THE SECOND LAW OF THEMRODYNAMICS

I. DIFFERENT WORDINGS OF THE SECOND LAW

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

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.**
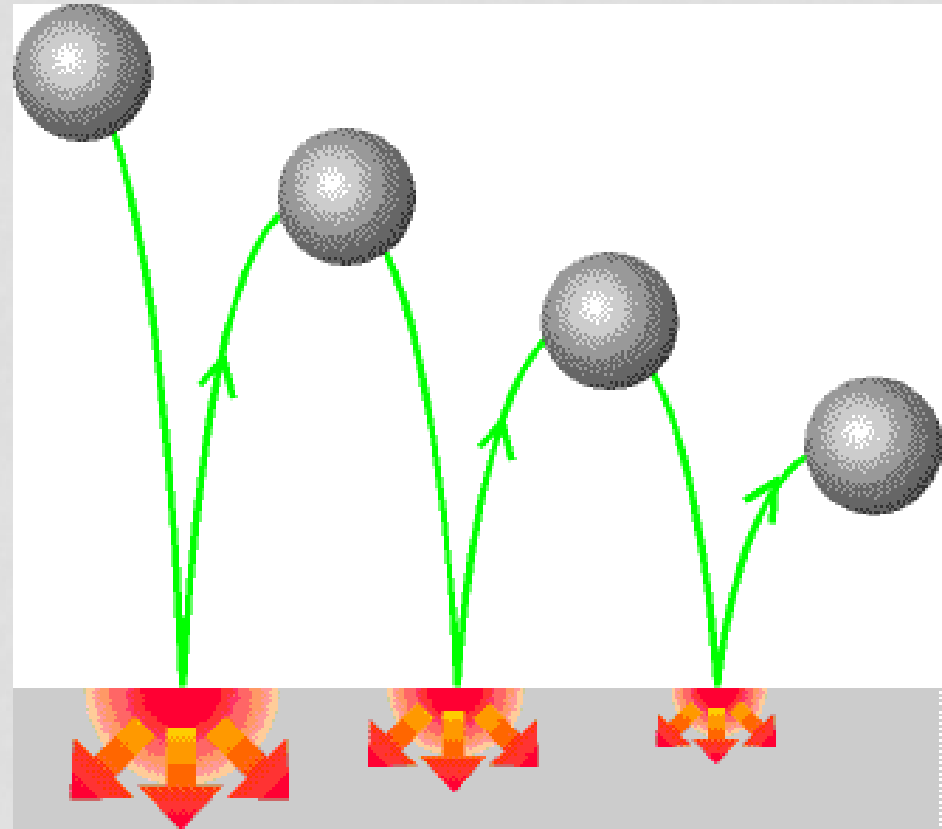
I. DIFFERENT WORDINGS OF THE SECOND LAW

- New concept: entrop

- „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: $\Delta S_{tot} > 0$.

- In the state of equilibrium, the entropy of a globally isolated system s 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,
  - $H_2 + Cl_2 \rightarrow 2\,HCl$ 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.

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: $\Delta S = \displaystyle\int_{i}^{f} \dfrac{dq_{rev}}{T}$

- 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.

II. THERMODYNAMIC AND STATISTICAL DEFINTION OF ENTROPY

$$S = k.\log W$$

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 DEFINTION OF ENTROPY

- **Entropy:**
  - <u>State function</u>: 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:

