
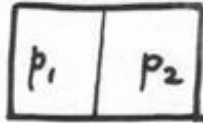
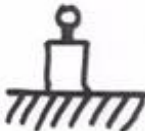
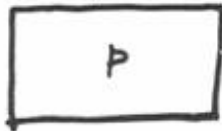


THE SECOND LAW OF THERMODYNAMICS

- 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

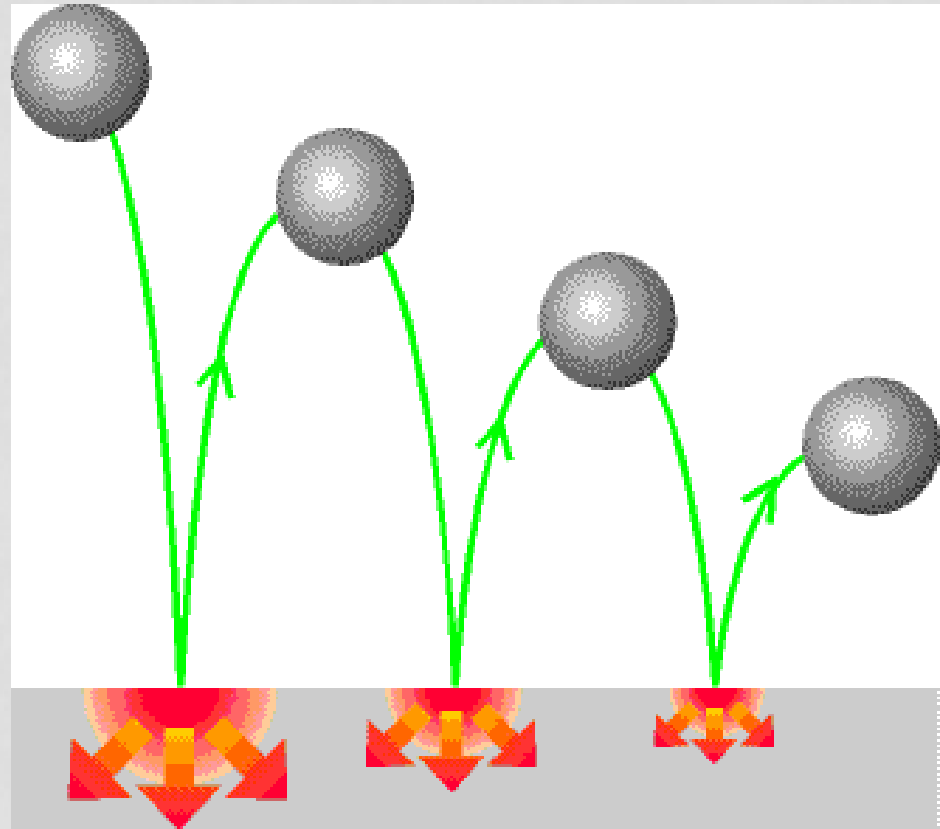
I. DIFFERENT WORDINGS OF THE SECOND LAW

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

	falling of an object	gas expansion	formation of hydrochloric acid
INITIAL			$H_{2(g)} + Cl_{2(g)} + H_2O(l)$
FINAL			$2 HCl_{aq}$

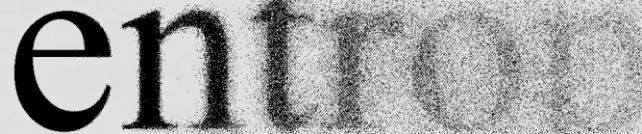
I. DIFFERENT WORDINGS OF THE SECOND LAW

- 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.**



I. DIFFERENT WORDINGS OF THE SECOND LAW

- New concept:



entropy

- „molecular disorder of substances”
(Rudolf Clausius)
- Greek: τροπή = „content of change”

I. DIFFERENT WORDINGS OF THE SECOND LAW

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

- **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,
 - $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$ 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.

II. THERMODYNAMIC AND STATISTICAL DEFINITION OF ENTROPY

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

II. THERMODYNAMIC AND STATISTICAL DEFINITION OF ENTROPY

$$S = k \cdot \log W$$

*Tombstone of
Ludwig Boltzmann*



- 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.

