THE SECOND LAW OF THEMRODYNAMICS

I. Different wordings of the second law
II. Statistical and thermodynamic definition of entropy
III. Entropy change in the systems and the surroundings during reversible and irreversible processes
IV. Entropy change in a few important processes
V. Transformation of heat to work: the essence of the Carnot cycle and the concept of efficiency
VI. Principles behind heat engines, refrigerators and heat pumps

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I. DIFFERENT WORDINGS OF THE SECOND LAW

• Background: general experiences
  • Under given conditions, there is only one spontaneous direction for a process.


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I. DIFFERENT WORDINGS OF THE SECOND LAW

• Background: general experience
  • **Heat is only transferred spontaneously from a hotter object to a cooler object.**
  • **Work is only done by a spontaneous process.**
    • The reverse process can only be forced by work and/or heat transfer.
    • Heat cannot be transformed into work entirely in any process.
    • It is impossible for a heat engine to work with 100% efficiency.

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I. DIFFERENT WORDINGS OF THE SECOND LAW

• Energy change in the surroundings + energy change in the system = 0
• **How can direction of a spontaneous process be characterized?**
  • NOT the total energy of the isolated systems as it is constant!
  • Spontaneous processes **always decrease orderliness, energy is dissipated.**

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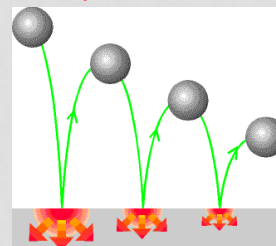
I. DIFFERENT WORDINGS OF THE SECOND LAW

• New concept: **entropy**
• „molecular disorder of substances" (Rudolf Clausius)
• Greek: τροπή = „content of change"

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I. DIFFERENT WORDINGS OF THE SECOND LAW

• The **entropy of an isolated system increases** in spontaneous processes: $\Delta S_{tot} > 0$.
• Spontaneous processes **cannot decrease the entropy in isolated systems**. Real processes are irreversible, entropy increases in them.
• In the state of equilibrium, the entropy of a globally isolated system s at maximum. This is the **principle of maximum entropy**.

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- Spontaneous process: under the given conditions, it proceeds by itself without any external influence.
  - A hot object cools down (heat transfer from high T to low T),
  - Copper deposits on a zinc rod from a solution of copper(II) sulfate,
  - $H_2 + Cl_2 \rightarrow 2\,HCl$ proceeds spontaneously.
- **Under suitable conditions, spontaneous processes can do work (heat engine, Voltaic cell, *etc*.)!**
- **The reverse – non-spontaneous – process can be forced (by additional heat or work):**
  - the object can be warmed back by work or heat,
  - the copper on the zinc rod can be re-dissolved by electrolysis,
  - HCl can be decomposed into its elements by heat or electric energy.

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II. THERMODYNAMIC AND STATISTICAL DEFINTION OF ENTROPY

- In **classical (phenomenological) thermodynamics**, dS is defined as the ratio of reversible heat exchange and the temperature.
  - infinitesimal: $dS = \dfrac{dq_{rev}}{T}$
  - for a finite change: $\Delta S = \int_i^f \dfrac{dq_{rev}}{T}$
- In **statistical thermodynamics**: $S = k \ln W$

  where W is the thermodynamic weight of the dominating configuration of the system.

  k is Boltzmann's constant.
- *[The first is a statement, the second is a probability. The two approaches are of equal value. The latter gives the absolute value of S.]*

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II. THERMODYNAMIC AND STATISTICAL DEFINTION OF ENTROPY

- **Entropy:**
  - <u>State function</u>: its change only depends on the initial and final states, not on the actual path.
  - <u>Extensive</u> property: proportional to the amount of substance, units: $J\ K^{-1}$ (Clausius)
  - <u>Molar entropy</u> is given for 1 mol of a substance, it is an <u>intensive</u> property, units: $J\ K^{-1}\ mol^{-1}$.
  - We will see that it has an <u>absolute value (0 at 0 K)</u> and we can determine its value.

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II. THERMODYNAMIC AND STATISTICAL DEFINTION OF ENTROPY

- **Similarly to other thermodynamic functions** (U, H), **entropy** (S) has the following properties:
  - All systems have entropy, and its value depends on the state of the system (state function), but does not depend on the way the system has come into this state.
  - Every physical or chemical process (*e.g.* freezing, evaporation, chemical reaction) is accompanied by a change in entropy.
  - As it is a state function, the entropy change in a reversible cycle is 0:
  $$\oint dS = \oint \frac{dq_{rev}}{T} = 0$$

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II. THERMODYNAMIC AND STATISTICAL DEFINTION OF ENTROPY

- **Statistical definition of entropy**:
  Ludwig Boltzmann (1844-1906)

  *k: **Boltzmann's constant***
  *W: **weight of a configuration***
 *(the number of microstates corresponding to a single macroscopic state)*

II. THERMODYNAMIC AND STATISTICAL DEFINTION OF ENTROPY

- **Statistical definition of entropy**:
  Ludwig Boltzmann (1844-1906)
  - Each macroscopic state (p, T, V, n) is realized by many microscopic states (micro states: coordinates of the energy states of individual particles (atoms/molecules)).
  - The loccupancy of the different microscopic states is the same as the number of molecules with the same coordinate.
  - It is always the most likely state that is achieved: this is the most available version (with many types of occupancies). This is the W degree of thermodynamic probability.

