SEMMELWEIS UNIVERSITY

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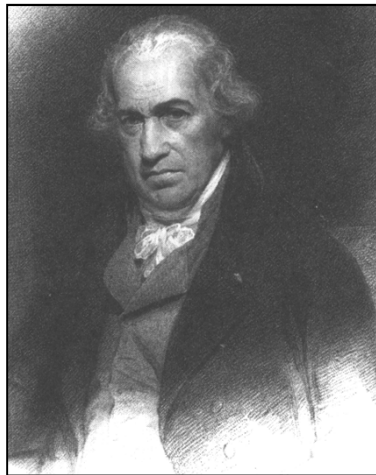
THERMODYNAMICS

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What is thermodynamics?

- *Classical definition:* branch of physics studying the effects of changes in temperature, pressure and volume (energy changes).

- *Therme* (Gr) heat, *dynamis* (Gr) power.

James Watt (1736-1819)

$$\Delta U = \Delta Q + \Delta W$$

Thermodynamics

- It reveals the driving forces behind natural phenomena.

- Due to its generalizations, it has abstract, complex and difficult-to-understand concepts.

- Classical thermodynamics, which was developed in the first half of the nineteenth century by Carnot, Clausius, Joule, Kelvin, and Mayer (and others), is a *phenomenological* theory, dealing with macroscopic phenomena, and avoiding atomic concepts.

- <u>Its strength</u> lies in the generality of its predictions, which are based on the small number postulates set out in the laws of thermodynamics, and apply to all macroscopic systems; e.g. solids, fluids and electromagnetic radiation.

Its weakness also lies in great generality, since it cannot be applied to real systems without auxiliary input, either experimental or theoretical.

For example: the equation of state of a fluid, linking pressure, volume and temperature, must be derived from experiment.

École Polytechnique	Glasgow school	Berlin school	Edinburgh school
Sadi Carnot (1796-1832)	William Thomson (1824-1907)	Rudolf Clausius (1822-1888)	James Maxwell (1831-1879)
Vienna school	Gibbsian school	Dresden school	Dutch school
Ludwig Boltzmann (1844-1906)	Willard Gibbs (1839-1903)	Gustav Zeuner (1828-1907)	Johannes der Waals (1837-1923)

- Temperature and heat are different.
  (**Joseph Black**)

- First thermometer
  (**Galileo Galilei**)

- First clinical thermometer
  (**Jean Rey** 1631)

- Early temperature scale
  (**Anders Celsius** 1742).

- Temperature scale
  (**Carl von Linne**)

$F = 1.8C + 32$

$K = C + 273.15$

Fahrenheit: water freezes at 32 °F; boils at 212 °F

Celsius: water freezes at 0 °C; boils at 100 °C
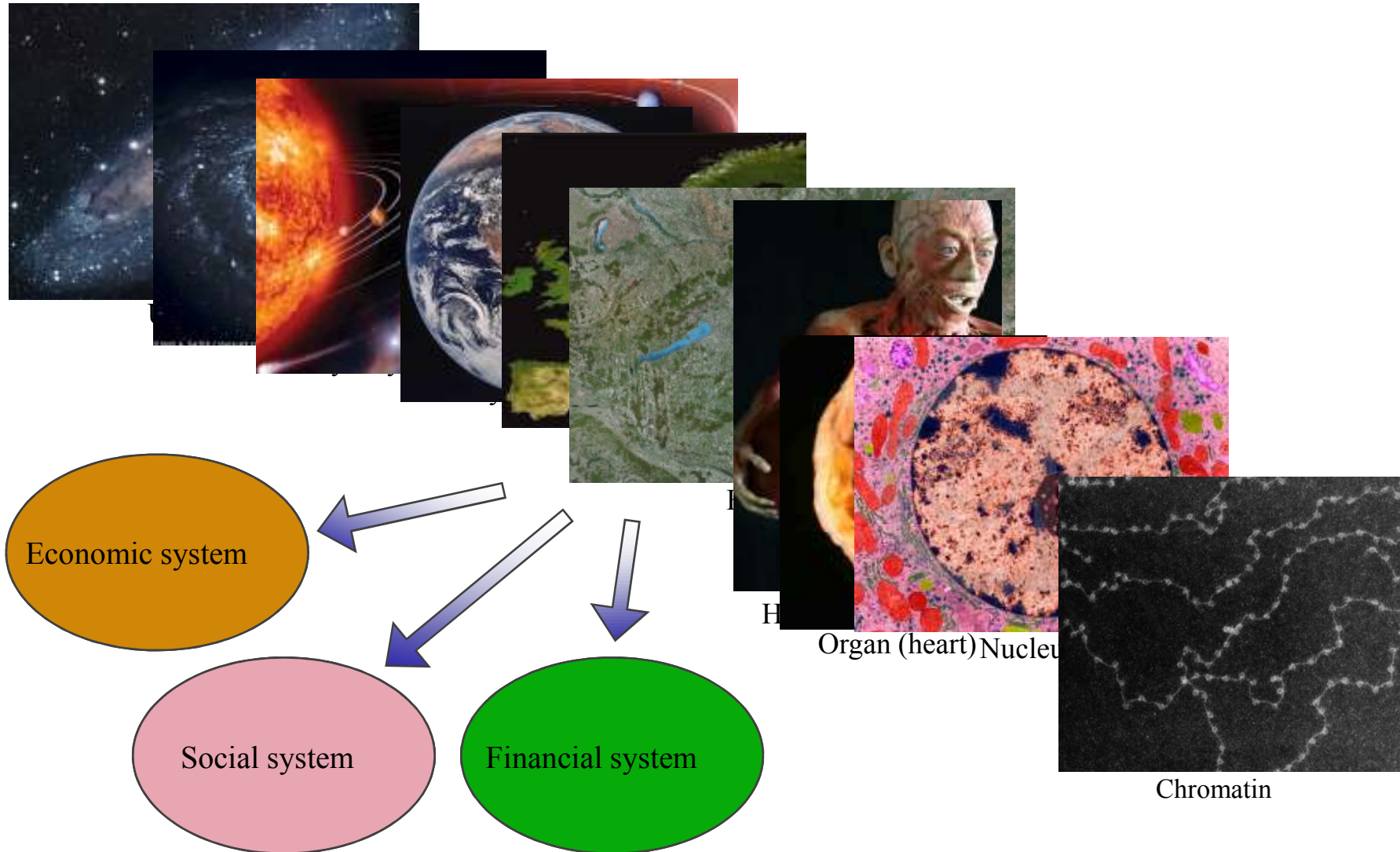
Kelvin: water freezes at 273.15 K; boils at 373.15 K

$$F = 1.8C + 32$$

$$K = C + 273.15$$

The Kelvin scale is setup so that its zero point is the coldest possible temperature--absolute zero, at which point a substance would have zero internal energy. This is -273.15 °C. Absolute zero can never be reached, but there is no limit to how close we can get to it. Scientists have cooled substances to within 10^{-5} kelvins of absolute zero. How do we know how cold absolute zero is, if nothing has ever been at that temperature?
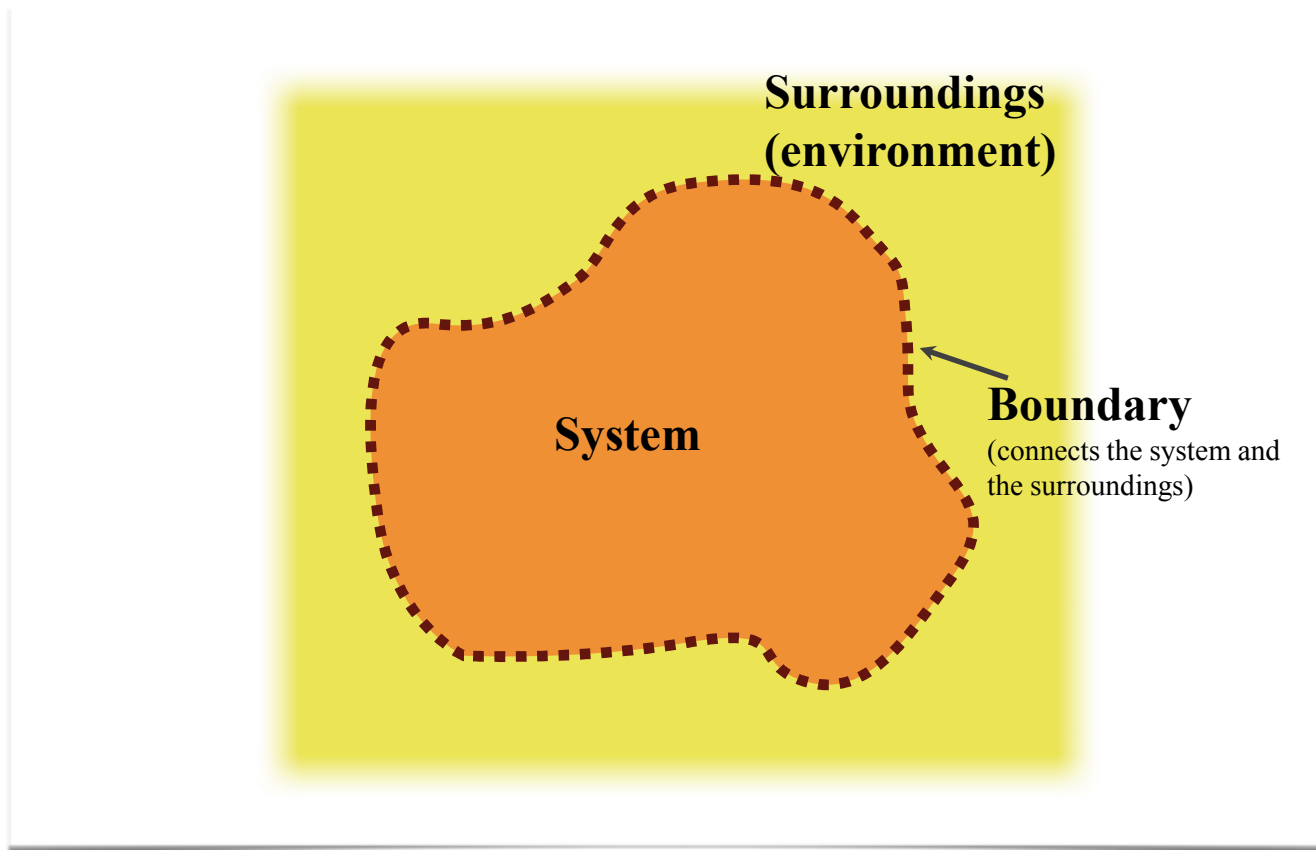

A gas exerts no pressure when at absolute zero.

P

gas A

gas B

gas C

T (°C)