II. THERMODYNAMIC AND STATISTICAL DEFINITION OF ENTROPY

- **Entropy:**

- State function: its change only depends on the initial and final states, not on the actual path.
- As it is a state function, the entropy change in a reversible cycle is 0:

$$\oint dS = \oint \frac{dq_{\text{rev}}}{T} = 0$$

- Extensive property: proportional to the amount of substance, units: J K^{-1} (Clausius)
- Molar entropy is given for 1 mol of a substance, it is an intensive property, units: $\text{J K}^{-1} \text{mol}^{-1}$.
- Every physical or chemical process is accompanied by a change in entropy.

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 entropy change both in the system (dS) and its surroundings (dS_{sur} or dS').

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:

$$dS \geq dq/T, \text{ i.e. } dS - (dq/T) \geq 0.$$

- 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

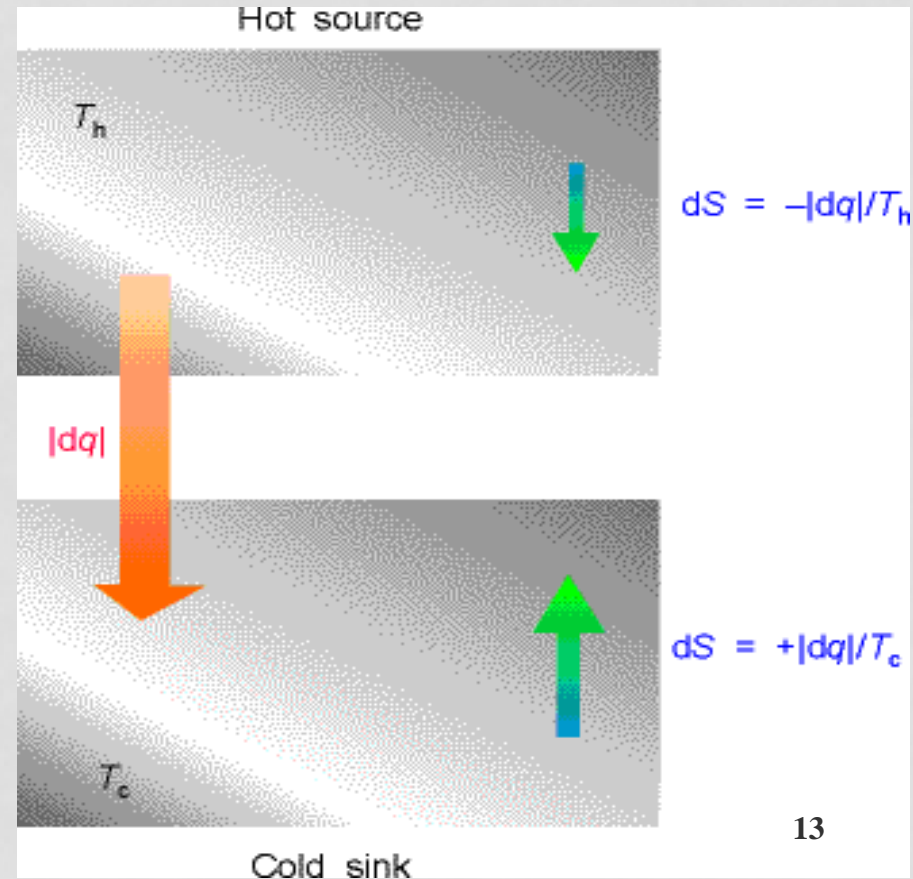
IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

a) Spontaneous heat exchange

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

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

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



IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

b) Adiabatic processes (no heat exchange)

- In adiabatic reversible processes, there is no entropy change as $q = 0$, so $\Delta S = q_{\text{rev}}/T = 0$.
These are **isentropic processes**.
- In adiabatic spontaneous processes, no heat is transferred into the surroundings, so the entropy of the surroundings does not change: $dS_{\text{sur}} = 0$.

IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

c) Entropy change in isothermal processes: 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):

$$q_{\text{rev}} = -w_{\text{rev}} = nRT \ln \left(\frac{V_f}{V_i} \right)$$

- for each step, integration of the ratio of the heat and the temperature is necessary.