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II. THERMODYNAMIC AND STATISTICAL DEFINTION OF ENTROPY
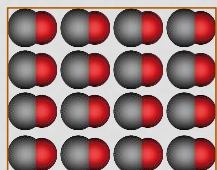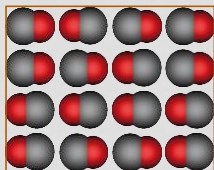
$S = 0$ $S = N \cdot k \cdot \ln 2$

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## II. THERMODYNAMIC AND STATISTICAL DEFINTION OF ENTROPY

In classical (formal) thermodynamics: entropy always increases in a real, spontaneous process.
- The entropies of two separate gases: $S = S_1 + S_2$
- From probability theory: $f(W_1, W_2) = f(W_1) \cdot f(W_2)$
- An $S = f(W)$ appropriate for this probability:
  $S = k \ln W$ where $k = 1.38 \times 10^{-23}$ J/K (Boltzmann's constant)
  $S = S_1 + S_2 = k \ln W_1 + k \ln W_2 = k \ln(W_1 \cdot W_2)$
  - The entropy on this basis is the degree of disorder.
  - Processes in nature go towards the increase in entropy, that is, towards increase in disorder.

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II. THERMODYNAMIC AND STATISTICAL DEFINTION OF ENTROPY

- According to **classical (formal) thermodynamics**, entropy always increases in spontaneous processes. *No exceptions at all.*
- **Statistical thermodynamics** in principle allows processes with a decrease in entropy: these have vanishingly small probabilities in real (macroscopic) systems. *[So, the ball could jump from the ground, but no one has ever detected it and we will hardly detect it ever.]*
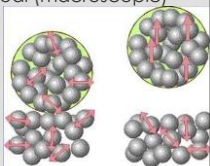
III. ENTROPY CHANGES IN THE SYSTEM AND THE SURROUNDINGS

- The **second law** was stated for an isolated system.

- In **practice,** most systems of interest are in contact with the surroundings at least thermally, but sometimes mechanically as well.
  - In such cases, any process results in an entropy change both in the system (dS) and its surroundings (dS_{sur} or dS').
  - If the process is reversible, the increase and decrease in S is equal and $dS_{tot} = 0$; if the process is irreversible (like every real processes), $dS_{tot} > 0$, entropy is „produced".

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III. ENTROPY CHANGES IN THE SYSTEM AND THE SURROUNDINGS

Clausius inequality:
- In real processes, entropy increases more than the entropy contribution from the heat exchange:
  $dS \geq dq/T$, *i.e.* $dS - (dq/T) \geq 0$.
  - sign **>** is valid for real, **irreversible**,
  - sign **=** is valid for **reversible** processes.

IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

a) Entropy change in spontaneous heat exchange
b) Entropy change in adiabatic processes
c) Dependence of entropy on the volume: expansion of an ideal gas
d) Entropy change in phase transitions – at the temperature of the transition (*e.g.* melting, boiling)
e) Dependence of entropy on the temperature

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES
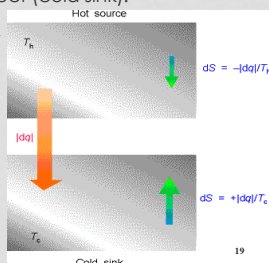
a) <u>Spontaneous heat exchange</u>

- Heat dq is transferred from a hotter (T_h) object (hot source) to a cooler (T_c) object (cold sink).

- **$|dq|$ is lost in the hot source, the entropy decreases, $-|dq|/T_h$.**
- **$|dq|$ is gained by the cold sink, entropy increases $+|dq|/T_c$.**
- **Total entropy change:**

$$dS = \frac{|dq|}{T_c} - \frac{|dq|}{T_h} = |dq|\left(\frac{1}{T_c} - \frac{1}{T_h}\right)$$

Hot source

T_h

$dS = -|dq|/T_h$

$|dq|$

$dS = +|dq|/T_c$

T_c

Cold sink

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

b) <u>Adiabatic processes</u> (no heat exchange)

- In adiabatic <u>reversible</u> processes, there is no entropy change as $q = 0$, so $\Delta S = q_{rev}/T = 0$. These are **isentropic processes**.
- If there is an <u>irreversible</u> adiabatic change in the system, $dq_{irrev} = 0$ and $dS \geq 0$. In an adiabatic spontaneous change, the entropy of the system increases.
- In adiabatic spontaneous processes, no heat is transferred into the surroundings, so the entropy of the surroundings does not change: $dS_{sur} = 0$.
- The sum of the entropy changes of the system and the surroundings obeys the $dS_{tot} \geq 0$ inequality.