-273.15 °C

0 °C
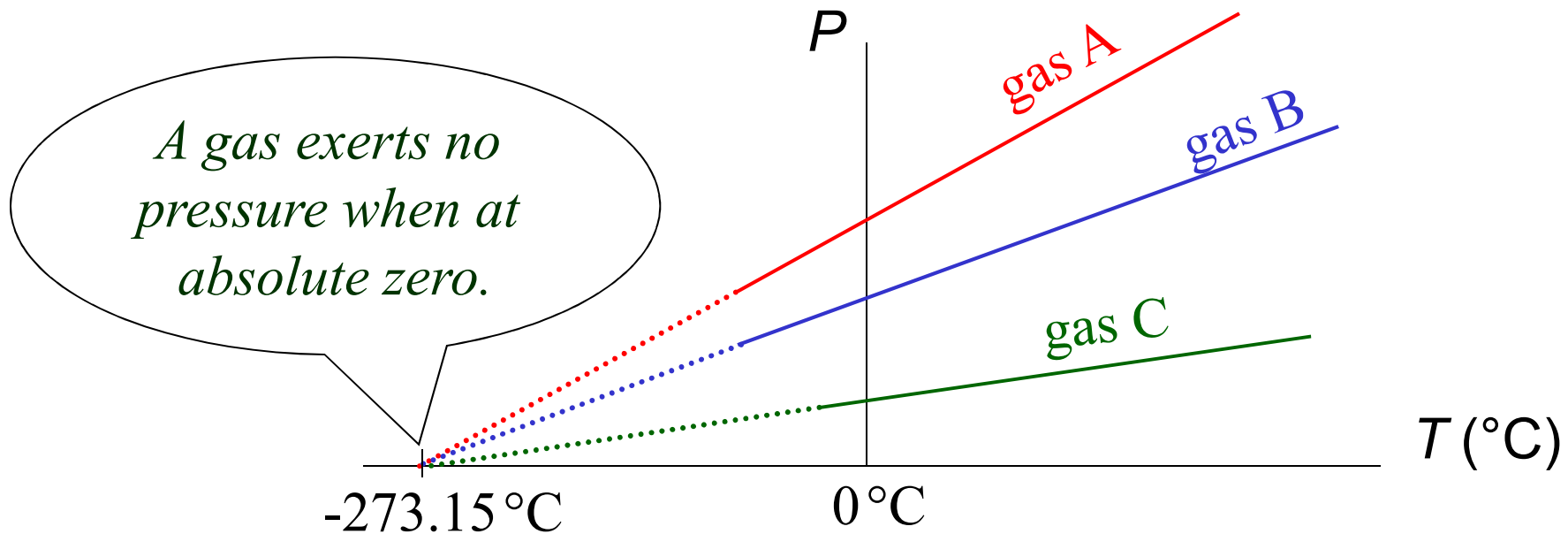
Thermodynamic system today

Economic system

Social system

Financial system
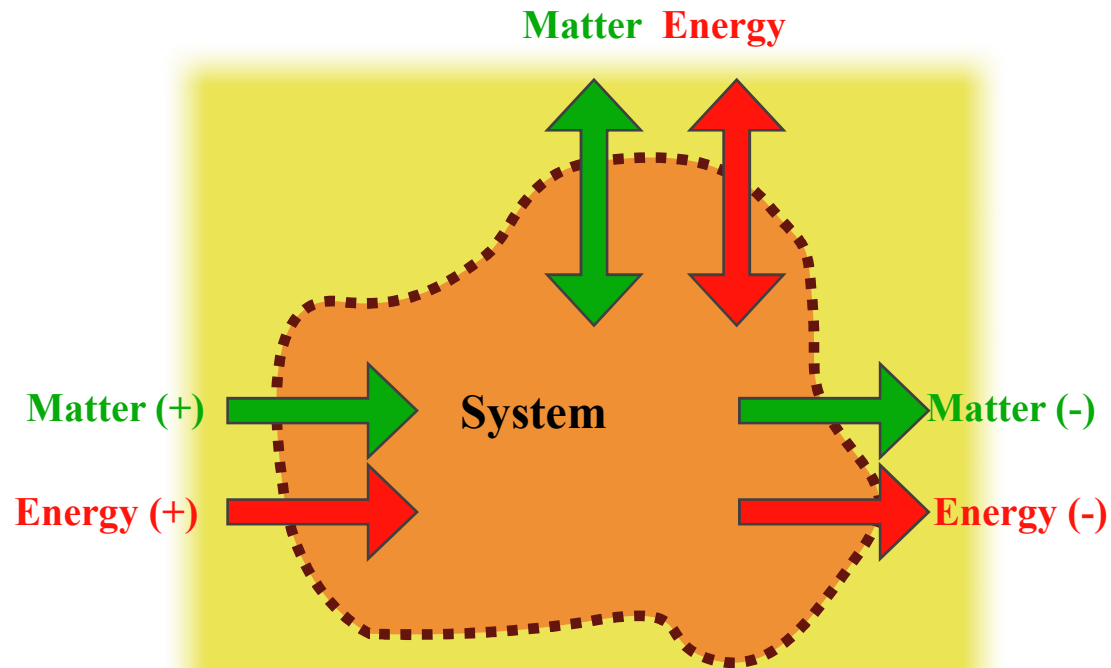
Organ (heart) Nucleus

Chromatin

Abstraction of the thermodynamic system

Definition: the thermodynamic system is the part of nature under investigation.

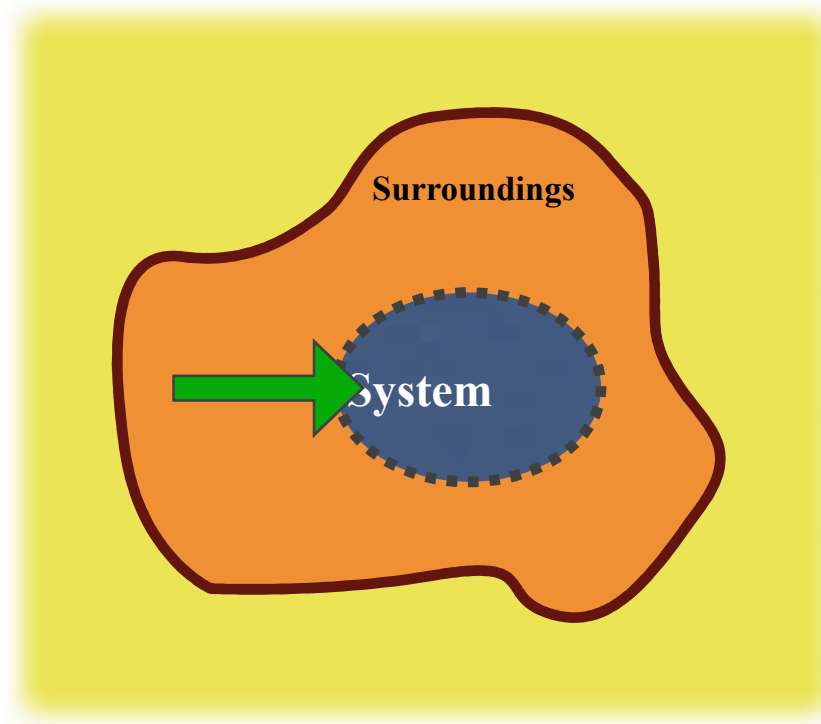# The thermodynamic system interacts with the surroundings

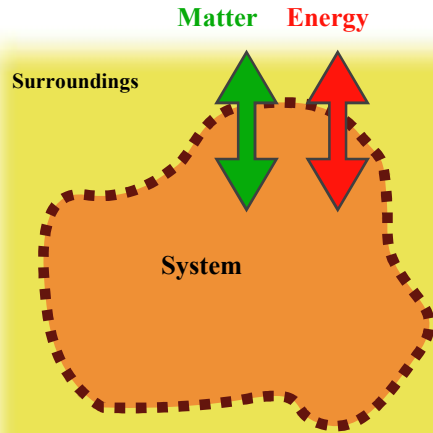Exchange of matter and energy may occur across the boundary.

The thermodynamic system interacts with the surroundings

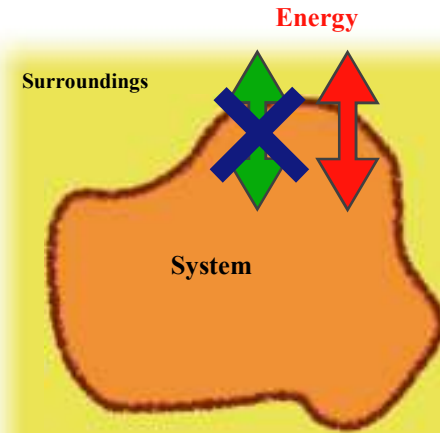Defining the thermodynamic system has consequences for processes.
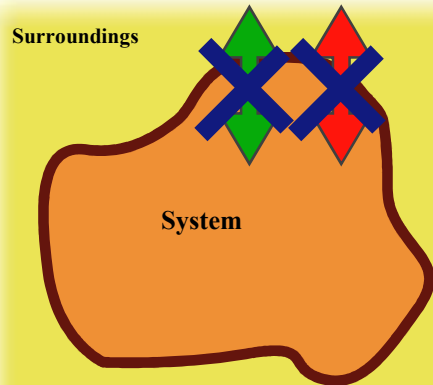
Types of thermodynamic systems
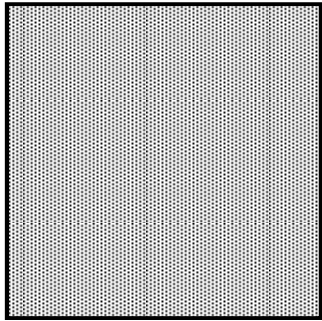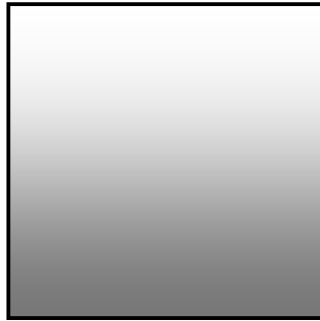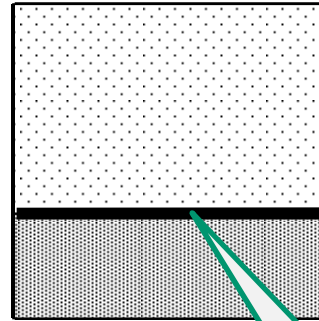
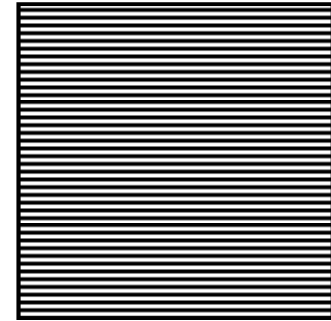# Types of thermodynamic systems

Homogeneous uniform   **inhomogeneous**   **heterogen**   **anisotropic**

interface

Characterization of the thermodynamic system

Macroscopic characterization: **state variables**
- explicitly determine the *state* of the system.

Pressure: p
Volume: V
Temperature: T
Concentration: c
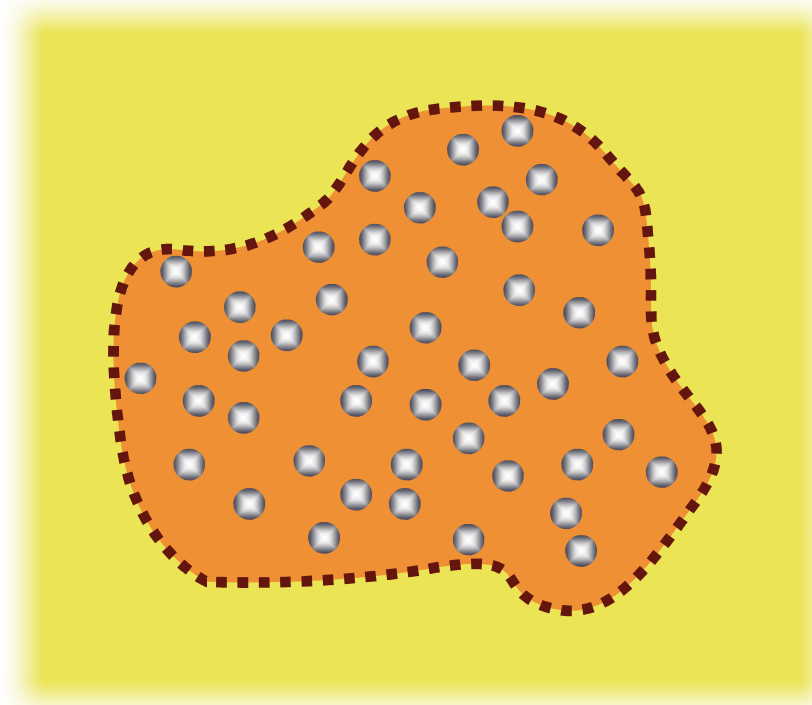
Universal gas law

$$pV=nRT$$

Isolated, Closed and Open Systems

- A *system* is the portion of the physical world being studied.
- The system plus surroundings comprise a *universe*.

- The boundary between a system and its surroundings is the *system wall*.

- If heat cannot pass through the system wall, it is termed an *adiabatic wall*, and the system is said to be *thermally isolated* or *thermally insulated*.

- If heat can pass through the wall, it is termed a *diathermal wall*.

- Two systems connected by a diathermal wall are said to be in *thermal contact*.

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Isolated, Closed and Open Systems

- An *isolated system* cannot exchange mass or energy with its surroundings.

- The wall of an isolated system <u>must</u> be adiabatic.

- A *closed system* can exchange energy, but not mass, with its surroundings.

- The energy exchange may be mechanical (associated with a volume change) or thermal (associated with heat transfer through a diathermal wall).

- An *open system* can exchange both mass and energy with its surroundings.

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Thermodynamic Variables

- ***Thermodynamic variables*** are the observable macroscopic variables of a system, such as P, V and T.

- If the are used to describe an equilibrium state of the system, they are known as **state variables**.

- ***Extensive variables*** depend on the size of the system; e.g. mass, volume, entropy, magnetic moment.

- ***Intensive variables*** do <u>not</u> depend on size; e.g. pressure, temperature, magnetic field.

- An extensive variable may be changed to an intensive variable, known as a ***specific value***, by dividing it by a suitable extensive variable, such as mass, no.of kmoles, or no. of molecules.

- Example: the specific heat is normally (heat capacity)/(mass).

Equilibrium

Macroscopic description: intensive variables are identical (between the system and surroundings, or between different parts of the system)

$p_k, \mu_k, \varphi_k, T_k$

$p_r, \mu_r, \varphi_r, T_r$

$p_k, \mu_k, \varphi_k, T_k = p_r, \mu_r, \varphi_r, T_r$
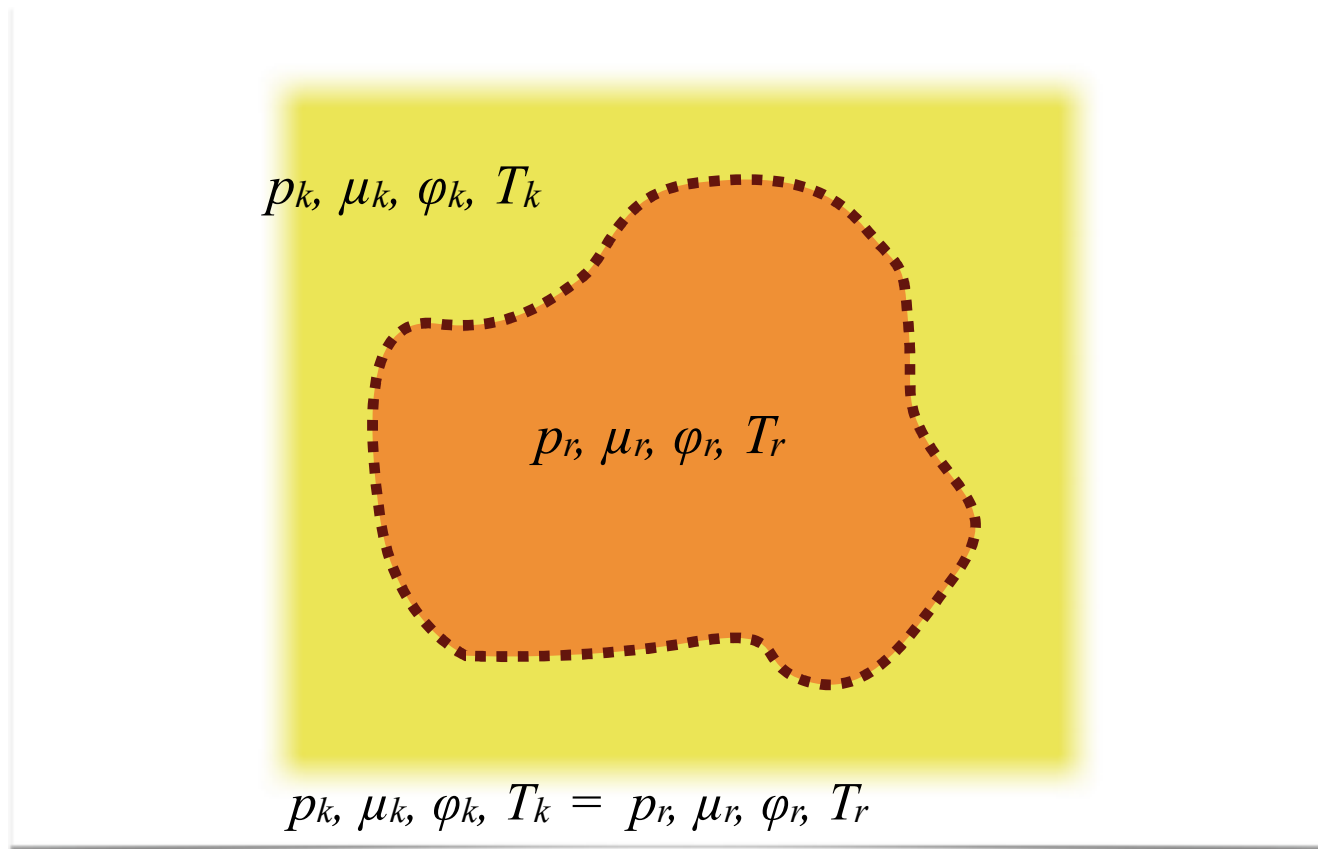
Equilibrium

Microscopic description: average rates of forward and reverse reactions are equal.