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

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

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:**

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

Hot source

T_h

$dS = -|dq|/T_h$

$|dq|$

$dS = +|dq|/T_c$

T_c

Cold sink
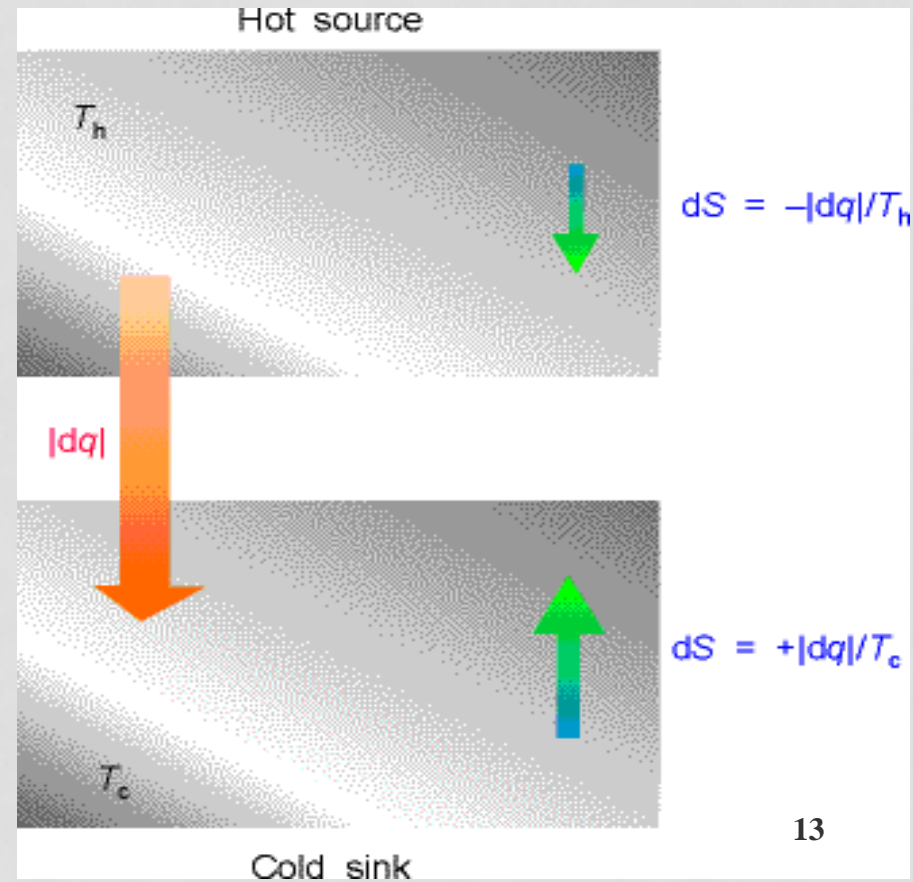
IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

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**.

- In adiabatic spontaneous processes, no heat is transferred into the surroundings, so the entropy of the surroundings does not change: $dS_{sur} = 0$.

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.

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

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:

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

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.

- <u>**Trouton's rule**</u> (observation): **most liquids have a standard molar entropy of evaporation at about +85 J K^{-1} 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

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

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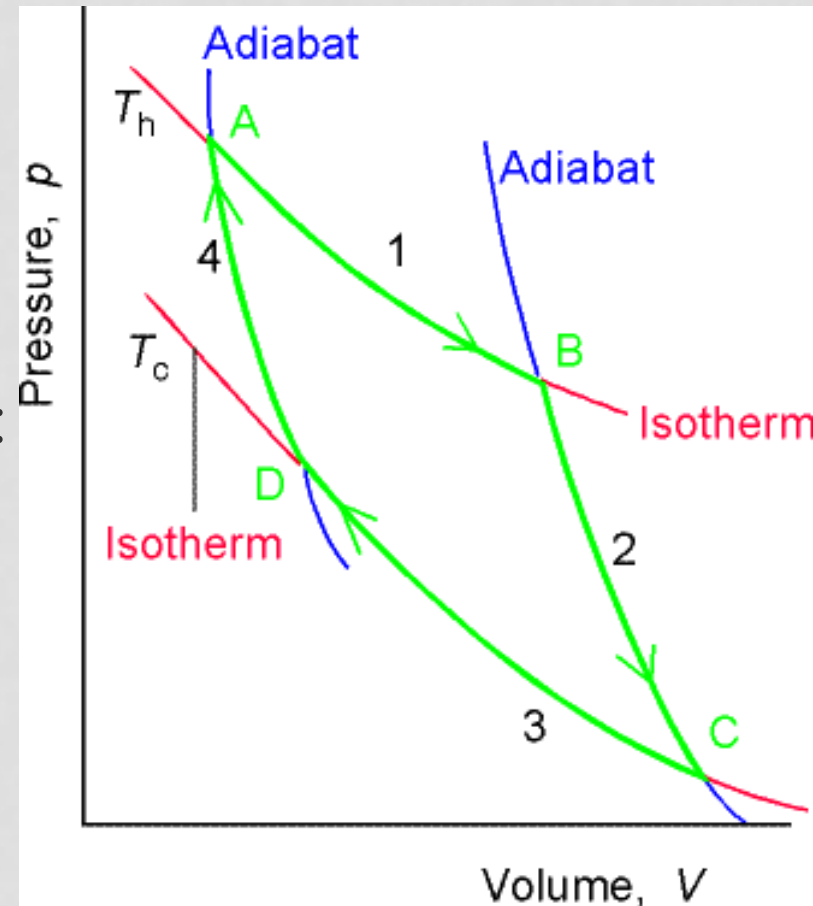
- **Trouton's rule** (observation): **most liquids have a standard molar entropy of evaporation at about +85 J K^{-1} mol^{-1}.** *Deviations can be interpreted microscopically.*

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IV. ENTROPY CHANGE IN A FEW IMPORTANT PROCESSES

e) Dependence of entropy on the <u>temperature</u>

- 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: $T_c \rightarrow T_h$.