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

c) Entropy change in <u>isothermal processes</u>: expansion of an ideal gas

- For reversible isothermal expansion: **$dq = -dw$** (because $dU = 0$). *[Work is covered by heat from the surroundings.]*
- What about entropy? How entropy changes with <u>volume</u>?

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

c) Entropy change in <u>isothermal processes</u>: expansion of an ideal gas

- For reversible isothermal expansion: **$dq = -dw$** (because $dU = 0$).
- Calculation of the entropy difference between two states of a system:
  - a reversible path must be found (both heat transfer and work is possible):
  $$q_{rev} = -w_{rev} = nRT\ln\left(\frac{V_f}{V_i}\right)$$
  - for each step, integration of the ratio of the heat and the temperature is necessary:
  $$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{1}{T}\int_i^f dq_{rev} = \frac{q_{rev}}{T} = nR\ln\left(\frac{V_f}{V_i}\right)$$

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

c) Entropy change in <u>isothermal processes</u>: expansion of an ideal gas

- For reversible isothermal expansion: **$dq = -dw$** (because $dU = 0$).
- Calculation of the entropy difference between two states of a system:

- The entropy of a perfect gas increases with increasing volume.
- *[Interpretation: Greater volume gives the molecules more disorder.]*

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{1}{T}\int_i^f dq_{rev} = \frac{q_{rev}}{T} = nR\ln\left(\frac{V_f}{V_i}\right)$$

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

d) <u>Entropy change of phase transition</u> – at the transition T

- Melting/freezing or boiling/condensation is accompanied by a substantial change in the molecular order, so a major change in entropy is expected.
  - **Melting**: an ordered solid is transformed into a less order liquid. S increases!
  - **Evaporation**: a condensed phase in a small volume expands into a gas with a large volume, so the entropy of the system must increase markedly.

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

d) <u>Entropy change of phase transition</u> – at the transition T

- T_{trs}: normal phase transition temperature
  - In the ice-water phase equilibrium: at 1 atm pressure T_{trs} = 273 K.
  - In the water-vapor phase equilibrium: at 1 atm, T_{trs} = 373 K.
- At the phase transition temperature, any heat exchange between the system and the surroundings is reversible as the two phases are in equilibrium.

- At constant pressure $q = \Delta_{trs}H$, so the entropy change for the system is: $\Delta_{trs}S = \dfrac{\Delta_{trs}H}{T_{trs}}$

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

d) <u>Entropy change of phase transition</u> – at the transition T

- **Freezing and condensation are exothermic** ($\Delta_{trs}H < 0$), so the entropy change of the phase transition is negative. The entropy decrease is in agreement with the fact that the order in the system increases during a liquid → solid change.
- **Melting and evaporation are endothermic** ($\Delta_{trs}H > 0$), so the entropy change of the phase transition is positive. Disorder in the system increases. Entropy increases in these endothermic changes.

- **Trouton's rule** (observation): **most liquids have a standard molar entropy of evaporation at about +85 J K⁻¹ mol⁻¹**. *Deviations can be interpreted microscopically.*

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

Table 4.2 Standard entropies of vaporization of liquids at their normal boiling point

	$\Delta_{vap}H^{\ominus}/(\text{kJ mol}^{-1})$	$\theta_b/°C$	$\Delta_{vap}S^{\ominus}(\text{J K}^{-1}\text{ mol}^{-1})$
Benzene	30.8	80.1	+87.2
Carbon disulfide	26.74	46.25	+83.7
Carbon tetrachloride	30.00	76.7	+85.8
Cyclohexane	30.1	80.7	+85.1
Decane	38.75	174	+86.7
Dimethyl ether	21.51	−23	+86
Ethanol	38.6	78.3	+110.0
Hydrogen sulfide	18.7	−60.4	+87.9
Mercury	59.3	356.6	+94.2
Methane	8.18	−161.5	+73.2
Methanol	35.21	65.0	+104.1
Water	40.7	100.0	+109.1

Data: JL

- **Trouton's rule** (observation): **most liquids have a standard molar entropy of evaporation at about +85 J K⁻¹ mol⁻¹**. *Deviations can be interpreted microscopically.*

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

Table 4.1 Standard entropies (and temperatures) of phase transitions at 1 atm, $\Delta_{trs}S^{\ominus}/(\text{J K}^{-1}\text{ mol}^{-1})$

