

2nd and 3rd Laws of Thermodynamics

Lectures in Physical Chemistry 3



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2nd Law of Thermodynamics

Several things are considered obvious,
but we cannot explain them without learning thermodynamics.

Throwing a snowball to a wall, the wall stops the snowball,
the snow is deformed and the wall gets warmer.

IT HAS NEVER BEEN OBSERVED that snow attached to a wall
collects energy from the wall and starts flying in the air as a snowball.

Ball rolling on a floor eventually stops due to friction.

IT HAS NEVER BEEN OBSERVED that
a standing ball cools the floor and starts rolling.

The ignited matchstick burns, and produces light, heat and smoke.

IT HAS NEVER BEEN OBSERVED that a burnt matchstick
collects light, heat and smoke from the air
and an unburnt matchstick is formed.

2nd Law of Thermodynamics

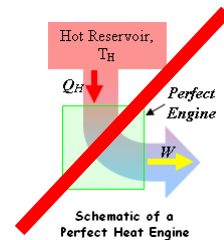
The processes listed on the previous slide obey the 1st Law, but do not occur.

All real processes are irreversible; they cannot be reversed in such a way that there is no change in either the system or in the surroundings.

2nd Law of Thermodynamics

Equivalent statements of the 2nd Law :

- Heat cannot be converted fully to work.
- Heat is transferred spontaneously only from a high temperature body to a low temperature body. (Spontaneously: without applying external work)
- Perpetuum mobile of the second kind does not exist: a machine does not exist that has only one heat reservoir and is able to convert heat to work in a cyclic process. (Cyclic process: the original state is restored after a full cycle.)
- Entropy of an isolated system does not decrease.



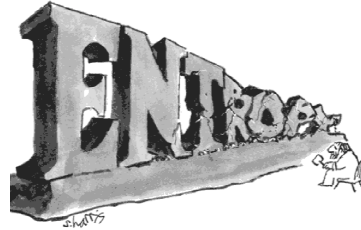
Entropy

DEF Definition of the change of entropy:

$$dS = \frac{\delta q_{\text{rev}}}{T}$$

δq_{rev} heat exchange of the system in a reversible process
 T temperature of the heat exchange

entropy is a **state function** and **extensive**
 Unit: J/K



Interpretation:

Well ordered system: small entropy (e.g. crystal)
 disordered system: large entropy (e.g. gases)

In spontaneous processes entropy increases or remains constant.

Entropy can be decreased using work cf. decreasing disorder in a room

Clausius suggested word „entropy” from Greek „en+tropein” : „transformation content”

Entropy theorem

2nd Law with entropy:

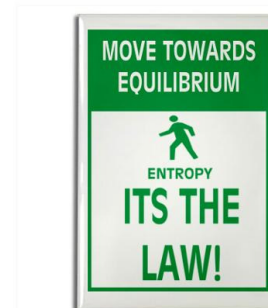
Entropy theorem: Entropy of an isolated system increases or remains constant in a spontaneous change.

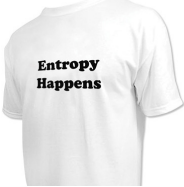
irreversible process: entropy increases
 reversible process: entropy remains constant

Consequence: perpetuum mobile of second kind does not exist

In an isolated system in an irreversible cyclic process entropy continuously increases
 \Rightarrow without applying work, the system cannot be transformed back to the state having the same entropy.

Entropy is different after each full cycle:
 \rightarrow the cycle cannot be repeated infinite times.





Entropy Happens

Clausius inequality

$$dS \geq \frac{\delta q}{T},$$


δq heat exchange
 T temperature of the heat exchange

δq in either reversible or irreversible process

δq in reversible process: $dS = \delta q / T$
 This is the definition of entropy!

δq in irreversible process: $dS > \delta q / T$

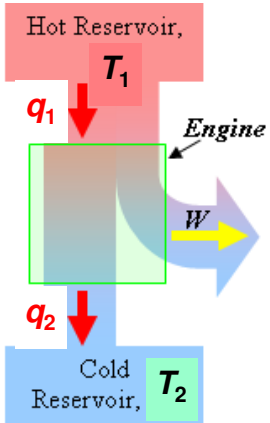
special case:
 irreversible process + adiabatic system
 $\Rightarrow \delta q = 0 \Rightarrow dS > 0$



Rudolf Julius Emmanuel Clausius
 (1822 –1888)
 German physicist ⁷

Heat engines

DEF Heat engine: a machine with two heat reservoirs.
 Heat is taken from the higher temperature reservoir and less heat is emitted to the lower temperature reservoir. The heat difference is converted to work.