Boundary

Surroundings

System

$k_{forward}$

$k_{backward}$

$$\overline{k}_{forward} = \overline{k}_{backward}$$
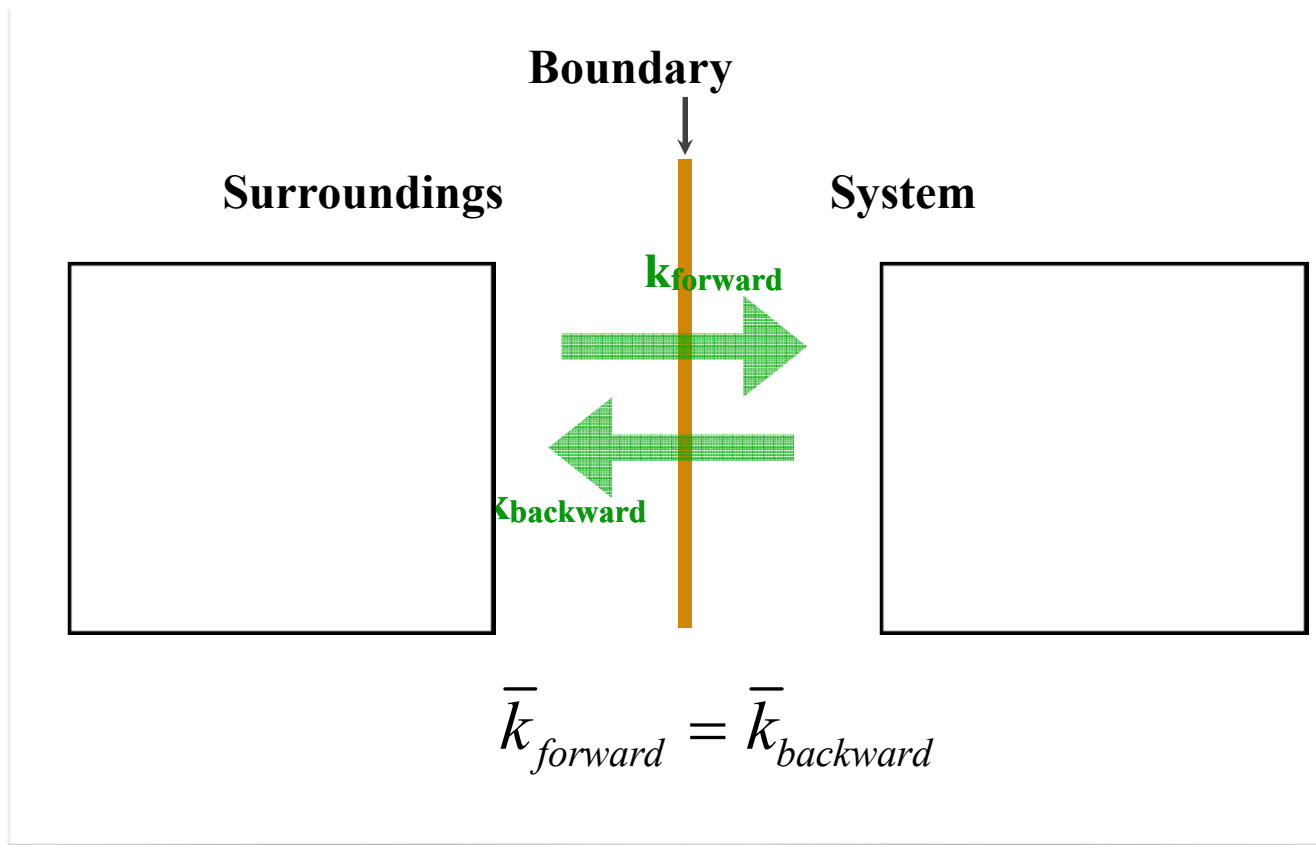
Equilibrium States

- An ***equilibrium state*** is one in which the properties of the system do not change with time.
- In many cases, an equilibrium state has intensive variables which are uniform throughout the system.

- A ***non-equilibrium state*** may contain intensive variables which vary in space and/or time.

- An ***equation of state*** is a functional relationship between the state variables; e.g. if P,V and T are the state variables, then the equation of state has the form f(P, V, T) =0.

- In 3-dimensional P-V-T space,

    an equilibrium state is represented by a point,

    and the equation of state is represented by a surface.

Zeroth law of thermodynamics

- If two systems (A and B) are independently in equilibrium with a third one (C), then they are in equilibrium with each other as well.
- Between different points of a system in equilibrium, the intensive variables are equal (there are no thermodynamic currents).
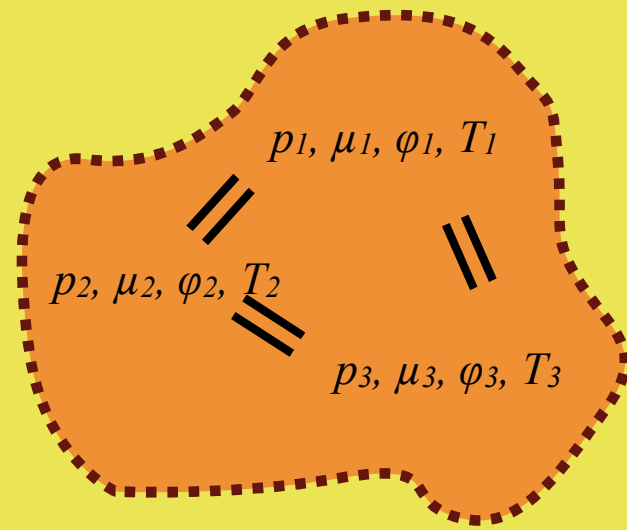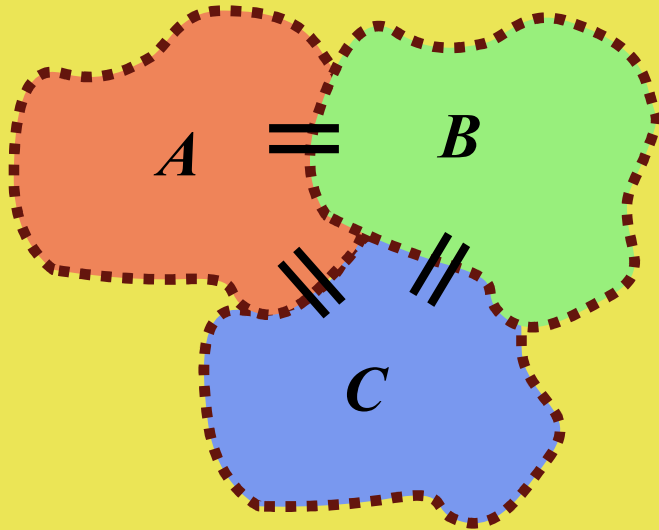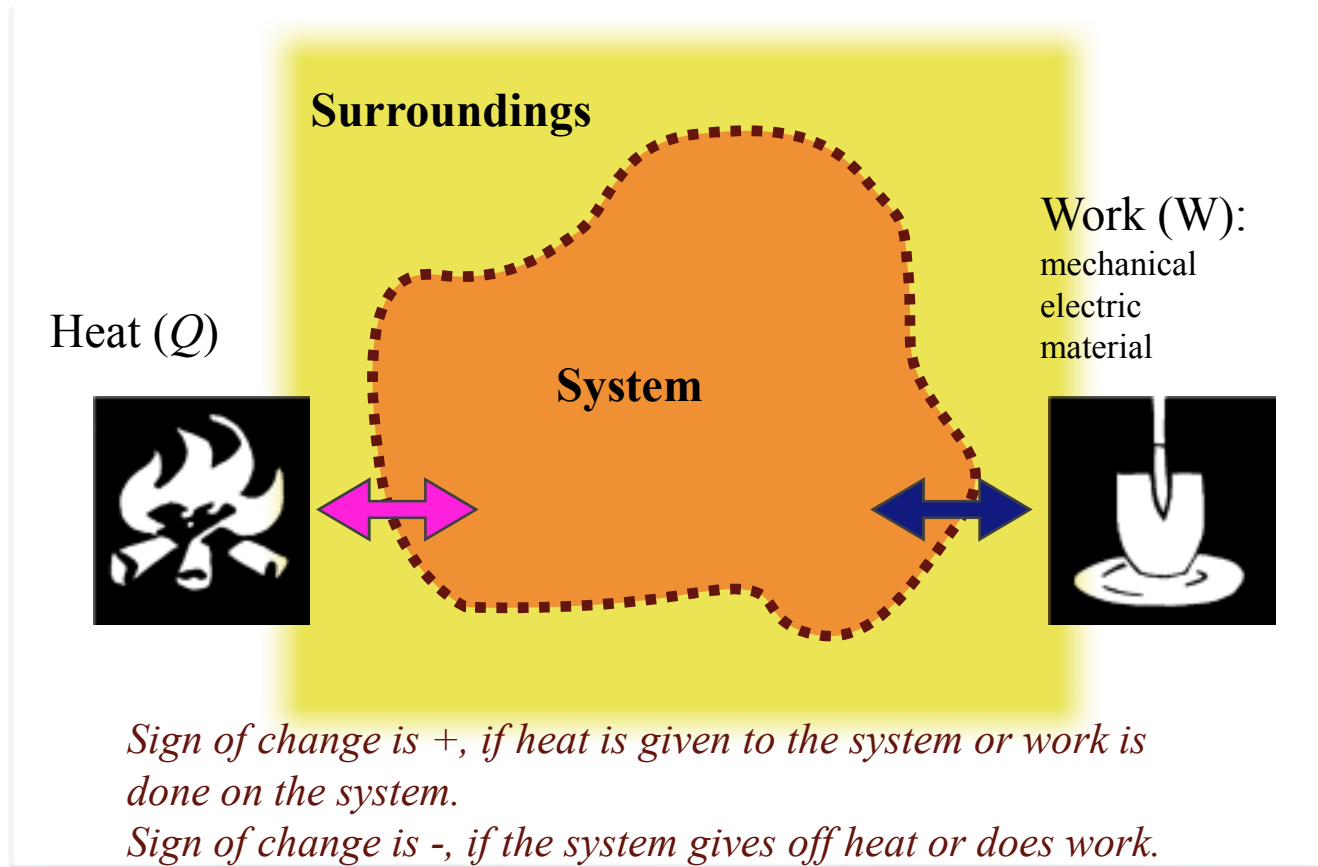
Change

Thermodynamics is interested in the changes within the system.
Changes may be evoked by: heating, work.
Result: **internal energy of the system changes**.

Surroundings

Heat (Q)

Work (W):
mechanical
electric
material

System

Sign of change is +, if heat is given to the system or work is done on the system.
Sign of change is -, if the system gives off heat or does work.

Thermodynamic processes

- *Isobaric:* at constant pressure.
- *Isochoric (isometric, isovolumetric):* at constant volume.
- *Isothermic:* at constant temperature.
- *Adiabatic:* no heat exchange.
- *Isentropic:* at constant entropy.
- *Isenthalpic:* at constant enthalpy.
- *"Steady state":* at constant internal energy.

Processes 1

- A *process* refers to the change of a system from one equilibrium state to another.
- The initial and final states of a process are its *end-points*.

- A *quasistatic process* is one that takes place so slowly that the system may be considered as passing through a succession of equilibrium states.
- A quasistatic process may be represented by a *path* (or line) on the equation-of-state surface.
- If it is *non-quasistatic*, only the end-points can be shown.

- A *reversible process* is one the direction can be reversed by an infinitessimal change of variable.
- A reversible process is a quasistatic process in which no dissipative forces, such as friction, are present.

- A reversible change must be quasistatic, but a quasistatic process need not be reversible; e.g. if there is hysteresis.

Processes 2

- An *isobaric* process is one in which the <u>pressure</u> is constant.
- An *isochoric* process is one in which the <u>volume</u> is constant.
- An *isothermal* process is one in which the <u>temperature</u> is constant.