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 THEMRODYNAMICS

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 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: $\Delta S \rightarrow 0$ 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 (meting, 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.

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}:

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

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

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

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:

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

III. ABSOLUTE AND STANDARD ENTROPIES

- Since $S(0) = 0$ J K^{-1} mol^{-1}, 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},

- physical or chemical <u>processes</u>: the change of entropy for the process is: *ΔS*.

III. 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
Liquids:	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

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:

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

- **$\Delta_r S^\theta$ 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 <u>Gibbs energy</u>

I. COMBINATION OF THE FIRST AND SECOND LAWS OF THERMODYNAMICS

- first law:

  $dU = dw + dq$

  $dw = -pdV$ (expansion work)

- second law:

  $dq = TdS$ (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 <u>system</u> 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

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

THERMODYNAMIC POTENTIAL FUNCTIONS

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

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

$$\left. \right\downarrow{}_{S = const.} \qquad \downarrow{}_{U = const.}$$

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

  - Heat transfer at <u>constant pressure</u>:

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

$$\downarrow{}_{S = const.} \qquad \downarrow{}_{H = const.}$$

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

- **IMPORTANT: Only the properties of the system** are given!

THERMODYNAMIC POTENTIAL FUNCTIONS

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

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

$$\boxed{\text{Rearr.}}$$

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

  - Heat transfer at <u>constant pressure</u>:

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

$$\boxed{\text{Rearr.}}$$

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

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

$H = U + pV$

pV

U

$A = U - TS$

TS

$G = H - TS$

TS
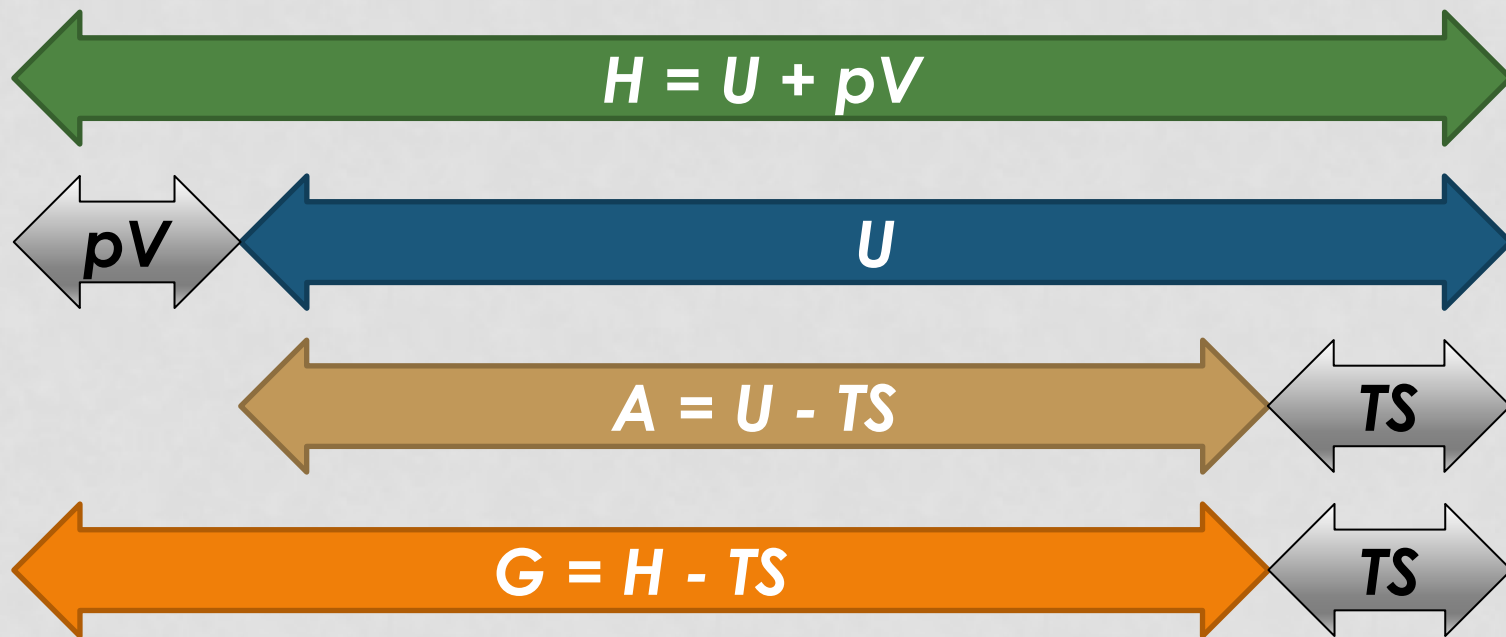
II. THE HELMHOLTZ AND GIBBS ENERGIES

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

III. PROPERTIES OF THE GIBBS ENERGY

- The Gibbs energy, G, is a very important thermo-dynamic 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, Δ_rG^{θ}

$$\Delta_rG^{\theta} = \Delta_rH^{\theta} - T\Delta_rS^{\theta} = \sum_{products} \nu\Delta_{form}G^{\theta} - \sum_{reactants} \nu\Delta_{form}G^{\theta}$$