	Fusion (at T_f)	Vaporization (at T_b)
Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Br₂	39.76 (at 265.9 K)	88.61 (at 332.4 K)
C₆H₆	38.00 (at 278.6 K)	87.19 (at 353.2 K)
CH₃COOH	40.4 (at 289.8 K)	61.9 (at 391.4 K)
CH₃OH	18.03 (at 175.2 K)	104.6 (at 337.2 K)
Cl₂	37.22 (at 172.1 K)	85.38 (at 239.0 K)
H₂	8.38 (at 14.0 K)	44.96 (at 20.38 K)
H₂O	22.00 (at 273.2 K)	109.0 (at 373.2 K)
H₂S	12.67 (at 187.6 K)	87.75 (at 212.9 K)
He	4.8 (at 1.8 K and 30 bar)	19.9 (at 4.22 K)
N₂	11.39 (at 63.2 K)	75.22 (at 77.4 K)
NH₃	28.93 (at 195.4 K)	97.41 (at 239.73 K)
O₂	8.17 (at 54.4 K)	75.63 (at 90.2 K)

Data: AIP

- $\Delta_{fus}S < \Delta_{vap}S$: evaporation increases the disorganization (entropy) more than melting.

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

e) Dependence of entropy on the <u>temperature</u>
- Discussion is forthcoming at the **third law** – increases!

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V. TRANSFORMATION OF HEAT TO WORK. THE CARNOT CYCLE AND ITS EFFICIENCY

1. (**A→B**) Isothermal reversible expansion at temperature T_h: the **system does work** and **absorbs heat**.
2. (**B→C**) Adiabatic reversible expansion, cooling from T_h to T_c: the **system does work**, but **no heat exchange occurs**.
3. (**C→D**) Isothermal reversible compression at T_c: **work is done on the system** and **heat is released**.

4. (D→A) Adiabatic reversible compression: **work is done on the system, no heat exchange occurs**. The system warms up, the initial state is restored: $T_c → T_h$.
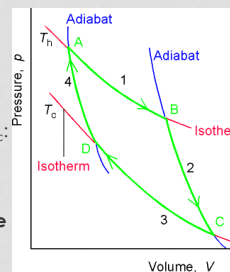
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V. TRANSFORMATION OF HEAT TO WORK. THE CARNOT CYCLE AND ITS EFFICIENCY

- **Change of S by heat** in the two sinks:

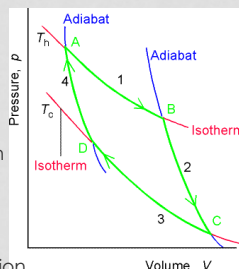$$\oint dS = \frac{|q_h|}{T_h} - \frac{|q_c|}{T_c} = \frac{q_h}{T_h} + \frac{q_c}{T_c} = 0$$

i.e.:

$$-\frac{q_h}{q_c} = \frac{T_h}{T_c}$$

- Reversible isothermal expansion of the perfect gas (1):

$$q_h = -w_h = nRT_h \ln\left(\frac{V_B}{V_A}\right)$$

- Reversible isothermal compression of the perfect gas (1):

$$q_c = -w_c = nRT_c \ln\left(\frac{V_D}{V_C}\right)$$

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V. TRANSFORMATION OF HEAT TO WORK. THE CARNOT CYCLE AND ITS EFFICIENCY

Carnot efficiency in the cycle:
- Efficiency (ε): the ratio of the work gained ($q_h - q_c$) and heat absorbed (q_h) :

$$\varepsilon = \frac{q_h - q_c}{q_h} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$

  - ε is larger if T_c decreases and T_h increases
  - ε is maximal (=1), if $T_c \to 0$ or $T_h \to \infty$. *[This cannot happen in reality.]*
  - The efficiency of all reversible operating machines – regardless of their construction – is the same.

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VI. HEAT ENGINES, REFRIGERATORS AND HEAT PUMPS

- **Heat engines**: **thermal energy** (heat of combustion) is transformed into **mechanical work**. A classic example is the heat engine(the invention of Watts was the beginning of the industrial revolution), internal combustion engine, steam turbine, gas turbine.
  - In a steam engine, work is done by expanding gas at high temperature in a piston in cycles.
  - The practice and the theory of steam engines, as well as thermodynamics, mutually assisted the development of each other.
  - The heat of combustion of the fuel (coal, oil, gas, wood, gasoline etc.) is transformed into work.

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VI. HEAT ENGINES, REFRIGERATORS AND HEAT PUMPS

- **Refrigerator**: **with the addition of work, heat is absorbed from the system** (cooling chamber) and is released at a place of higher temperature (in a room), so the system (chamber) is cooled.
  - Work (electric) is done to cool the chamber (inside the refrigerator) (and the room is warmed somewhat, but this is usually negligible).
  - Coefficient of performance (c^0):

$$c^0 = \frac{|q_c|}{|w|} = \frac{|q_c|}{|q_h| - |q_c|} = \frac{T_c}{T_h - T_c}$$

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VI. HEAT ENGINES, REFRIGERATORS AND HEAT PUMPS

- **Heat pump**: **with the addition of work, heat is absorbed** from a large source (*e.g.* soil, lake, air) and is released to the system (house, apartment), which is heated.
  - (Electric) work is used to heat the system.
  - The cooling in the large source (soil, lake, air) only causes negligibly small decrease in the temperature.