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

IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

d) Entropy change of phase transition – 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:

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

IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

d) Entropy change of phase transition – at the transition T

- **Freezing and condensation are exothermic** ($\Delta_{\text{trs}}H < 0$), 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 \rightarrow solid change.
- **Melting and evaporation are endothermic** ($\Delta_{\text{trs}}H > 0$), 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 $+85 \text{ J K}^{-1} \text{ mol}^{-1}$.**

Deviations can be interpreted microscopically.

IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

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

	$\Delta_{\text{vap}}H^\circ / (\text{kJ mol}^{-1})$	$\theta_b / ^\circ\text{C}$	$\Delta_{\text{vap}}S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
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

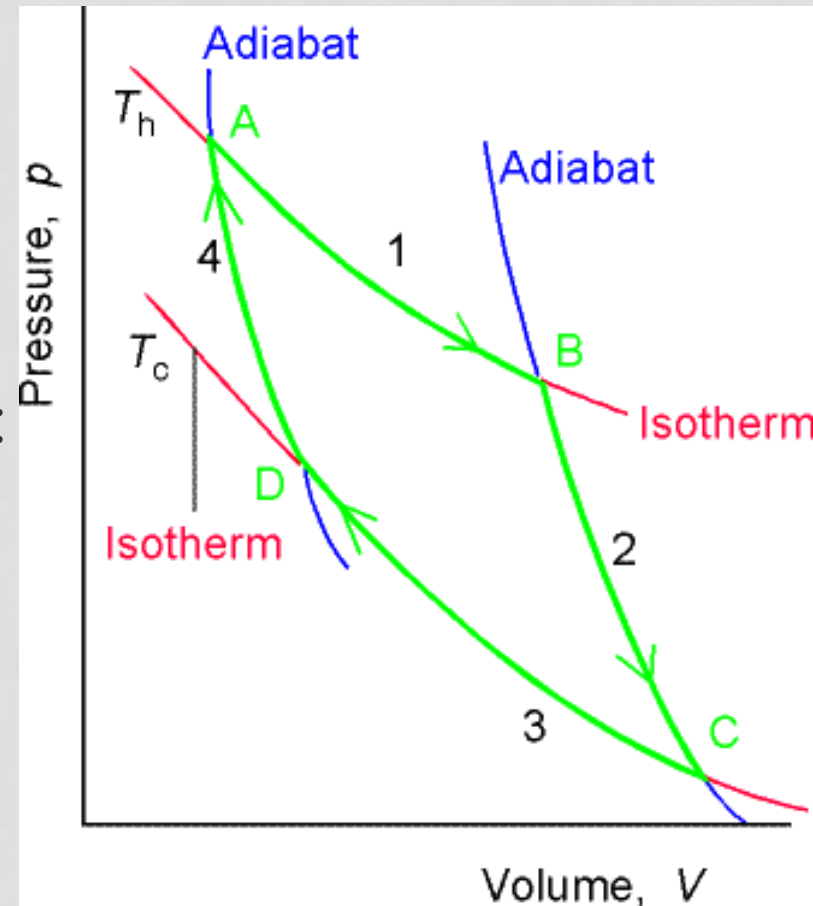
- **Trouton's rule** (observation): most liquids have a standard molar entropy of evaporation at about $+85 \text{ J K}^{-1} \text{ mol}^{-1}$.
Deviations can be interpreted microscopically.

IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

- e) Dependence of entropy on the temperature
- Discussion is forthcoming at the **third law**

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: $T_c \rightarrow T_h$.



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 T_c decreases and T_h increases
- ε is maximal ($=1$), if $T_c \rightarrow 0$ or $T_h \rightarrow \infty$.
[This cannot happen in reality.]

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 heat of combustion of the fuel (coal, oil, gas, wood, gasoline etc.) is transformed into work.

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:

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

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 (apartment), which is heated.
 - (Electric) work is used to heat the system.
 - The cooling in the large source only causes negligibly small decrease in the temperature.