We expect two things from a heat engine:

- 1) Follows the First Law:
 $|q_1| = |q_2| + |W|$
- 2) Follows the Second Law:
 entropy production during the operation
 $(|q_2|/T_2 - |q_1|/T_1) > 0$

Schematic of a Heat Engine

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Maximal efficiency of heat engines

There is entropy production if the machine is operating

$$(|q_2|/T_2 - |q_1|/T_1) > 0$$

T_1 temperature of the warm reservoir

T_2 temperature of the cold reservoir

q_1 heat taken from the warm reservoir

q_2 heat emitted to the cold reservoir

Less entropy production = better efficiency

In the extreme case (when the machine is just not working) $\Delta S=0$

Then:

$$|q_2|/T_2 - |q_1|/T_1 = 0 \Rightarrow |q_2| = |q_1|T_2/T_1$$

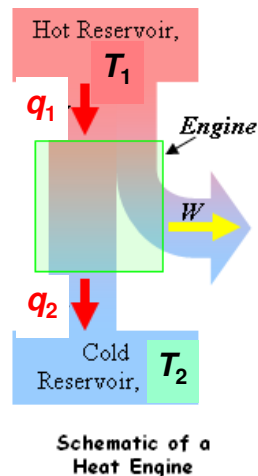
Using the principle of energy conservation:

$$|w| = |q_1| - |q_2| = |q_1| - |q_1|T_2/T_1 = |q_1|(1 - T_2/T_1)$$

$$\eta_C = |w| / |q_1| = (1 - T_2/T_1)$$

This is the maximum efficiency of a heat engine (η_C , „Carnot efficiency“)

This can be calculated knowing only temperatures T_1 and T_2 !



Carnot cycle with ideal gas

Carnot efficiency is independent of the

- the technical details of the heat engine
- material used

Carnot cycle using ideal gas:

1 → 2 isotherm expansion (heat uptake)

2 → 3 adiabatic expansion

3 → 4 isotherm compression (heat loss)

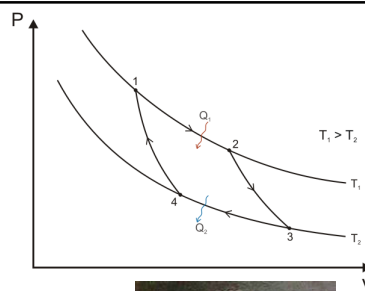
4 → 1 adiabatic compression

1 → 3 work is done by the machine

3 → 1 we do work to restore the initial state

Can be proved that in this special case also

$$\eta_C = |w| / |q_1| = (1 - T_2/T_1)$$



Nicolas Léonard Sadi Carnot
(1796 – 1832)
French physicist



Thermodynamic temperature scale

for a reversible Carnot cycle $(|q_2|/T_2 - |q_1|/T_1) = 0$

Rearranging:

$$\frac{|q_1|}{|q_2|} = \frac{T_1}{T_2}$$

The ratio of heats is equal to the ratio of temperatures!

Temperature can be measured by measuring amounts of heat, and the temperature obtained is identical to the Kelvin scale.

(Kelvin defined his temperature scale on the basis of the volume change of ideal gases).

⇒ the „thermodynamic“ temperature scale is identical to the Kelvin scale!

Note:

this is a theoretical possibility; nobody ever measured temperature this way¹¹

Refrigerator, air conditioner, heat pump

Refrigerators, air conditioners, and heat pumps are based on the same thermodynamic principles (and the actual machinery is also almost identical).

By applying work, heat is transferred from a cold reservoir to a warm reservoir. This is a spontaneous process and associated with entropy production.

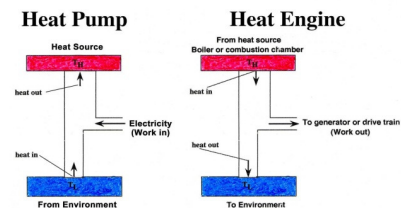
COP: coefficient of performance of a heat pump

$$\text{COP} = |q_1|/|w|$$

domestic heat pump: COP≈3.5
public building heat pump: COP≈6

fridge
air conditioner
heat pump

heat engine
power station



Consider that electricity is about 3.5 times more expensive than gas (for the same energy content).