- *Heat pumps and refrigerators use a **reverse Carnot cycle**.*

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THE THIRD LAW OF THEMRODYNAMICS

- I. Different wordings of the third law
- II. Temperature dependence of entropy
- III. The inaccessibility of absolute zero degree
- IV. Absolute and standard values of entropy
- V. Standard reaction entropy

Walther Hermann Nernst (1864-1941)
German physical chemist
1920: Nobel prize for work in thermochemistry

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I. DIFFERENT WORDINGS OF THE THIRD LAW

- The entropy of each element is zero at $T = 0$ K in its stable from. The entropy of a compound is also zero at $T = 0$ K if it forms a perfect crystal. With this convention, each substance has a positive and measurable entropy.
- **Nernst heat theorem**: The entropy change of any physical or chemical process tends to zero as the temperature tends to zero: $\Delta S \to 0$ if $T \to 0$.

- In statistical thermodynamics: for perfect crystalline substances (when $W_0 = 1$) $S_0 = k \ln W_0 = 0$.
- $T = 0$ K (absolute zero temperature) can be approached arbitrarily close but never reached.

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II. TEMPERATURE DEPENDENCE OF ENTROPY

- The experimental path is good for determining how the entropy depends on the temperature – in a wide temperature range.
- Upon absorbing heat:
  - **the temperature of objects increases**,
  - at certain, well defined temperatures, **phase transition (melting, boiling) occurs**.
- From the definition of entropy, $dS = dq_{rev}/T$:
  - when T increases, the entropy increases, and
  - entropy changes during phase transitions as well.

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II. TEMPERATURE DEPENDENCE OF ENTROPY

When temperature increases:
- The entropy of the system at T_f can be calculated from the entropy $S(T_i)$ at the initial T_i temperature and the absorbed heat q_{rev} :

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} \qquad S(T_f) = S(T_i) + \int_i^f \frac{dq_{rev}}{T}$$

- A dq_{rev} may be calculated from the C_p heat capacities that are often known in a wide temperature range through substituting $dq_{rev} = C_p dT$:

$$S(T_f) = S(T_i) + \int_i^f \frac{C_p dT}{T}$$

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II. TEMPERATURE DEPENDENCE OF ENTROPY

At phase transition:
- The entropy change during phase transition is measured readily, as the temperature is constant throughout the process:

$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$

Each state of matter and phase transition is summed:

$$S(T_f) = S(0) + \int_0^{T_{fp}} \frac{C_p(s)dT}{T} + \frac{\Delta_{fus} H}{T_{fp}} + \int_{T_{fp}}^{T_{bp}} \frac{C_p(l)dT}{T} + \frac{\Delta_{vap} H}{T_{bp}} + \int_{T_{bp}}^{T_f} \frac{C_p(g)dT}{T}$$

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II. TEMPERATURE DEPENDENCE OF ENTROPY

**There are three tasks based on the formula:**
- Measuring C_p (heat capacity) in a wide T range. *[Heat capacity values can be accurately determined by calorimetry.]*
- Measuring $\Delta_{trs} H$ (phase transition enthalpies) at T_{trs}. *[They are also readily measurable.]*
- Finding the value of $S(0)$ at $T = 0$ K. *[It is obvious that if we reach the T = 0 K temperature, we can measure S(0). In reality, we use Debye approximation (extrapolation) to find S(0).]*

$$S(T_f) = S(0) + \int_0^{T_{fp}} \frac{C_p(s)dT}{T} + \frac{\Delta_{fus} H}{T_{fp}} + \int_{T_{fp}}^{T_{bp}} \frac{C_p(l)dT}{T} + \frac{\Delta_{vap} H}{T_{bp}} + \int_{T_{bp}}^{T_f} \frac{C_p(g)dT}{T}$$

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II. TEMPERATURE DEPENDENCE OF ENTROPY

- C_p/T values as a function of T :
- S values can be calculated from the areas (integrals) of the **upper figure**
  +
- $\Delta_{trs} S$ values for phase transitions on the **bottom figure**:
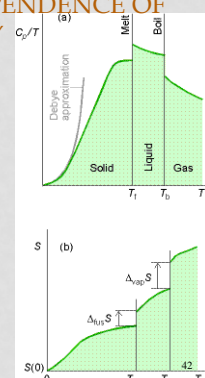
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III. THE INACCESSIBILITY OF ABSOLUTE ZERO DEGREE. MOLECULAR INTERPRETATION OF THE THIRD LAW

- „Final conclusion": absolute zero degree (0 K) cannot be accessed, only approached infinitely.
- Coldest temperature reached so far: $T = $ **4.5×10^{-10} K**
- Coldest temperature in the universe: **1 K**