THE THIRD LAW OF THERMODYNAMICS

- I. Different wordings of the third law
- II. Temperature dependence of entropy
- III. Absolute and standard values of entropy
- IV. Standard reaction entropy

Walther Hermann Nernst (1864-1941)
German physical chemist

1920: Nobel prize for work in thermochemistry



I. DIFFERENT WORDINGS OF THE THIRD LAW

- The entropy of each element is zero at $T = 0$ K in its stable form. 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: $\Delta S \rightarrow 0$ if $T \rightarrow 0$.
- In statistical thermodynamics: for perfect crystalline substances (when $W_0 = 1$): $S_0 = k \ln W_0 = 0$.

II. TEMPERATURE DEPENDENCE OF ENTROPY

- Upon absorbing heat:
 - **the temperature of objects increases,**
 - at certain, well-defined temperatures, **phase transition (melting, boiling) occurs.**
- From the definition of entropy, $dS = dq_{\text{rev}}/T$:
 - when T increases, the entropy increases, and
 - entropy changes during phase transitions as well.

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} :

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

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

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

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:

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

Each **state of matter** and **phase transition** is summed:

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

III. ABSOLUTE AND STANDARD ENTROPIES

- Since $S(0) = 0 \text{ J K}^{-1} \text{ mol}^{-1}$, entropy values have an absolute value (unlike U and H .)

The entropy can be given for

- substances (elements and compounds): this is given at standard state and any temperature as: S_m^θ ,
- physical or chemical processes: the change of entropy for the process is: ΔS .

III. ABSOLUTE AND STANDARD ENTROPIES

- Standard entropies for some substances at 25 °C

		$S_m^\ominus / (\text{J K}^{-1} \text{mol}^{-1})$
Solids:	graphite, C(s)	5.7
	diamond, C(s)	2.4
Liquids:	water, H ₂ O(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

IV. STANDARD ENTROPIES FOR CHEMICAL PROCESSES

- **In a chemical reaction:** standard reaction entropy, $\Delta_r S^\theta$ is the difference of entropies for products and reactants:

$$\Delta_r S^\theta = \sum_{\text{products}} \nu \cdot S_m^\theta - \sum_{\text{reactants}} \nu \cdot S_m^\theta$$

- $\Delta_r S^\theta$ 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**.

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

I. COMBINATION OF THE FIRST AND SECOND LAWS OF THERMODYNAMICS

- first law:

$$dU = dw + dq$$

$$dw = -pdV \quad (\text{expansion work})$$

- second law:

$$dq = TdS \quad (\text{reversible heat transfer})$$

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

$$dU = TdS - pdV$$

THERMODYNAMIC POTENTIAL FUNCTIONS

- Our investigation focuses on the system only.
- 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

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

THERMODYNAMIC POTENTIAL FUNCTIONS

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

$$dS - \frac{dU}{T} \geq 0 \xrightarrow{\cdot T} TdS - dU \geq 0 \xrightarrow{\text{Rearr.}} TdS \geq dU$$

\downarrow
 $S = \text{const.}$

\downarrow
 $U = \text{const.}$

$0 \geq dU_{V,S}$

$dS_{V,U} \geq 0$

- Heat transfer at constant pressure:

$$dS - \frac{dH}{T} \geq 0 \xrightarrow{\cdot T} TdS - dH \geq 0 \xrightarrow{\text{Rearr.}} TdS \geq dH$$

\downarrow
 $S = \text{const.}$

\downarrow
 $H = \text{const.}$

$0 \geq dH_{p,S}$

$dS_{p,H} \geq 0$

IMPORTANT: Only the properties of the system are given!