- An *adiabatic* process is one in which no heat enters or leaves the system; i.e. $Q = 0$.
- If a system is left to itself after undergoing a non-quasistatic process, it will reach equilibrium after a time t much longer than the <u>longest</u> *relaxation time* τ involved; i.e. $t \gg \tau$.
- *Metastable equilibrium* occurs when one particular relaxation time τ_0 is much longer than the time Δt for which the system is observed; i.e. $\tau_0 \gg \Delta t$.
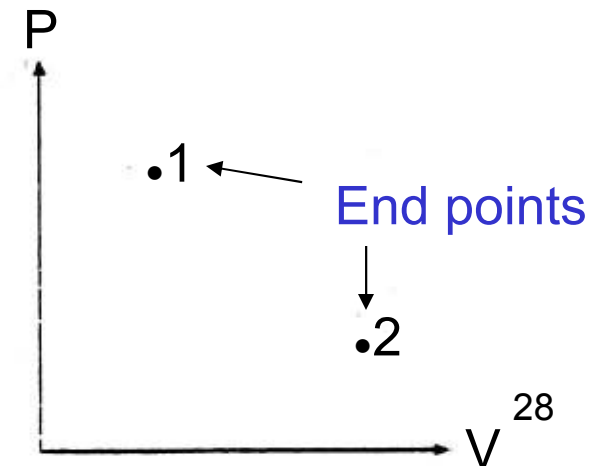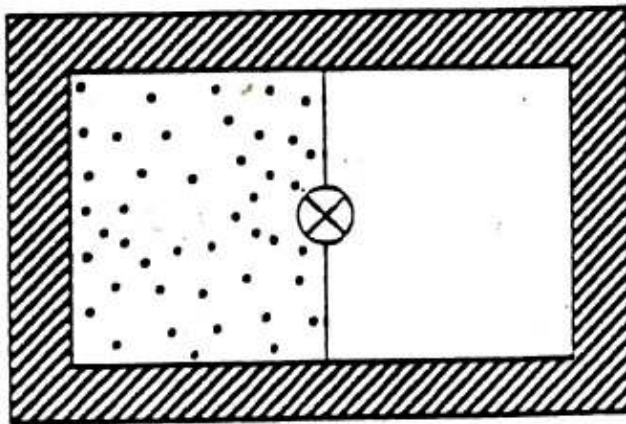
Three Types of Process

Isothermal process

System

Heat bath or reservoir

P

Adiabat

Isotherm

V
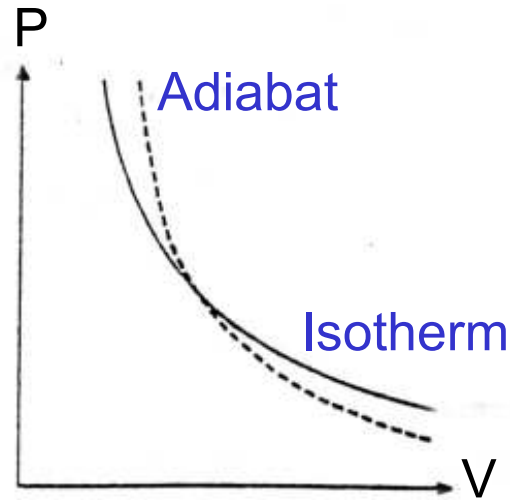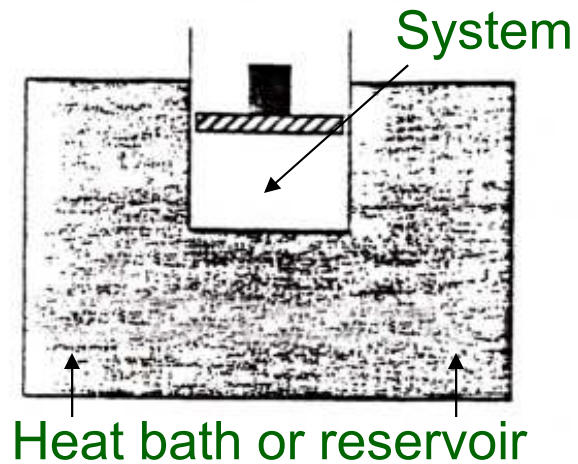
Adiabatic process
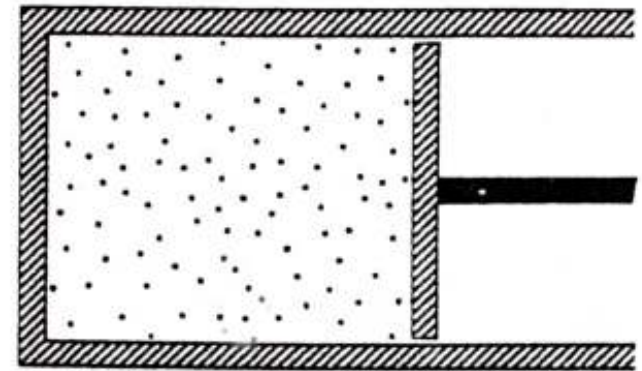
Adiabatic free expansion
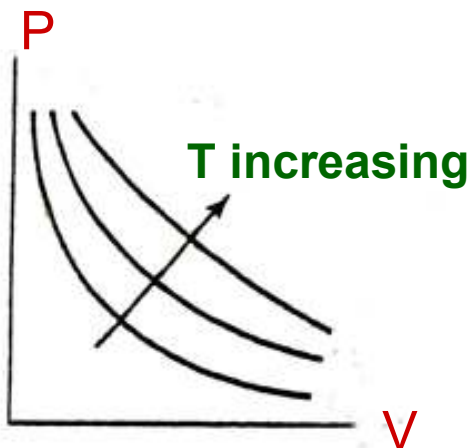

P

•1

End points

•2

V

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The Ideal Gas Law

- <u>Ideal gas law</u> $PV = nRT$ or $PV_m = RT$,

- where n is the no. of kmoles, v is the volume per kmole, T is the absolute temperature in K, and the gas constant $R = 8.314 \times 10^3$ J/(K.kmol).

- For a constant quantity of gas, $P_1 V_1/T_1 = P_2 V_2/T_2$.
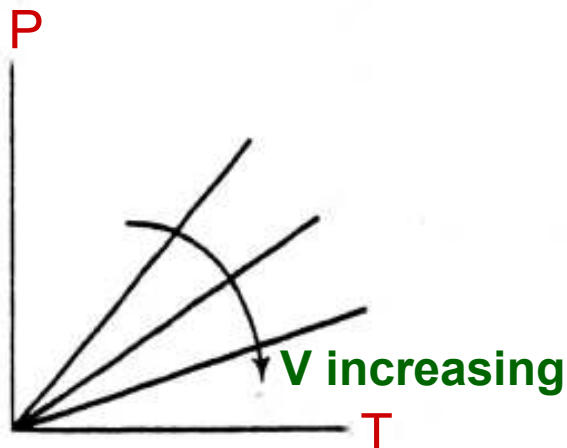
<u>Boyle's Law</u>
$P_1 V_1 = P_2 V_2$
(T constant)

<u>Gay-Lussac Law</u>
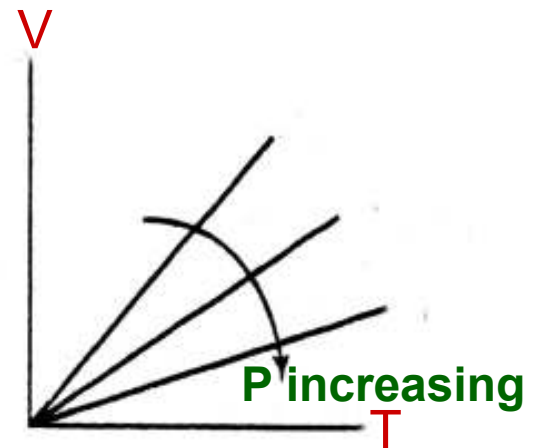$P_1/T_1 = P_2/T_2$
(V constant)

<u>Charles' Law</u>
$V_1/T_1 = V_2/T_2$
(P constant)

Internal energy

Internal energy is the energy an object or substance is due to the molecular **kinetic** and **potential** energies associated with the random motions of all the particles that make it up.
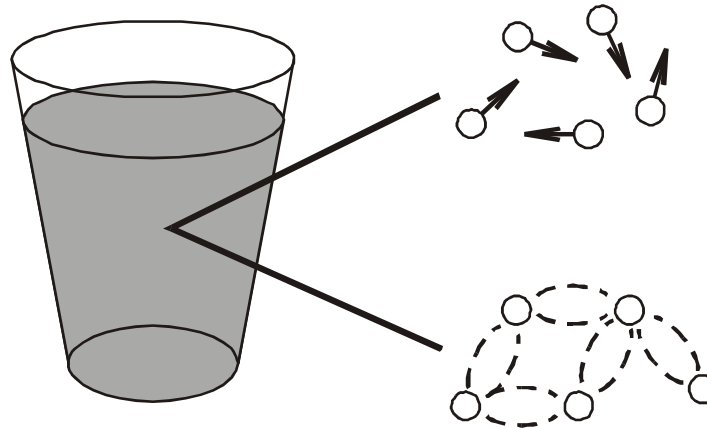
The kinetic energy is due to the motion of the particles. The potential energy is due to interactions between atoms, ions and molecules.
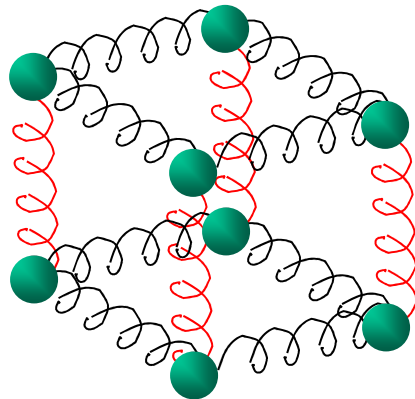
$$E = E_{pot} + E_{kin} + U$$

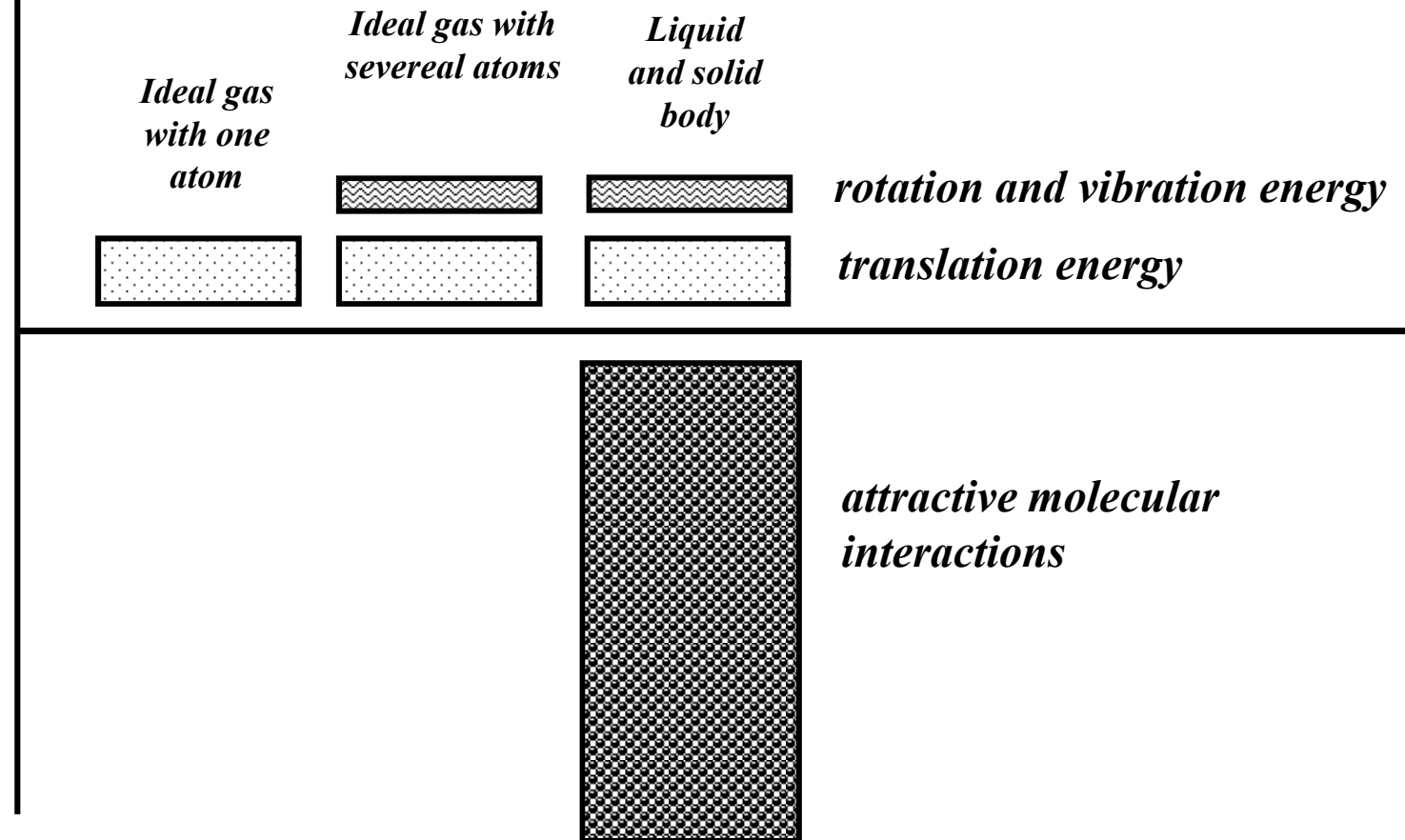Microscopic characterization: **internal energy (U)**

Macroscopic potential- and kinetic energies are not included in the internal energy.