Statistical interpretation of entropy

Let N , E , V be constant (isolated system with rigid walls)

N particles in the system

E total energy of the system

V volume of the system

- particles are not distinguishable
- energy levels exist in the system (according to the quantum theory)



Ludwig Eduard Boltzmann
(1844-1906)

Austrian physicist

Boltzmann equation: $S = k \ln \Omega$

Ω is the number of different ways in which the energy of the system can be achieved by rearranging the atoms or molecules among their available states.

$k = R/N_A$ Boltzmann constant

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



Third Law of thermodynamics

Third Law of thermodynamics:

entropy of chemically pure perfect crystals is zero at temperature $T = 0$ K.

(1) chemically pure (2) perfect crystal (3) $T = 0$ K $\Rightarrow S = 0$ J/K.

Consequence:

The absolute value of entropy is known at $T = 0$ K (S is zero)

+ equation for entropy change is known ($dS = \delta q_{rev} / T$)

\Rightarrow the absolute value of entropy can be determined at any temperature

Statistical explanation to the 3rd Law:

At temperature $T = 0$ K

all particles of a perfect crystal are at the lowest energy level:

this is possible in a single way: $\Omega = 1 \Rightarrow \ln 1 = 0$

$S = k \ln \Omega \Rightarrow S = 0$ J/K.

0 K is the lowest temperature

According to the experiments, the heat capacity of solids approaches zero as $T \rightarrow 0$ K

⇒ large amount of extracted heat causes small decrease of the temperature

⇒ it is impossible to cool a body to reach $T = 0$ K

The world record is 4.5×10^{-10} K (MIT, 2003)



Cosmic background temperature: 2.725 K

The lowest temperature found in the space is 1.00 K

(5000 light years from here, Boomerang Nebula, in constellation Centaurus)

I found it in an astronomical blog:

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.

One of the comments:

COO



Boomerang nebula⁵

Combining the First and Second Laws

This is the traditional, but a misleading title.

The point is the derivation of a new exact differential of U and H .

The First Law:

$$dU = -p_{ex}dV + \delta w_{other} + \delta q$$

$$dH = \delta w_{other} + \delta q + Vdp$$

In a reversible process $\delta q = TdS$

$$dU = -pdV + \delta w_{other} + TdS$$

$$dH = Vdp + \delta w_{other} + TdS$$

If there is no other work, $\delta w_{other} = 0$

$$dU = -pdV + TdS$$

$$dH = Vdp + TdS$$

These equations will be frequently used.

These are the exact differentials of U and H with variables V, p, S

(Previously: exact differentials of U and H with variables V, p, T)

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Thermodynamic potential functions

- 1) The system can decrease the energy and there is no change in the structure
 ⇒ the final state is determined by the minimum of energy U min
Example: marble in a concave plate

- 2) The total energy of the system is constant and the structure of the system may change
 ⇒ the final state is determined by the maximum of entropy S max
Examples: coloured marbles in a box; all isolated systems

- 3) Closed system with constant volume and temperature (V, T, n constant)
 ⇒ the final state is determined by the minimum of $F=U-TS$ F min
Example: all „ V, T, n constant” thermodynamic systems

- 4) Closed system with constant pressure and temperature (p, T, n constant)
 ⇒ the final state is determined by the minimum of $G=H-TS$ G min
Example: all „ p, T, n constant” thermodynamic systems

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Free energy or Helmholtz free energy

DEF Definition: $F = U - TS$
 features: state function and extensive
 unit: J

Change of F in a reversible process, in the absence of other work:

$$dF = dU - TdS - SdT = -pdV - SdT$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -p; \quad \left(\frac{\partial F}{\partial T}\right)_V = -S.$$

- using equation $dU = TdS - pdV$ (cf. slide combining the 1st and 2nd Laws)
- this is the exact differential of F with variables V and T
- provides the dependence of F on the change of V and T

The change of free energy from the actual state till reaching the equilibrium at constant volume and temperature

provides the maximal work that the system can do

origin of the name: „free energy” that can be extracted from the system

Free energy 2

In reversible processes,
the change of free energy is equal to the useful work.

In irreversible processes,
the obtainable useful work is less than the change of the free energy.

In an isochoric, isothermal, closed system without other work
(i.e. V , T , n are constant)

F is a monotonically decreasing potential function.