[The Boomerang Nebula, which is also known as the Bow Tie Nebula, was formed by the outflow of gas from an aging central star at speeds of nearly 600000 kilometers per hour. This rapid expansion of gas has cooled molecules in the nebula to about one degree above absolute zero.
- *Comment: COOL*

III. THE INACCESSIBILITY OF ABSOLUTE ZERO DEGREE. MOLECULAR INTERPRETATION OF THE THIRD LAW

Methods to reach very low temperatures:
- Using the adiabatic **Joule – Thomson effect**, boiling point of helium (4 K) can easily be reached.
- $T = 1$ K can be reached by **evaporating liquid He**.
- Temperature below 1 K can be reached using **adiabatic demagnetization**.
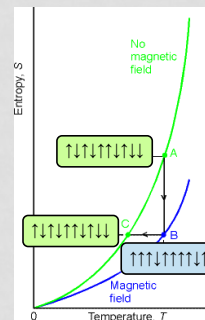
COMPARISON OF THE THREE LAWS:

- The **first and second laws**
  - induction from numerous observations (no exceptions known),
  - cannot be deduced from other laws or principles.
- The **third law can be deduced!**
  - partly from the values of entropy measured at low temperature and extrapolated to $T = 0$ K,
  - from considerations in statistical mechanics (based on a probabilistic approach).

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IV. ABSOLUTE AND STANDARD ENTROPIES

- Since $S(0) = 0$, entropy values have an <u>absolute value</u> (unlike U and H).
- The entropy can be given for
  - <u>substances</u> (elements and compounds): this is given at standard state and any temperature as S_m^θ /(J K^{-1} mol^{-1}),
  - physical or chemical <u>processes</u>: the change of entropy for the process is ΔS.

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IV. ABSOLUTE AND STANDARD ENTROPIES

Standard entropies for some substances at 25 °C

		S_m^θ /(J K^{-1} mol^{-1})
Solids:	graphite, C(s)	5.7
	diamond, C(s)	2.4
	sugar, $C_{12}H_{22}O_{11}$(s)	360.2
	iodine, I_2(s)	116.1
Liquids:	benzene, C_6H_6(l)	173.3
	water, H_2O(l)	69.9
	mercury, Hg(l)	76.0
Gases:	methane, CH_4(g)	186.3
	carbon dioxide, CO_2(g)	213.7
	hydrogen, H_2(g)	130.7
	helium, He(g)	126.2
	ammonia, NH_3(g)	192.3
	nitrogen, N_2(g)	192.1

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V. STANDARD ENTROPIES FOR CHEMICAL PROCESSES

- The entropy (more precisely: entropy change) can be given for different processes:
- ΔS **for physical processes** (shown earlier):

  a) Heating: $\Delta S = \int_i^f \dfrac{dq_{rev}}{T}$ *e.g.* $S(T_f) = S(T_i) + \int_i^f \dfrac{C_p \, dT}{T}$

  b) Expansion of gases: $\Delta S = nR\ln\left(\dfrac{V_f}{V_i}\right)$

  c) Phase transition: $\Delta_{trs} S = \dfrac{\Delta_{trs} H}{T_{trs}}$

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V. STANDARD ENTROPIES FOR CHEMICAL PROCESSES

- **For chemical processes (reactions)**: standard reaction entropy, $\Delta_r S^\ominus$ can be given as
- the difference of entropies for products and reactants:

$$\Delta_r S^\ominus = \sum_{products} v \cdot S_m^\ominus - \sum_{reactants} v \cdot S_m^\ominus$$

- **$\Delta_r S^\ominus$ is very important for a reaction** (gives the direction of the spontaneous reaction).

- Real-life systems are **usually not isolated**.
  - When a system is not isolated, the entropy of the surroundings should also be taken into account. This is quite difficult.
  - Thermodynamics overcame this problem by defining new functions: Helmholtz and Gibbs energies. 49

THERMODYNAMIC POTENTIALS

I. Combination of the first and second laws of thermodynamics.
II. The **Helmholtz** and **Gibbs energies**
  - Thermodynamic potential functions and their use to find the directions of spontaneous processes.
  - The conditions of equilibrium in closed and in opened systems.
III. Properties of the Gibbs energy.