Molecular potential- and kinetic energies are in the internal energy.

Internal energy does not contain the potential and kinetic energy of the macroscopic body.

Standard internal energy (298 K)

Ideal gas with
severeal atoms

Liquid
and solid
body

Ideal gas
with one
atom

rotation and vibration energy

translation energy
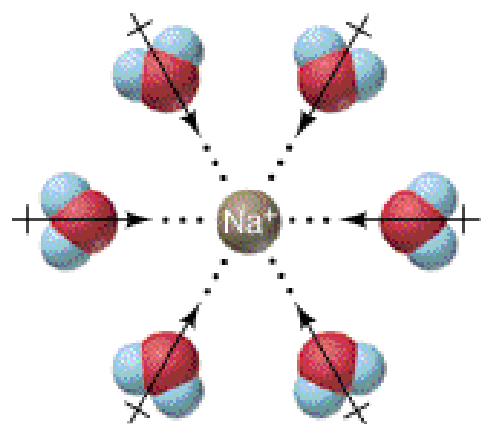
attractive molecular
interactions

The **van der Waals force** is the attractive force between molecules (or between parts of the same molecule) other than those due to covalent bonds or to the electrostatic interaction of ions with one another or with neutral molecules. The term includes interactions of:
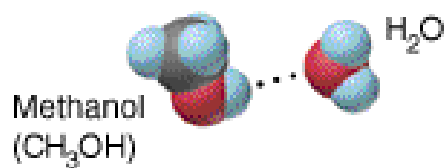
- ion – permanent dipole
- ion – induced dipole
- permanent dipole – permanent dipole
- permanent dipole – induced dipole
- instantaneous induced dipole-induced dipole
- H bond
- *hydrofobic*

Van der Waals forces are relatively weak compared to normal chemical bonds, but play a fundamental role

Ion-dipole

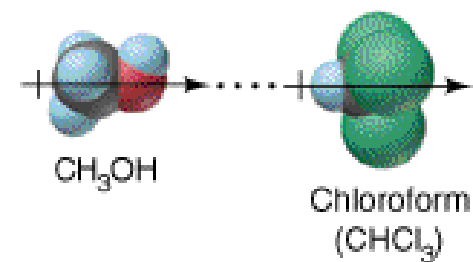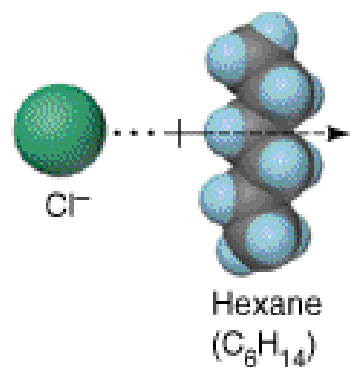Methanol
(CH$_3$OH)

H$_2$O

H bond

CH$_3$OH

Chloroform
(CHCl$_3$)

Dipole-dipole

Cl$^-$

Hexane
(C$_6$H$_{14}$)

Ion-induced dipole

Acetone
(C$_3$H$_6$O)

C$_6$H$_{14}$

Dipole-induced dipole

Octane
(C$_8$H$_{18}$)

C$_6$H$_{14}$

Dispersion

Interaction	Energy in RT units
chemical reaction	40 - 200
ion-ion	80 - 100
ion – dipole	10 - 20
H-bond	10 - 15
dipole –dipole	0,5 - 2
induced dipole –dipole	0,3 - 2
induced dipole – induced dipole	0,2 - 2

Dipole – charge interaction

ε_o

Permittivity of vaccuo: ε_o

Relative permittivity: ε_r

Energy of ionization: I

Distance between molecules: r

ion-ion

$$\left(\frac{1}{4\pi\varepsilon_0\varepsilon_{rel}}\right)\cdot\frac{q_1 q_2}{r}$$

ion-dipole

$$-\left(\frac{1}{4\pi\varepsilon_0}\right)^2\frac{\mu_1 q_2}{r^2}$$

dipole-dipole

$$-\left(\frac{1}{4\pi\varepsilon_0}\right)^2\cdot\frac{2}{3k_B T}\cdot\frac{\mu_1^2 \mu_2^2}{r^6}$$
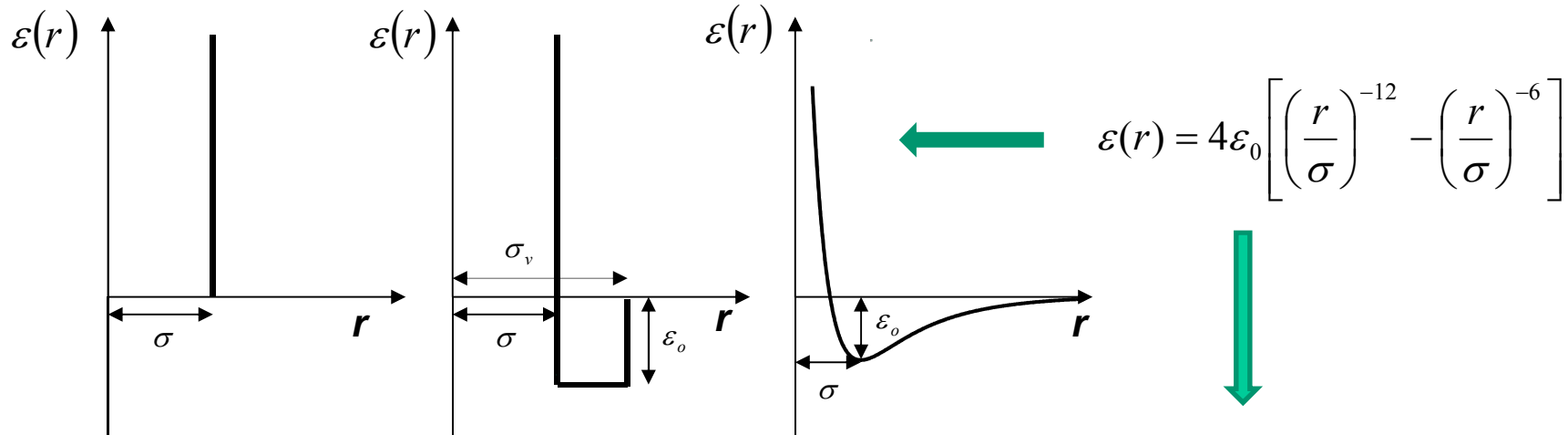
induced dipole-dipole

$$-\left(\frac{1}{4\pi\varepsilon_0}\right)^2\cdot\frac{\mu_1^2 \alpha_2}{r^6}$$

induced dipole-induced dipole

$$-\left(\frac{1}{4\pi\varepsilon_0}\right)^2\cdot\frac{3}{2}\cdot\frac{I_1 I_2}{I_1+I_2}\frac{\alpha_1 \alpha_2}{r^6}$$
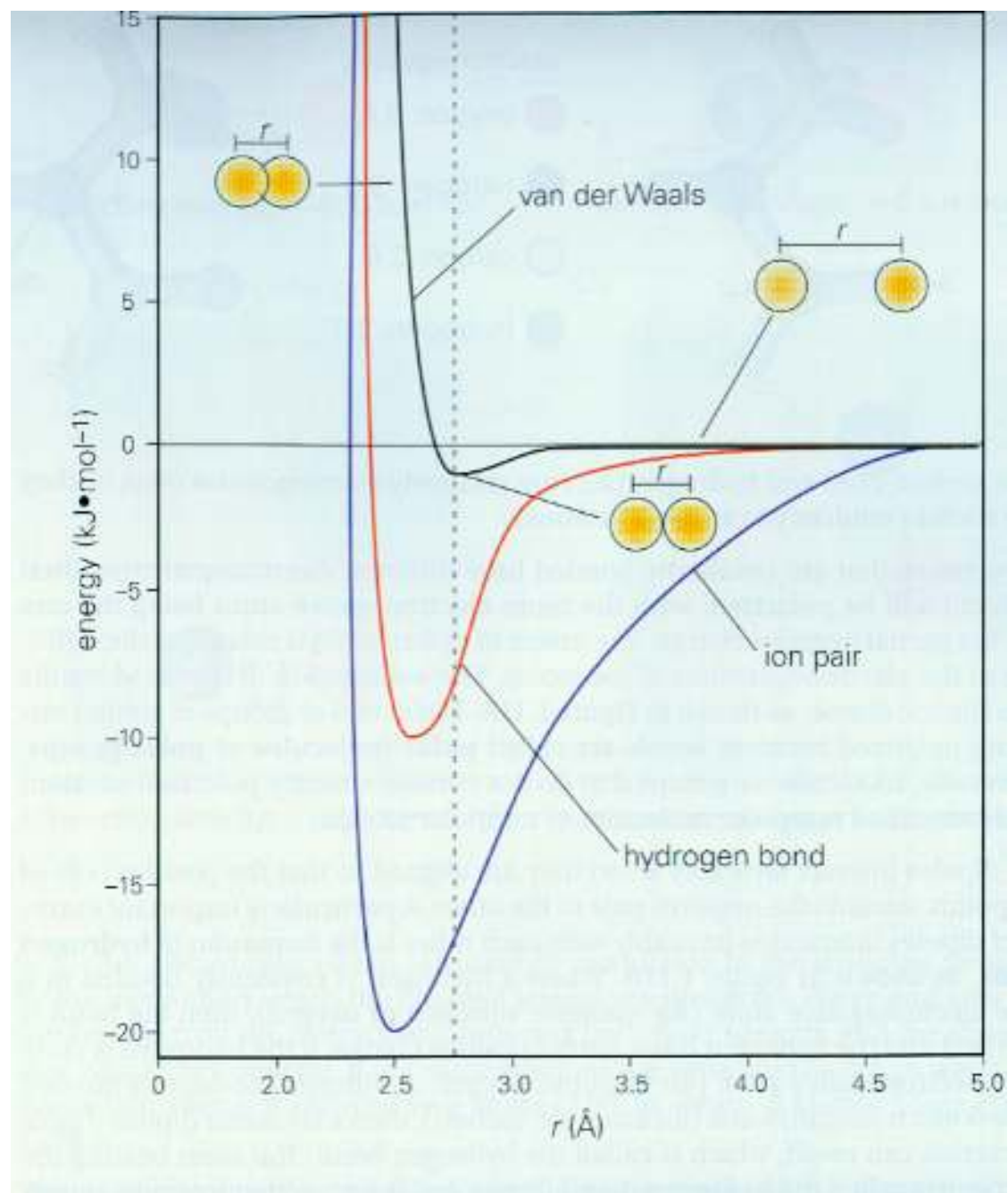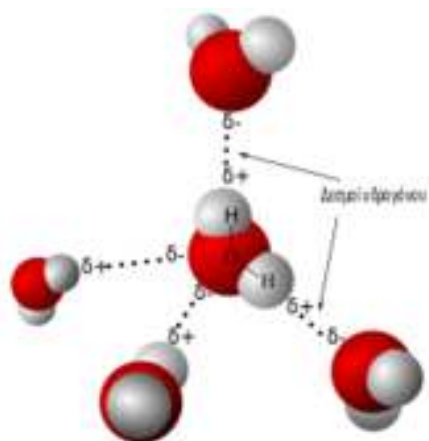
Modelling molecular interactions

$$\varepsilon(r)$$

$$\varepsilon(r)$$

$$\varepsilon(r)$$

$$\sigma$$

$$\sigma_v$$

$$\sigma$$

$$\varepsilon_o$$

$$\sigma$$

$$\varepsilon_o$$

$$r$$

$$r$$

$$r$$

$$\varepsilon(r) = 4\varepsilon_0 \left[\left(\frac{r}{\sigma} \right)^{-12} - \left(\frac{r}{\sigma} \right)^{-6} \right]$$

$$
U = \sum_{i<j} \sum 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]
$$

$$
+ \sum_{i<j} \sum \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}}
$$

$$
+ \sum_{bonds} \frac{1}{2} k_b (r - r_0)^2
$$

$$
+ \sum_{angles} \frac{1}{2} k_\theta (\theta - \theta_0)^2
$$

$$
+ \sum_{torsions} k_\phi \left[1 + \cos(n\phi - \delta) \right]
$$

Internal energy (U) is "state function"

State functions: single-value functions of the state variables
(independent variables) of the system.
Change in the state functions depend only on the initial and final
states of the system; it is independent of the path.

