the entropy of surroundings.

System + surroundings = Universe

$$\Delta S_{Universe} = \delta Q\left(\frac{1}{273.15} - \frac{1}{298.15}\right) \quad \ldots > 0$$

In the example, the entropy of the Universe increases. Once the thermal equilibrium was attained, the entropy remains constant – no processes can occur till the end of time. This situation is called *the thermal death of the Universe*.

The case of isothermal-isobaric process: Gibbs energy

Universe = system + surroundings

Therefore: $\Delta S_{universe} = \Delta S_{system} + \Delta s_{surroundings}$
$\Delta s_{universe} > 0$ for spontaneous process

If the process is isothermal, $\Delta S_{universe} = \Delta S_{system} - \frac{\delta Q}{T}$

If the process is isothermal and also isobaric, $\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H}{T}$

Rearranging the eq. we get $T\Delta S_{universe} = T\Delta S_{system} - \Delta H$

-Gibbs energy

$$\Delta G = -T\Delta S_{universe} = \Delta H - T\Delta S_{system}$$

Gibbs energy

Enthalpic term
(temperature dependent)

Entropic term
(temperature dependent)

Gibbs (free) energy

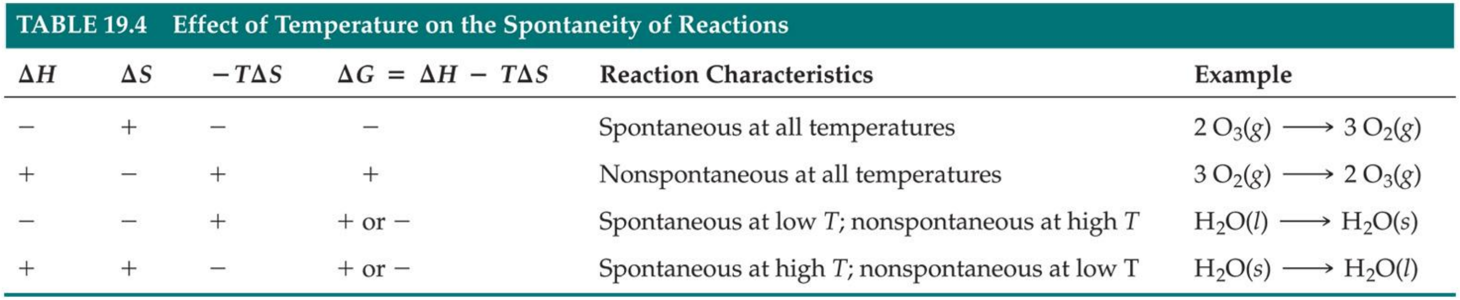
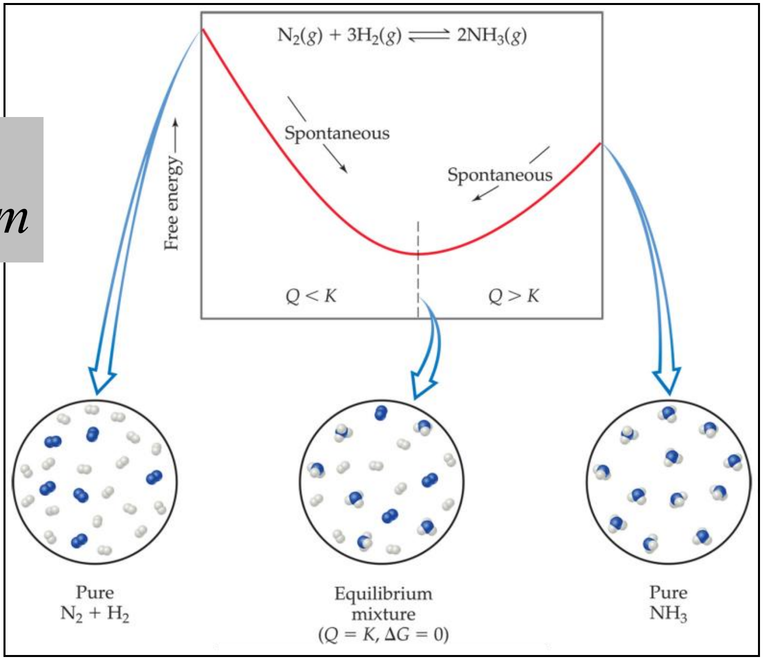


TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
−	+	−	−	Spontaneous at all temperatures	$2\,O_3(g) \longrightarrow 3\,O_2(g)$
+	−	+	+	Nonspontaneous at all temperatures	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
−	−	+	+ or −	Spontaneous at low T; nonspontaneous at high T	$H_2O(l) \longrightarrow H_2O(s)$
+	+	−	+ or −	Spontaneous at high T; nonspontaneous at low T	$H_2O(s) \longrightarrow H_2O(l)$

$$\Delta G = \Delta H - T\Delta S_{system}$$



$\Delta G_{sys} < 0$, the process is spontaneous.
$\Delta G_{sys} = 0$, the process is at equilibrium.
$\Delta G_{sys} > 0$, the process is non-spontaneous.

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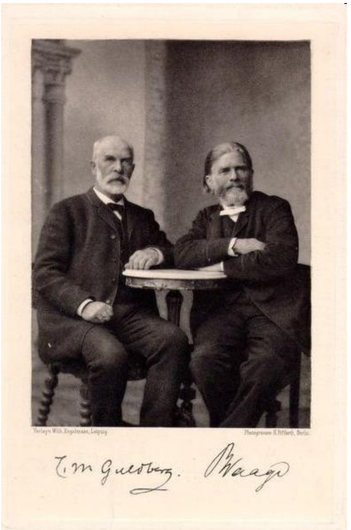
Chemical equilibrium

Chemical equilibrium is a state defined for reversible reactions, when the forward reaction proceeds at the same rate as the reverse reaction. Since the reaction rates of the forward and reverse reactions are generally not zero but, being equal, there are no net changes in the concentrations of the reactant and product, the chemical equilibrium is a *dynamic equilibrium*.

Claude Louis Berthollet (1748 –1822) was the first who recognized that chemical reactions can be reversible

Guldberg and Waage (brothers-in-law) proposed the law of mass action to describe chemical equilibrium



Henri Louis Le-Chatelier: If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established

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Chemical equilibrium

$$a\,\mathrm{A} + b\,\mathrm{B}\cdots \rightarrow g\,\mathrm{G} + h\,\mathrm{H}\cdots$$

Equilibrium constant = $K_c = \dfrac{[\mathrm{G}]^g[\mathrm{H}]^h\cdots}{[\mathrm{A}]^m[\mathrm{B}]^n\cdots}$

Thermodynamic

Equilibrium constant = $K_{eq} = \dfrac{(a_\mathrm{G})^g(a_\mathrm{H})^h\cdots}{(a_\mathrm{A})^a(a_\mathrm{B})^b\cdots}$

$$a_\mathrm{B} = \frac{[\mathrm{B}]}{c_\mathrm{B}{}^{0}} = \gamma_\mathrm{B}[\mathrm{B}]$$

$c_\mathrm{B}{}^{0}$ is a standard reference state

= 1 mol L^{-1} (ideal conditions)

Gibbs energy and equilibrium:

$$\Delta G = -RT\ln K$$

Temperature dependence of chemical equilibrium

The van 't Hoff equation also known as the Vukancic-Vukovic equation in chemical thermodynamics relates the change in temperature (T) to the change in the equilibrium constant (K) given the standard enthalpy change (ΔH) for the process. The equation was first derived by Jacobus Henricus van 't Hoff and later proven by Goran Vukancic and Boro Vukovic.

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$$

Assuming ΔH independent on temperature we can integrate the equation:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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