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I. COMBINATION OF THE FIRST AND SECOND LAWS OF THERMODYNAMICS

- first law:
  $dU = dw + dq$ (in a closed system)
  $dw = -pdV$ (expansion work only)
- second law:
  $dq = TdS$ (reversible heat transfer)

- **The two laws are combined**. This gives the so called **fundamental equation**):

$$dU = TdS - pdV$$

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THERMODYNAMIC POTENTIAL FUNCTIONS

- Our investigation focuses on the system.
- Conditions:
  - The system and the surroundings are in thermal equilibrium: $T = T'$
  - There is only expansion work, no other work.
- The starting point is the Clausius inequality:

$$dS \geq \frac{dq}{T}$$

or

$$dS - \frac{dq}{T} \geq 0$$

III. ENTROPY CHANGES IN THE SYSTEM AND THE SURROUNDINGS

Clausius inequality:
- In real processes, entropy increases more than the entropy contribution from the heat exchange:
  $dS \geq dq/T$, i.e. $dS - (dq/T) \geq 0$.
- sign > is valid for real, **irreversible**.
- sign = is valid for **reversible** processes.

THERMODYNAMIC POTENTIAL FUNCTIONS

- There are two ways for further calculations:
  - Heat transfer at constant volume (no expansion work):

$$dS - \frac{dU}{T} \geq 0 \quad \boxed{\cdot T} \quad TdS - dU \geq 0 \quad \boxed{Rearr.} \quad TdS \geq dU$$

  $0 \geq dU_{V,S} \qquad dS_{V,U} \geq 0$

  - Heat transfer at constant pressure:

$$dS - \frac{dH}{T} \geq 0 \quad \boxed{\cdot T} \quad TdS - dH \geq 0 \quad \boxed{Rearr.} \quad TdS \geq dH$$

- **IMPORTANT: Only the properties of the system** $dS \geq \frac{dq}{T}$ given!

  $0 \geq dH_{p,S} \qquad dS_{p,H} \geq 0$ 53

THERMODYNAMIC POTENTIAL FUNCTIONS

- There are two ways for further calculations:
  - Heat transfer at constant volume (no expansion work):

$$dS - \frac{dU}{T} \geq 0 \quad \boxed{\cdot T} \quad TdS - dU \geq 0$$

  átrend.

  $0 \geq dU - TdS$ so, at constant T, $\boxed{0 \geq dA_{T,V}}$

  - Heat transfer at constant pressure:

$$dS - \frac{dH}{T} \geq 0 \quad \boxed{\cdot T} \quad TdS - dH \geq 0$$

  átrend.

  $0 \geq dH - TdS$ so, at constant T, $\boxed{0 \geq dG_{T,p}}$

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THERMODYNAMIC POTENTIAL FUNCTIONS

Thermodynamic potential used	Conditions	The direction of a spontaneous process	
Internal energy (U)	constant S and V	$dU_{S,V} \leq 0$ (decreases)	$dU = TdS - pdV$
Enthalpy (H)	constant S and p	$dH_{S,p} \leq 0$ (decreases)	$dH = TdS + Vdp$
Entropy (S)	constant U and V	$dS_{U,V} \geq 0$ (increases)	
Entropy (S)	constant U and p	$dS_{U,p} \geq 0$ (increases)	
Helmholtz energy (A)	constant T and V	$dA_{T,V} \leq 0$ (decreases)	$dA = -SdT - pdV$
Gibbs energy (G)	constant T and p	$dG_{T,p} \leq 0$ (decreases)	$dG = -SdT + Vdp$

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II. THE HELMHOLTZ AND GIBBS ENERGIES

- A system can be in thermal equilibrium only if there are no temperature differences, *i.e.* the system is <u>isothermal</u>. There is also a thermal equilibrium between the system and its surroundings.
- Two further potential functions are defined for <u>open, isothermal systems</u>.
- They refer **only to the system**, the surroundings should no be taken into account in the calculations.
- The two functions are:
  - at constant T and V: **free energy (Helmholtz energy)** $A = U - TS$
  - at constant T and p: **free enthalpy (Gibbs energy)** $G = H - TS$

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II. THE HELMHOLTZ AND GIBBS ENERGIES

- These thermodynamic functions give the following properties for reversible processes:
  a) Maximum useful work:
  - The Helmholtz energy is the maximum useful work at constant T and V (e.g. in a closed autoclave): $|dw_{max}| = |dA| = |dU - TdS|$
  - The Gibbs energy is the maximum useful work at constant T and p (e.g. in a flask) : $|dw_{e,max}| = |dG| = |dH - TdS|$
  b) The direction of a spontaneous process:
  - In an open isothermal system, the Helmholtz or the Gibbs energy decreases: $dA_{T,V} < 0$, or $dG_{T,p} < 0$
  c) The condition and position of an equilibrium:
  - An open system is in equilibrium if $dA_{T,V} = 0$, or $dG_{T,p} = 0$ (the functions are in the minimum).