"A" state

$$\Delta U = U_B - U_A$$

ΔU
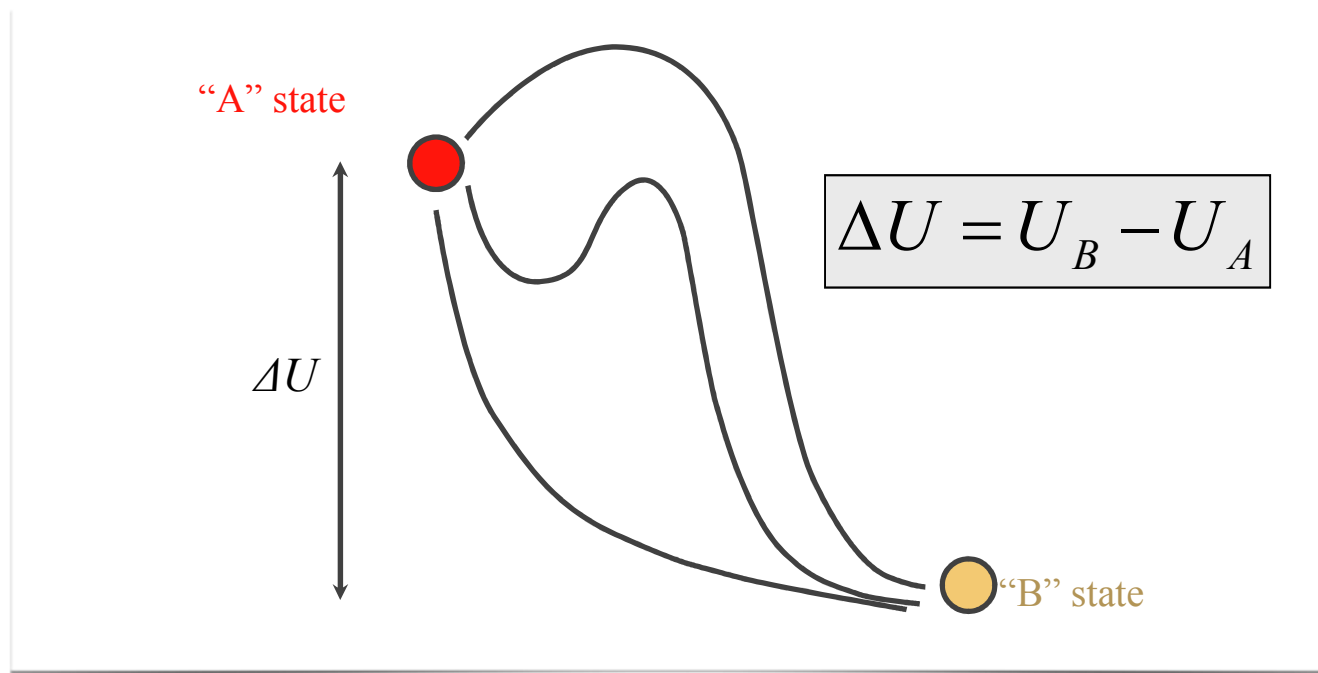
"B" state

Other state functions: enthalpy (H), Helmholtz free energy (F), Gibbs free energy (G), entropy (S)

Change of internal energy

BIO-THERMODYNAMIC SYSTEM

O_2

heat

food

BODY

metabolism

work *(movement)*

heat

end product
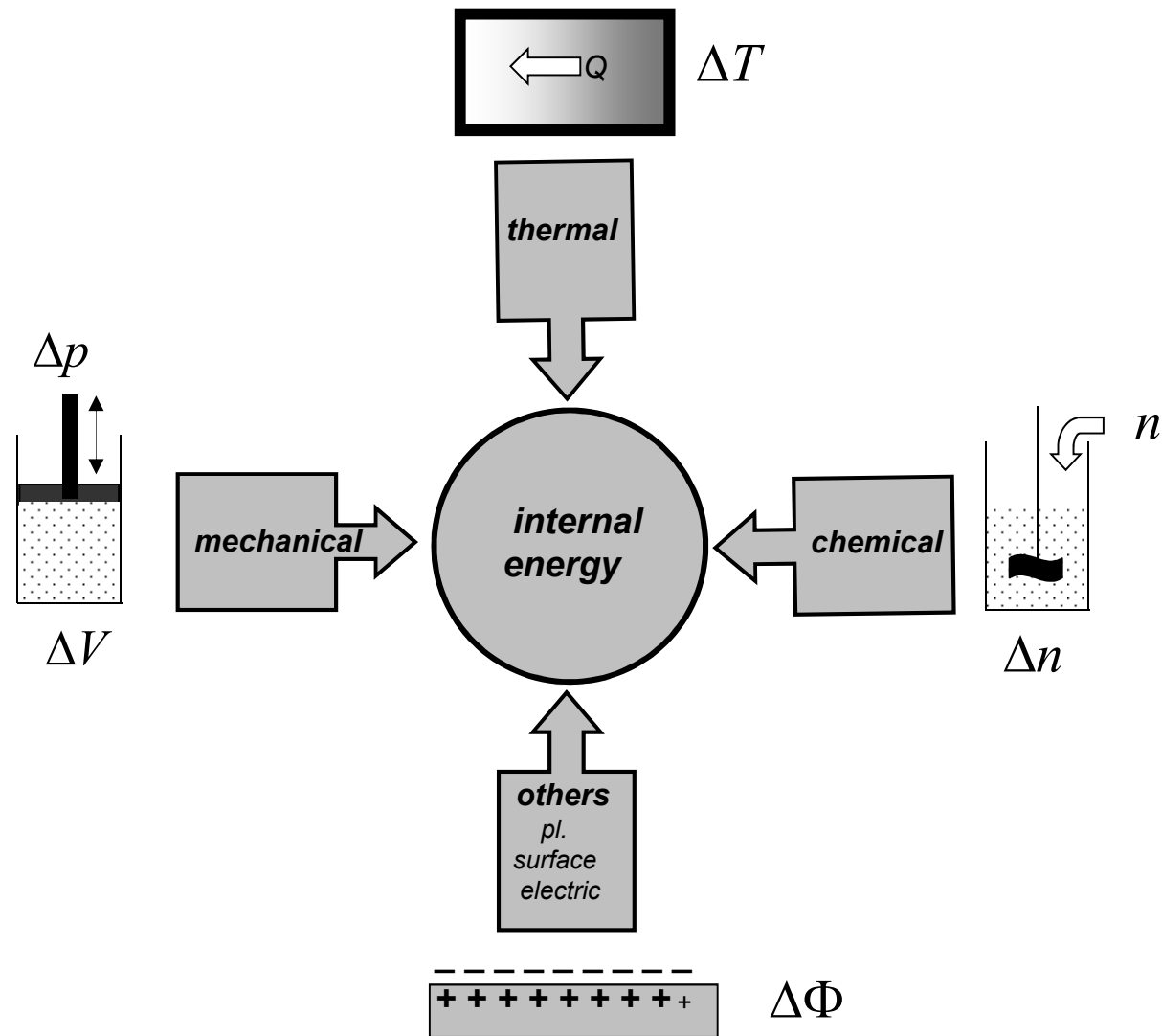
Heat and temperature play essential role !

$0 \; C^o \longrightarrow T \longrightarrow 42 \; C^o$

Biological Thermodynamics

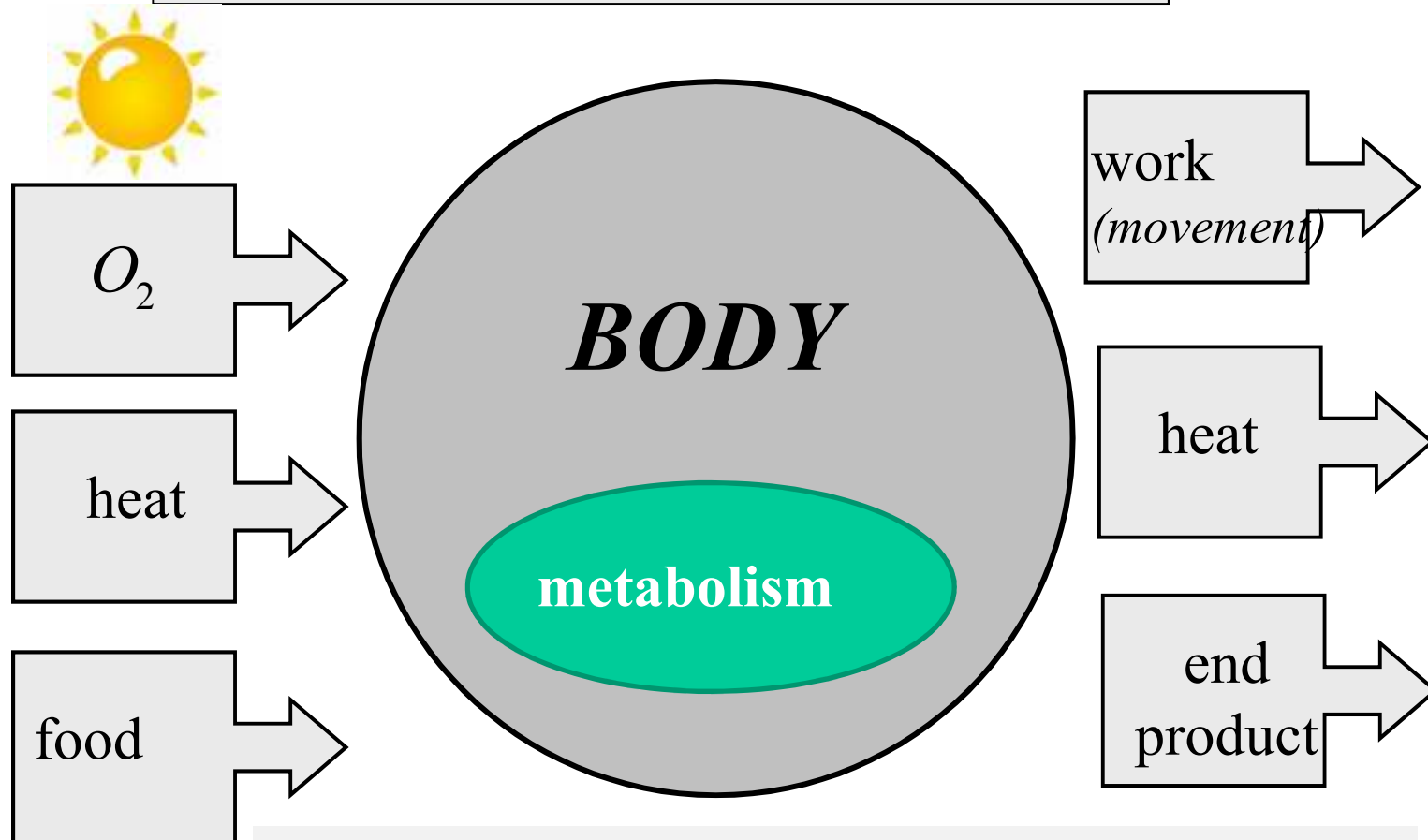## Mechanical interactions (1)

- mechanikai work
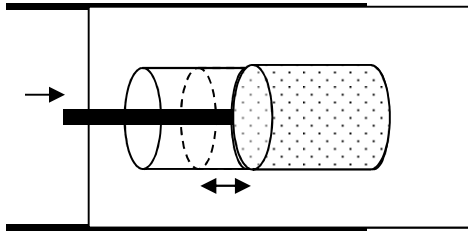
$$dW_{mech} = -f(x) \cdot dx$$

$$W_{mech} = -\sum_{x_k}^{x_v} f(x) \Delta x$$

- Volumertic work

$$f(x) = p(V) \cdot A_s$$

$$dW_{térf} = -p(V) A_s dx = -p(V) dV$$

The work is not state function!

$$W_{mech} = -\sum_{x_k}^{x_v} p(V) \Delta V$$

compression: $V_v < V_k$ $\quad W_{vol} > 0$

Isothermal process

p

V_v $\qquad$ V_k $\qquad$ V

$$W = -nRT\ln\frac{V_V}{V_k}$$

Isobaric process

p

izochor

V_v $\qquad$ V_k $\qquad$ V
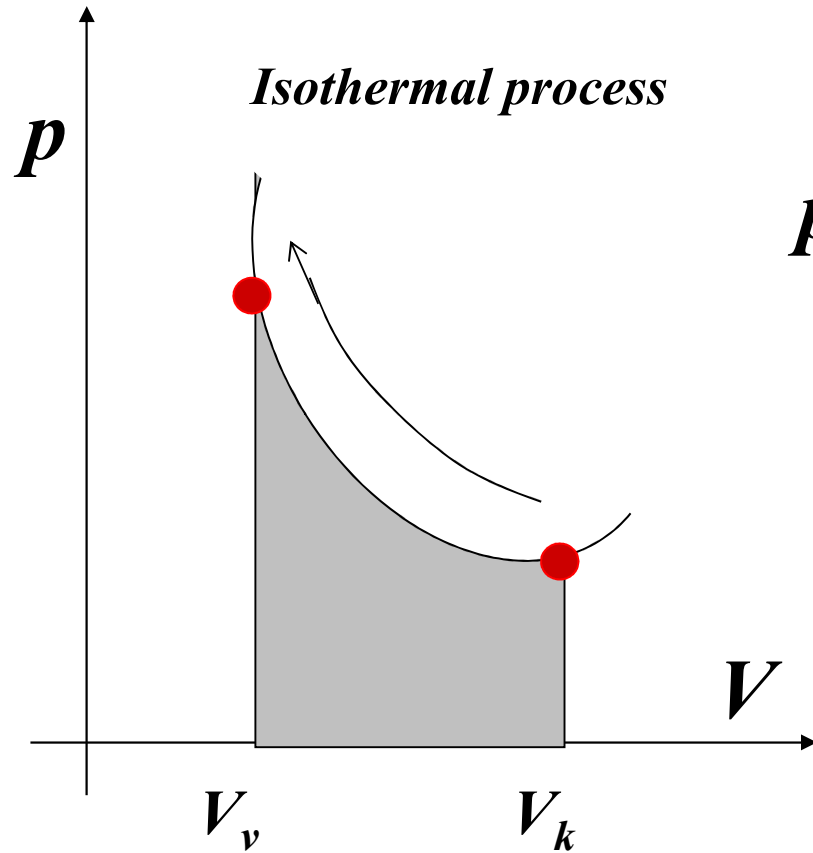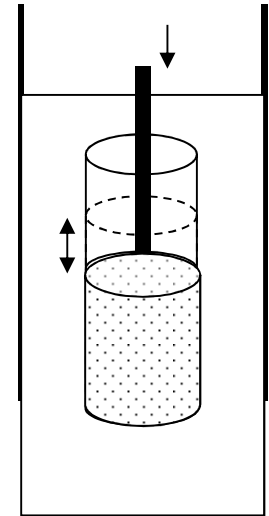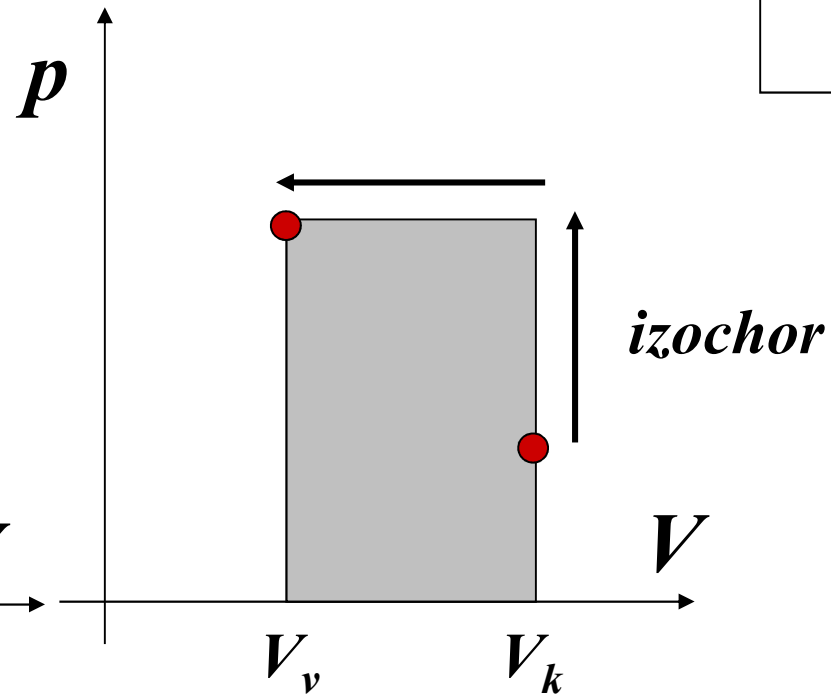
$$W = -p\cdot\Delta V$$