THERMODYNAMIC POTENTIAL FUNCTIONS

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

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



$$TdS - dU \geq 0$$



$$0 \geq dU - TdS \text{ so, at constant } T, \quad 0 \geq dA_{T,v}$$

- Heat transfer at constant pressure:

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



$$TdS - dH \geq 0$$

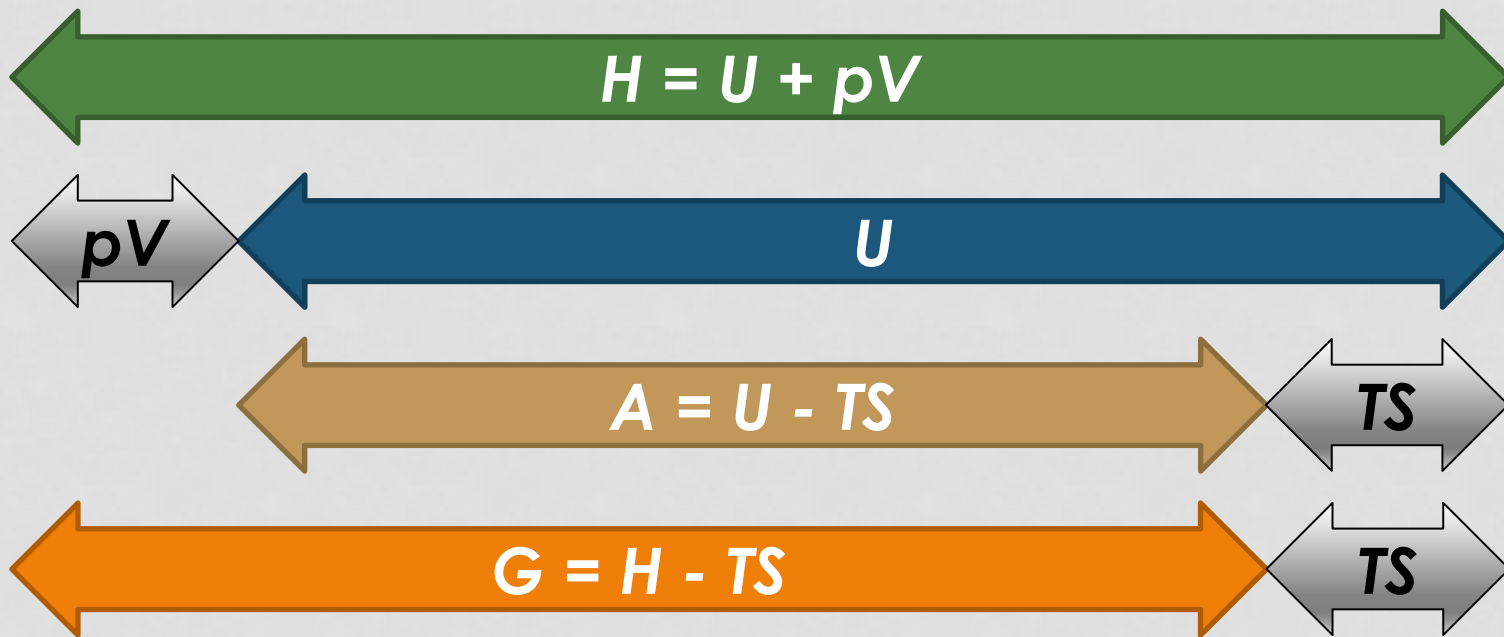


$$0 \geq dH - TdS \text{ so, at constant } T, \quad 0 \geq dG_{T,p}$$

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)	$dG = -SdT + Vdp$

RELATIONSHIP BETWEEN DIFFERENT THERMODYNAMIC POTENTIAL FUNCTIONS



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).

III. PROPERTIES OF THE GIBBS ENERGY

The G Gibbs energy – similarly to U , H , S and A – can be given for

- pure substances, like
 - elements ($G = 0$ by definition) and
 - compounds: this is called standard Gibbs energy of formation: $\Delta_{\text{form}} G^\theta$.
- processes, such as
 - physical processes, e.g. phase transition: $\Delta_{\text{trs}} G^\theta$
 - chemical reactions: this is called standard reaction Gibbs energy: $\Delta_r G^\theta$.