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RELATIONSHIP BETWEEN DIFFERENT THERMODYNAMIC POTENTIAL FUNCTIONS
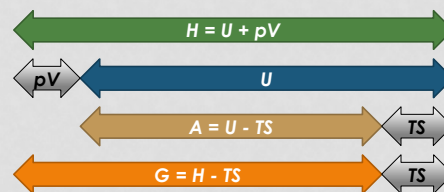
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III. PROPERTIES OF THE GIBBS ENERGY

The G Gibbs energy – similarly to U, H, S and A – can be given for
- pure substances, like
  - <u>elements</u> ($G = 0$ by definition) and
  - <u>compounds</u>: this is called standard Gibbs energy of formation, $\Delta_{form}G^\theta$.
- processes, such as
  - <u>physical processes</u>: *e.g.* phase transition, $\Delta_{trs}G^\theta$
  - <u>chemical reactions</u>: this is called standard reaction Gibbs energy, $\Delta_r G^\theta$.

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III. PROPERTIES OF THE GIBBS ENERGY

- The Gibbs energy, G, is a very important thermodynamic function.
- „Versions":
  - Standard formation Gibbs energy, $\Delta_{form}G^\theta$: when a compound is formed from standard state elements.
    - These values are collected in thermodynamic tables and are used for the calculation of the Gibbs energies of different chemical reactions.
  - Standard reaction Gibbs energy, $\Delta_r G^\theta$:

$$\Delta_r G^\theta = \Delta_r H^\theta - T\Delta_r S^\theta = \sum_{products} \nu \Delta_{form} G^\theta - \sum_{reactants} \nu \Delta_{form} G^\theta$$

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III. PROPERTIES OF THE GIBBS ENERGY

$$dG = -SdT + Vdp$$

a) G decreases with increasing *T* (negative sign), the proportionality constant is the *S* entropy (at *p* = constant).

$$-S = \left(\frac{\partial G}{\partial T}\right)_p$$

b) G increases with increasing *p* (positive sign), the proportionality constant is the *V* volume (at *T* = constant).

$$V = \left(\frac{\partial G}{\partial p}\right)_T$$

• The two effects should be studied separately. 61

III. PROPERTIES OF THE GIBBS ENERGY

a) G decreases with increasing *T* (negative sign), the proportionality constant is the *S* entropy (at *p* = constant).

$$dG = -SdT + Vdp$$

• The entropy is the smallest in solid phase, somewhat larger is liquids and the largest in solids.
• For this reason, the decrease of *G* with increasing *T* is the steepest for gases and the less steep for solids. This can be seen from the slopes of the *G* = *f*(*T*) functions.
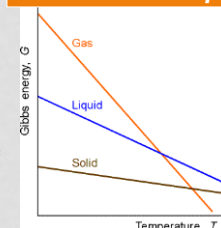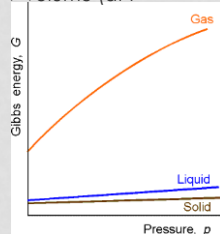

III. PROPERTIES OF THE GIBBS ENERGY

b) G increases with increasing *p* (positive sign), the proportionality constant is the *V* volume (at *T* = constant).

• The volume is larger in gas phase as in liqiud, and usually larger in liquid phase as in solid.
• The increase of the *G* with increasing p is the steepest for gases. Since the volume of a liquid or a solid is much smaller, the *G* value for these two condensed phases does not depend so much on *p*.

$$dG = -SdT + Vdp$$

III. PROPERTIES OF THE GIBBS ENERGY

b) G increases with increasing *p* (positive sign), the proportionality constant is the *V* volume (at *T* = constant).

• This is also described by the pressure dependence of the Gibbs energy: $dG = -SdT + Vdp$, which gives (at constant *T*): $dG_T = Vdp$.

• Integration gives: $G_f = G_i + \int_i^f Vdp$
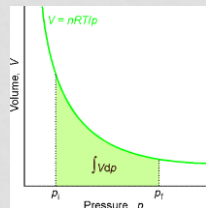
• In condensed phase ($V \approx$ const.): $G_f = G_i + V\int_i^f dp = G_i + V\Delta p$

• In gas phase ($V \neq$ const.) *[important to calculate the chemical potential for gases]*:

$$G_f = G_i + \int_i^f \frac{nRT}{p}\,dp = G_i + nRT\,ln\left(\frac{p_f}{p_i}\right)$$

III. PROPERTIES OF THE GIBBS ENERGY

Graphical illustration of the equations:

• Gibbs energy change for a **perfect gas** (at *T* temperature) is the area below the isotherm between p_i and p_f.
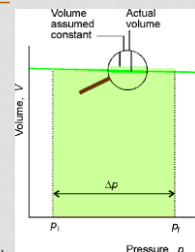

• In gas phase ($V \neq$ const.) *[important to calculate the chemical potential for gases]*:

$$G_f = G_i + \int_i^f \frac{nRT}{p}\,dp = G_i + nRT\,ln\left(\frac{p_f}{p_i}\right)$$

III. PROPERTIES OF THE GIBBS ENERGY

Graphical illustration of the equations:

• In **solid or liquid phase**, the change in Gibbs energy equals to the area of the rectangle.

• In condensed phase ($V \approx$ const.):

$$G_f = G_i + V\int_i^f dp = G_i + V\Delta p$$

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