At these conditions,
all processes decrease the free energy!



Hermann Ludwig Ferdinand von Helmholtz
(1821–1894)
German physician and physicist

Gibbs free energy or free enthalpy

DEF Definition: $G = H - T S$
features: state function and extensive
unit: J

Change of G in a reversible process, in the absence of other work:

$$dG = dH - TdS - SdT = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V; \quad \left(\frac{\partial G}{\partial T}\right)_p = -S.$$

- using equation $dH = TdS + Vdp$ (cf. slide combining the 1st and 2nd Laws)
- this is the exact differential of G with variables p and T
- provides the dependence of G on the change of p and T
- the corresponding equation for molar quantities: $dG_m = V_m dp - S_m dT$

The change of Gibbs free energy from the actual state till reaching the equilibrium at constant pressure and temperature provides the maximal work that the system can do

origin of the name: „free enthalpy” that can be extracted from the system

Gibbs free energy 2

In reversible processes,
the change of Gibbs free energy is equal to the useful work.

In irreversible processes,
the obtainable useful work is less than the change of the Gibbs free energy.

In an isobaric, isothermal, closed system without other work
(i.e. p , T , n are constant)

G is a monotonically decreasing potential function.

At these conditions,
all processes decrease the Gibbs free energy!



Josiah Willard Gibbs
(1839–1903)
USA physicist

Pressure dependence of the Gibbs free energy

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

V is always positive, therefore if the pressure increases
→ Gibbs free energy always increases at constant temperature T

Integration of volume V with respect p gives the change of G
for the change of pressure Δp .

Example for an ideal gas:

The Gibbs free energy at temperature T and standard pressure p^\ominus : $G(p^\ominus, T)$

Calculation of the change of Gibbs free energy, if the new pressure is p :

$$G(p, T) - G(p^\ominus, T) = \int_{p^\ominus}^p V dp = \int_{p^\ominus}^p \frac{nRT}{p} dp = nRT \ln \frac{p}{p^\ominus}$$

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Temperature dependence of the Gibbs free energy

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

S is always positive \rightarrow increasing $T \rightarrow G$ surely decreases at constant p

Integrating the expression above:

$$G(T_2, p) - G(T_1, p) = -\int_{T_1}^{T_2} S dT$$

Another temperature dependence: relation among G , H , and T :

Gibbs–Helmholtz equation:

$$\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = -\frac{H}{T^2}$$

Derivation (based on $(u/v)' = (v u' - v' u)/v^2$; $u = G$, $v = T$;
derivation not needed on the test/exam):

$$\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = \frac{T(\partial G/\partial T)_p - G}{T^2} = \frac{-TS - G}{T^2} = -\frac{G + TS}{T^2} = -\frac{H}{T^2}$$

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Thermochemistry with Gibbs free energy

DEF standard reaction Gibbs free energy: Gibbs free energy change due to a reaction that transforms standard state reactants to standard state products
denoted by $\Delta_r G^\ominus$ unit: J mol^{-1}

DEF standard molar Gibbs free energy of formation: Gibbs free energy of a reaction in which one mole compound is formed from its reference state elements
denoted by $\Delta_f G^\ominus$ unit: J mol^{-1}

standard molar Gibbs free energy of formation of reference state elements
is always zero (a consequence of the definition)

**Calculating standard reaction Gibbs free energy
from the standard molar Gibbs free energy of formation of the species:**

$$\Delta_r G^\ominus = \sum_j \nu_j \Delta_f G_{rj}^\ominus$$

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Direction of chemical reactions

Several reagents are mixed and chemical reactions occur.

What will be the final composition?

Answer:

A chemically reacting system behaves like any other thermodynamic system:

1) **isolated system**: in the final state entropy S has a maximum

2) **isothermal, isochoric (T, V constant) closed system**:
in the final state free energy F has a minimum

3) **isothermal, isobaric (T, p constant) closed system**
in the final state Gibbs free energy G has a minimum
 $\Rightarrow \Delta_r G^\ominus$ is always negative

← most systems
we interest in
are of this kind
(lab experiments,
animal bodies)

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

for an endothermic reaction:

$\Delta_r G^\ominus$ negative, $\Delta_r S^\ominus$ positive and $\Delta_r H^\ominus$ positive

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THE END

of topic

2nd and 3rd Laws of Thermodynamics



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