- Surface interaction
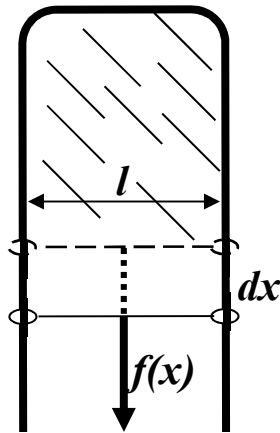
$$f(x) = -2\gamma \cdot l$$

$$dW_{fel} = 2\gamma l dx = \gamma dA_s$$

$$\boxed{W_{fel} = \gamma \cdot \Delta A_s}$$

- Chemical change

$$\Delta W_{k\acute{e}m} = \sum_{i=1}^{K} \left(\frac{\Delta U}{\Delta n_i} \right) \Delta n_i = \sum_{i=1}^{K} \mu_i \Delta n_i$$

μ_i: chemical potential

The change of internal energy is the sum of individual energy exchanges

$$\Delta U = \sum_i \Delta W_i = \sum_i y_i \cdot \Delta x_i$$

$$\Delta U = -p\Delta V + \gamma \Delta A_s + \Phi \Delta q + \mathbf{H}\Delta \mathbf{M} + \mathbf{E}\Delta \mathbf{P} + \sum_{i=1}^{K} \mu_i \Delta n_i$$

volumetric

surface

electric

magnetic

electrostatic

chemical

Where is the thermal interaction????

Characterization of the thermodynamic system

Macroscopic characterization: **extensive** and **intensive** variables
Extensive variables: their value is proportional to the size of the system
Intensive variables: their value is independent of the size of the system

Extensive variable	Intensive variable	Product: energy change
Volume (V) Matter (n) Charge (Q) Entropy (S)	Pressure (p) Chemical potential (μ) Electric potential (φ) Temperature (T)	Volumetric work (pΔV) Work of material transport ($\mu\Delta n$) Electric work ($\varphi\Delta Q$) **Hea**t ???

$$\Delta U = -p\Delta V + T\Delta S$$

more often

$$\Delta U = -p\Delta V + T\Delta S + \Phi\Delta q + \mathbf{H}\Delta\mathbf{M} + \mathbf{E}\Delta\mathbf{P} + \sum_{i=1}^{K} \mu_i \Delta n_i$$

$$\Delta W_i = y_i \cdot \Delta x_i$$

$$\Delta Q = T\Delta S$$

- Thermal interactions $\Delta Q = T \Delta S$ ⬅ **entropy**
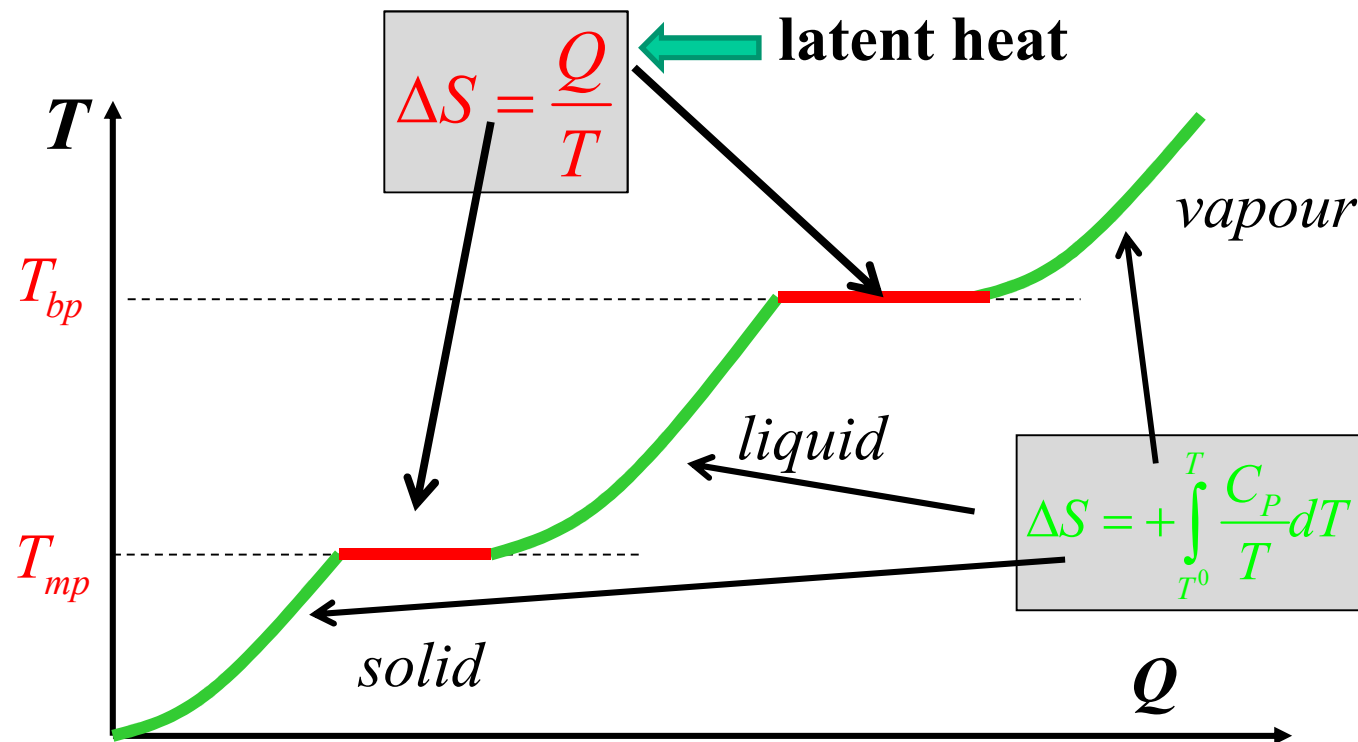
$$\Delta U = -p\Delta V + T\Delta S + \sum_{i=1}^{K} \mu_i \Delta n_i + ... +$$

Chemical potential

$$\Delta Q = T \Delta S$$

Thermal interactions

→ *temperature changes*

→ *temperature does not change*

$$\Delta S = \frac{Q}{T}$$

latent heat

vapour

T_{bp}

liquid

$$\Delta S = + \int_{T^0}^{T} \frac{C_P}{T} dT$$

T_{mp}

solid

T

Q

First law of thermodynamics

- Law of conservation of energy.
- Energy may be converted into different forms, but the total energy of the system remains constant.
- The change in the internal energy of the system is the sum of the supplied heat (Q_E) and the work (W) done on the system.

Work parts:

Volumetric work

$$W_V = -p\Delta V$$

Negative, because in the case of work done on the system $V_2 - V_1 < 0$.

Electric work:

$$W_Q = \varphi \Delta Q$$

Material transport:

$$W_n = \mu \Delta n$$

Generalized:

$$W^i = y_{int}^i \Delta x_{ext}^i$$

$$\Delta U = -p\Delta V + T\Delta \textcolor{red}{S} + \sum_{i=1}^{K} \mu_i \Delta n_i + ... +$$

Izochoric process ($\Delta V = 0$):

$$\Delta E = Q_V$$

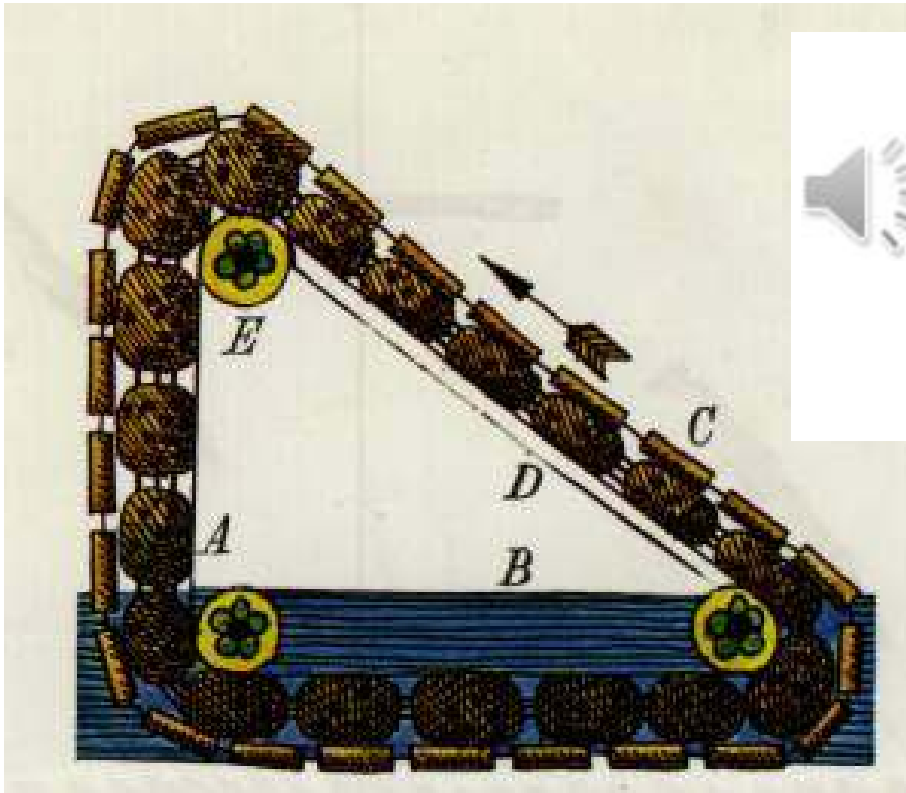Change in internal energy is caused only by the heat exchange.

Izobaric process (p=constant):

$$\Delta E = Q_p + W_V = Q_p - p\Delta V$$

First law of thermodynamics

Conservation of energy → no perpetuum mobile

Entropy change in isolated system when the temperature equalizes

$$\Delta U = -p\Delta V + T\Delta S$$

$$\Delta U = Q = T\Delta S$$

$$\Delta S_1 = \frac{1}{T_1}\Delta U_1$$

Thermal isolation

T_1
U_1
S_1

Q

T_2
U_2
S_2

Heat conducting wall

$$\Delta S_2 = \frac{1}{T_2}\Delta U_2$$
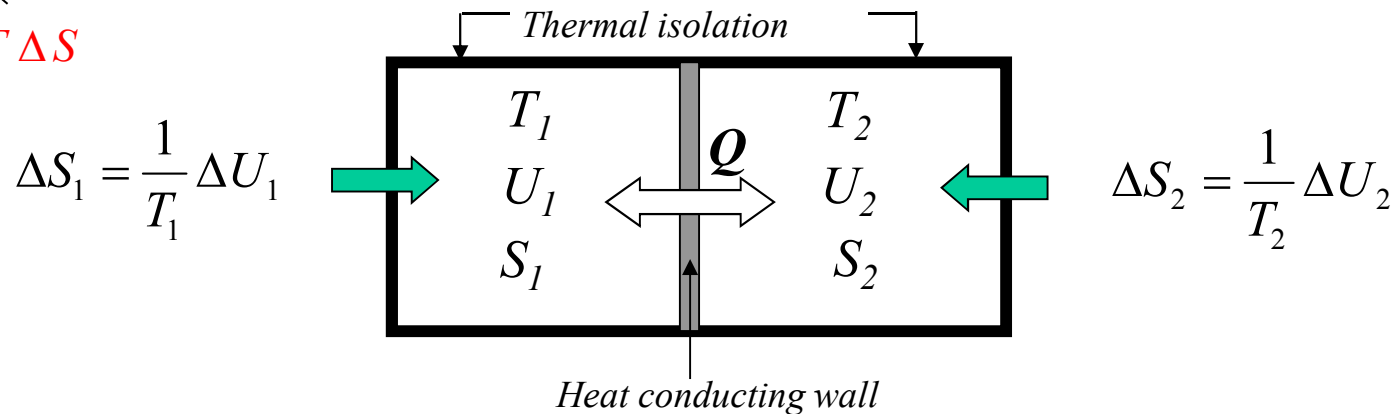
$$U = U_1 + U_2 = \text{állandó} \qquad \Delta U = 0 \qquad \longrightarrow \qquad \Delta U_1 = -\Delta U_2$$

$$\boxed{S = S_1 + S_2 = ?} \qquad \Delta S = \Delta S_1 + \Delta S_2 = ? \qquad \Delta S = \frac{1}{T_1}\Delta U_1 + \frac{1}{T_2}\Delta U_2 = \frac{T_2 - T_1}{T_2 T_1} \cdot \Delta U_1 \neq 0$$

$$ha \quad T_2 \rangle T_1 \quad akkor \quad \frac{T_2 - T_1}{T_2 T_1} > 0 \quad és \quad \Delta U_1 > 0 \quad \Longrightarrow \quad \Delta S > 0$$

$$ha \quad T_2 < T_1 \quad akkor \quad \frac{T_2 - T_1}{T_2 T_1} < 0 \quad és \quad \Delta U_1 < 0 \quad \Longrightarrow \quad \Delta S > 0$$

$$ha \quad T_2 = T_1 \quad akkor \quad \frac{T_2 - T_1}{T_2 T_1} = 0 \quad és \quad \Delta U_1 = 0 \quad \Longrightarrow \quad \Delta S = 0$$

Due to temperature equalization the entropy increases!