III. PROPERTIES OF THE GIBBS ENERGY

- The Gibbs energy, G , is a very important thermodynamic function.
- „Versions“:
 - Standard formation Gibbs energy, $\Delta_{\text{form}}G^\theta$: 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, $\Delta_r G^\theta$

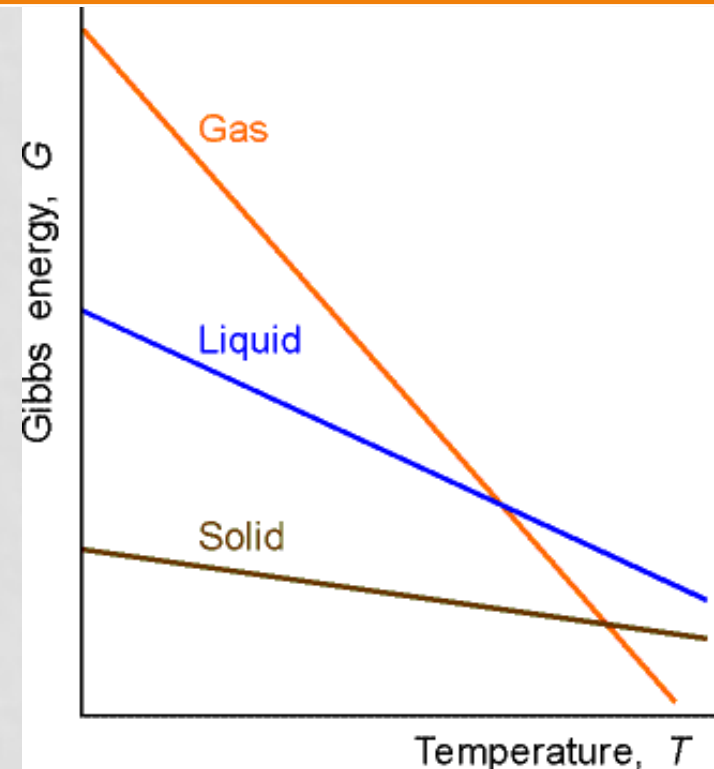
$$\Delta_r G^\theta = \Delta_r H^\theta - T\Delta_r S^\theta = \sum_{\text{products}} \nu \Delta_{\text{form}} G^\theta - \sum_{\text{reactants}} \nu \Delta_{\text{form}} G^\theta$$

III. PROPERTIES OF THE GIBBS ENERGY

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

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

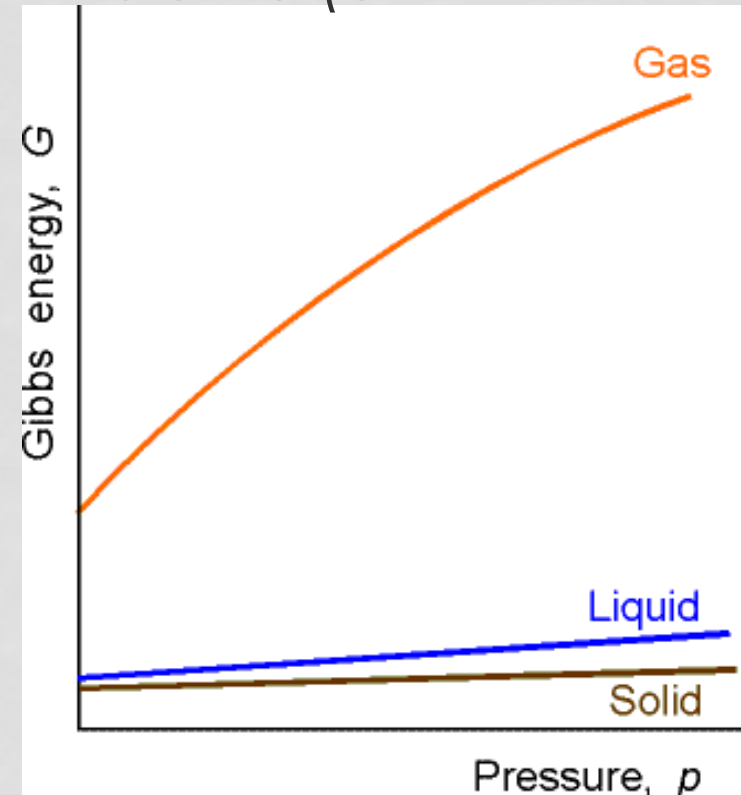
$$dG = -SdT + Vdp$$



III. PROPERTIES OF THE GIBBS ENERGY

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

- The volume is larger in gas phase as in liquid, 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 .



$$dG = -SdT + Vdp$$