III. PROPERTIES OF THE GIBBS ENERGY

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

$$dG = - SdT + Vdp$$

- 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.
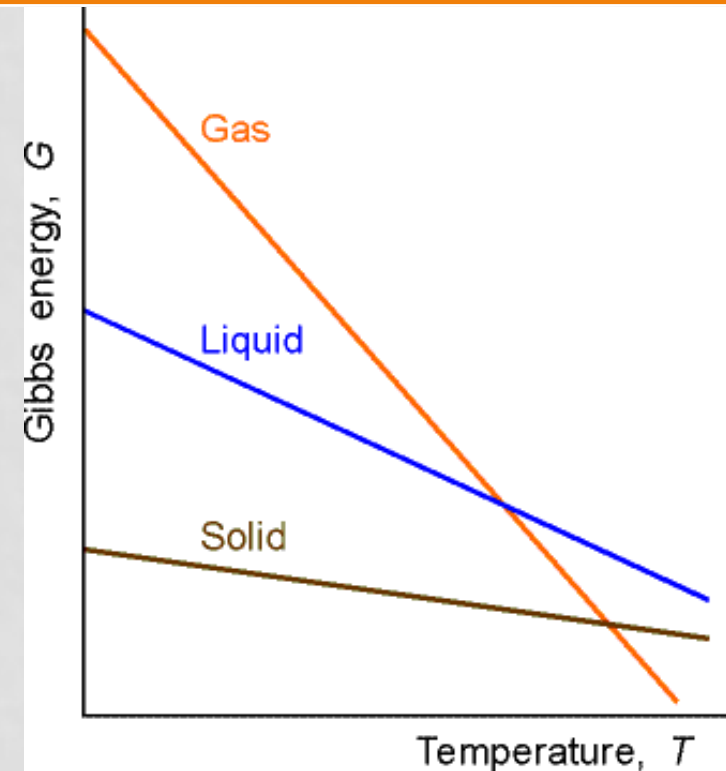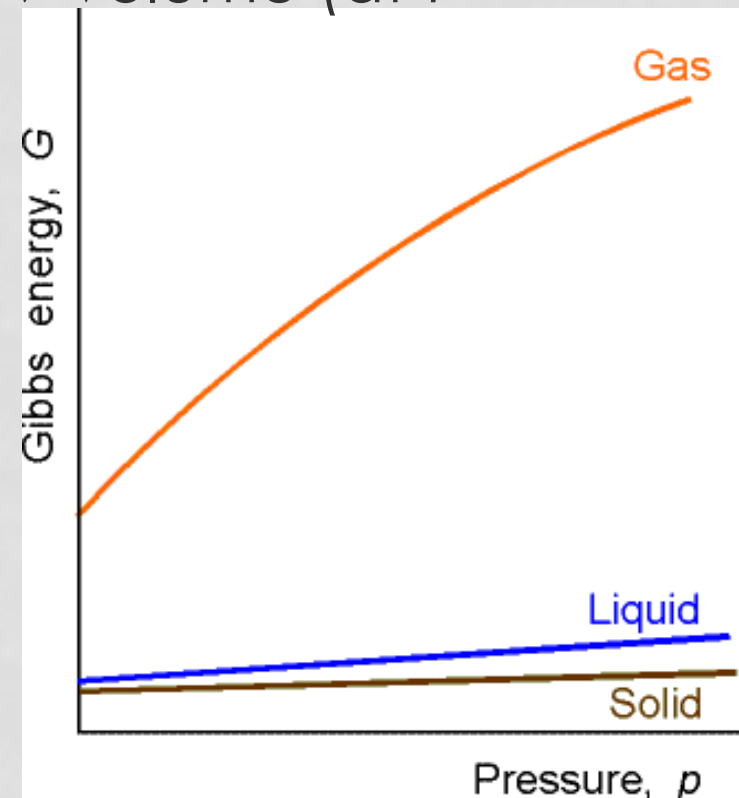
III. PROPERTIES OF THE GIBBS ENERGY

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*.

$$dG = - SdT + Vdp$$