Entropy is an **extensive** variable.
Is it conservative, like energy ?

Entropy change in isolated system when the pressure equalizes

$$\Delta U = T\Delta S - p\Delta V + \sum_{i=1}^{K} \mu_i \Delta n_i + \ldots +$$

$\implies$

$$\Delta S = \frac{\Delta U}{T} + \frac{p}{T}\Delta V - \sum_{i=1}^{K} \frac{\mu_i}{T}\Delta n_i + \ldots +$$

$$\Delta S = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta U_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\Delta n_1$$

Isotherm equalisation process :

ha $p_1 > p_2$ *akkor* $\dfrac{p_1}{T} - \dfrac{p_2}{T} > 0$ *és* $\Delta V_1 > 0$ $\implies$ $\Delta S > 0$

ha $p_1 < p_2$ *akkor* $\dfrac{p_1}{T} - \dfrac{p_2}{T} < 0$ *és* $\Delta V_1 < 0$ $\implies$ $\Delta S > 0$

ha $p_1 = p_2$ *akkor* $\dfrac{p_1}{T} - \dfrac{p_2}{T} = 0$ *és* $\Delta V_1 > 0$ $\implies$ $\Delta S = 0$
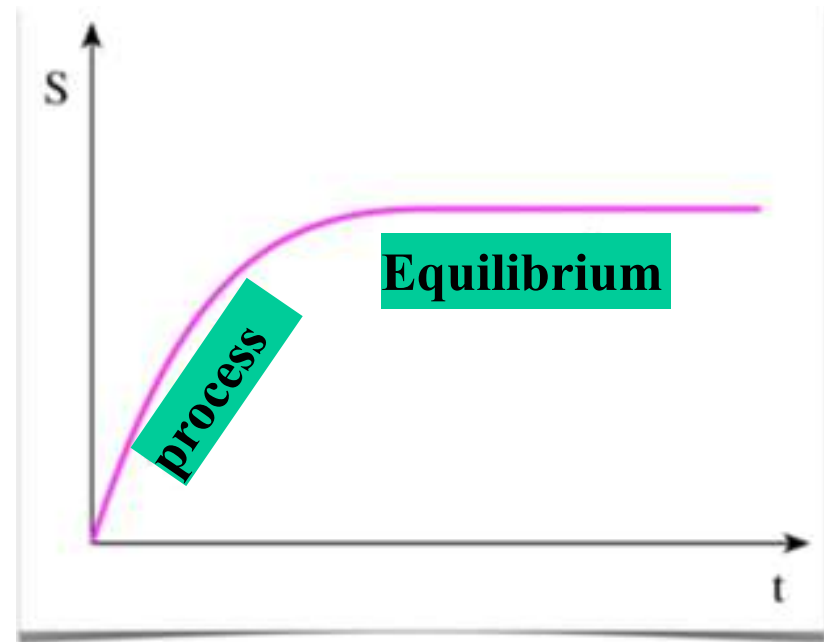
In isolated system during temperature and/or pressure equalization process the entropy increases!

Second Law of Thermodynamics

- The entropy of an isolated system never decreases; i.e.

$$\Delta S \geq 0,$$

approaching equilibrium, $S \rightarrow S_{max}.$

- **Examples of real processes:**
- i.   temperature equalization;
- ii. mixing of gases;
- iii. conversion of macroscopic (ordered) KE to thermal (random) KE.

Second law of thermodynamics

- **During spontaneous processes entropy increases. Thermodynamic equilibrium is characterized by entropy maximum.**
- Heat flows spotaneously from regions of high to low temperature.
- In an isolated system only such processes occur spontaneously which tend to equilibrate the respective intensive variables. .
- Spontaneous processes proceed towards the most probably state.
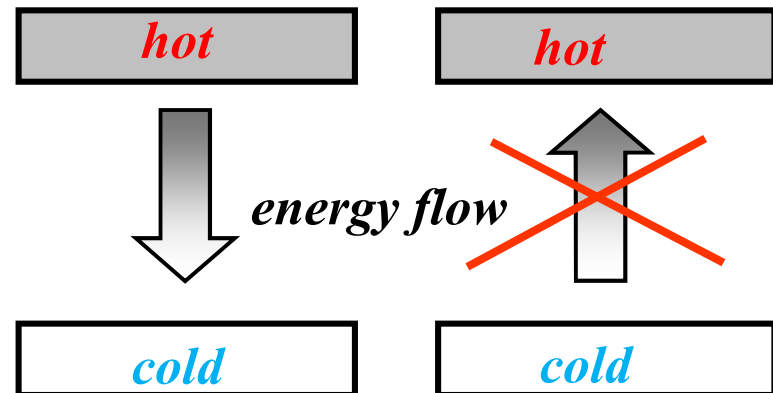
The essentially endless heat content of oceans cannot be used to spontaneously produce useful work.

entropy ⟶ *arrow of time*

Third law of thermodynamics

- The entropy of one-component, crystallizing material at 0 K temperature is 0.

- The 3rd Law fixes the absolute value of the entropy; i.e.

$$S \rightarrow 0 \text{ as } T \rightarrow 0.$$

The unattainability of absolute zero

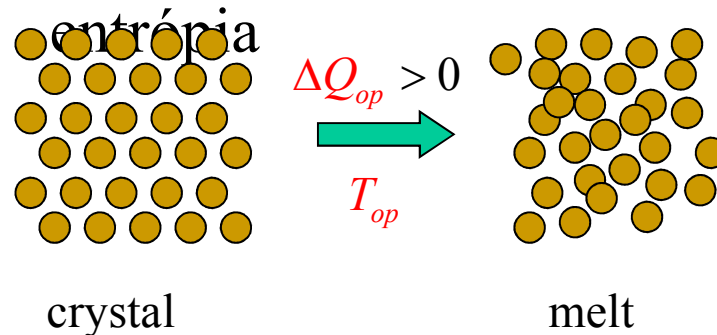It is impossible to reach T = 0 in a finite number of steps.

entropy

Thermal entropy

Configurational entropy
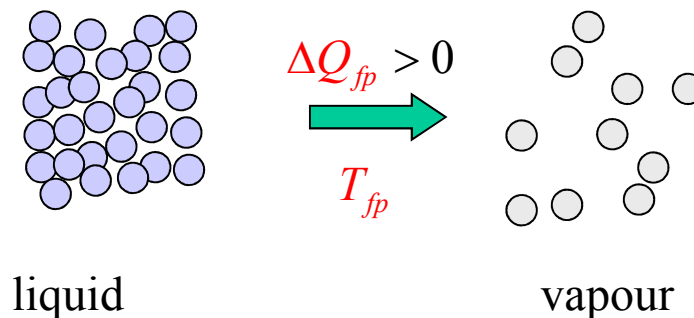
$$\Delta S = \Delta S_{term} + \Delta S_{konf}$$

entrópia

melting:

$\Delta Q_{op} > 0$

T_{op}

crystal   melt

$$\Delta S_{konf}\left(T_{op}\right) = \frac{\Delta Q_{op}}{T_{op}} > 0$$

$$\Delta Q = T\Delta S$$

boyling:

$\Delta Q_{fp} > 0$
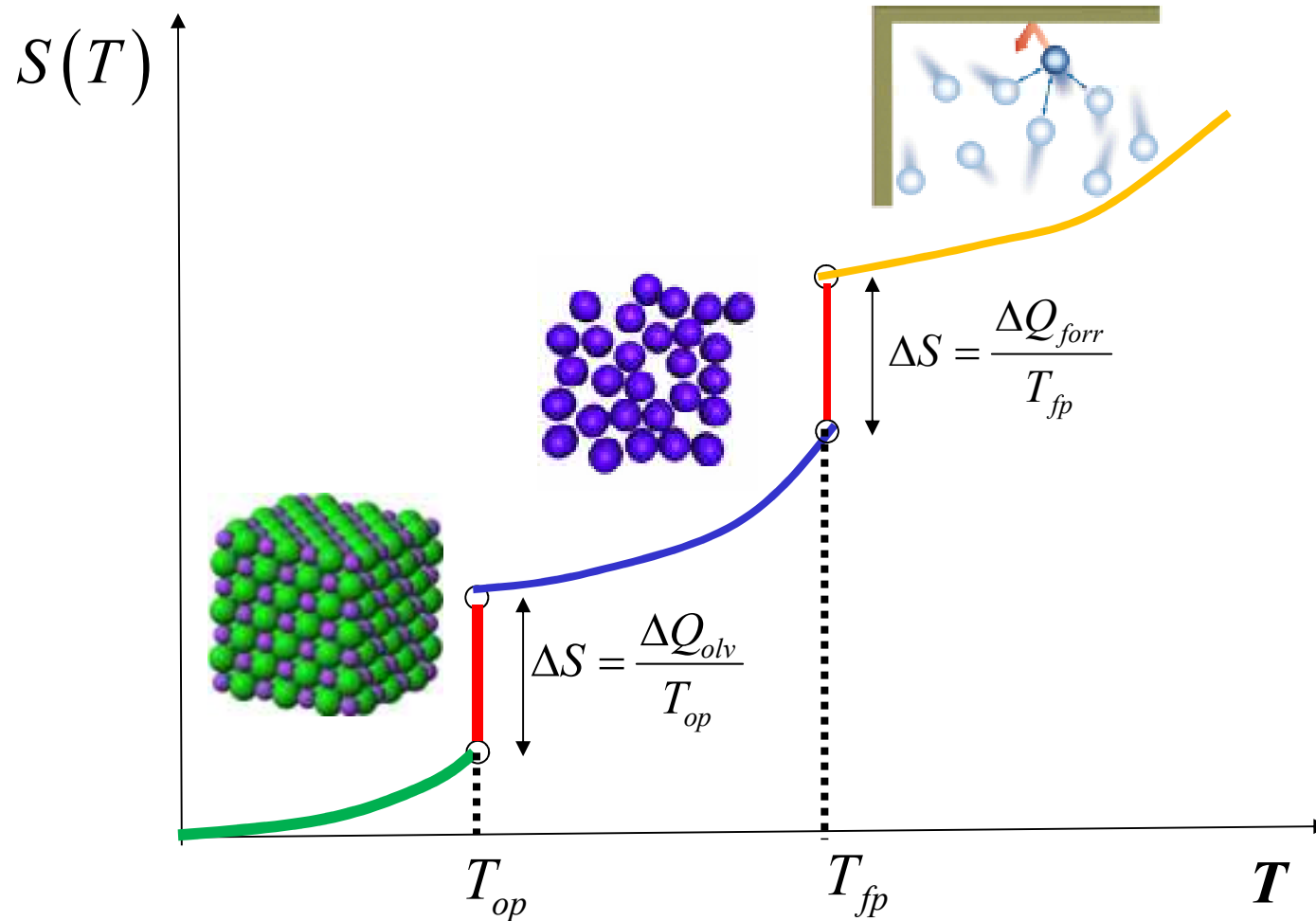
T_{fp}

liquid   vapour

$$\Delta S_{konf}\left(T_{fp}\right) = \frac{\Delta Q_{fp}}{T_{fp}} > 0$$

During phase transition the entropy increases at connstatnt T.

Entropy is a measure of local order or disorder!

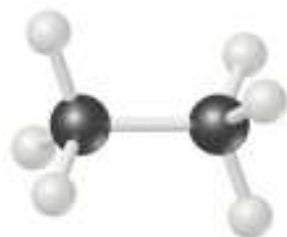# Dependence of entropy on the temperature
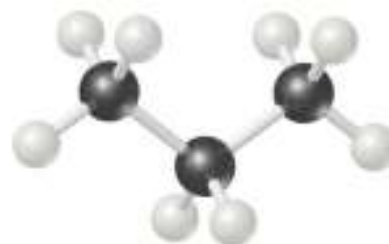
Entropy is a measure of local order or disorder!

Standard entropy at 298 K in unit of *J/molK*

Methane, CH_4
$S° = 186.3$ J mol^{-1} K^{-1}

Ethane, C_2H_6
$S° = 229.6$ J mol^{-1} K^{-1}

Propane, C_3H_8
$S° = 270.3$ J mol^{-1} K^{-1}

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	$S°$, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

solid		liquid		vapour	
C diamond	2,4	benzene	173,3	benzene vapour	269,3
C lead	5,7	water	69,9	steam	188,8