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Physical Chemistry 1

2018

1. Basic thermodynamics

1.1.Terms in thermodynamics

1. ***System*** *is the part of the world which we have a special interest in. E.g. a reaction vessel, an engine, an electric cell.*

There are two point of view for the description of a system:

Phenomenological *view: the system is a continuum, this is the method of thermodynamics.*

Particle view: *the system is regarded as a set of particles, applied in statistical methods and quantum mechanics.*

2. ***Surroundings***: *everything outside the system.*

***Isolated**: neither material nor energy cross the wall.*

Fig. 1.1.

***Closed**: energy can cross the wall.* W: work, Q: heat

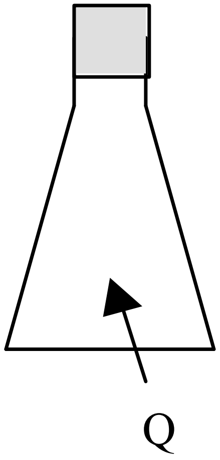


Fig. 1.2a

a) constant volume

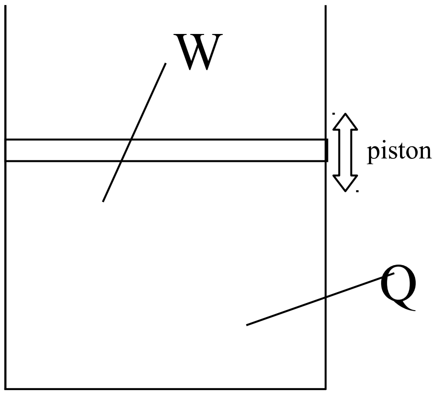
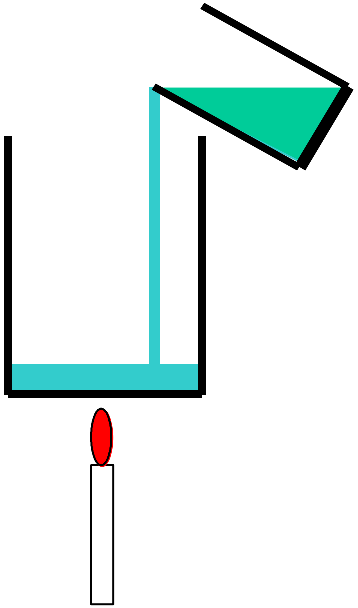


Fig. 1.2b.

b) changing volume

Open system



Transport of material and energy is possible

Fig. 1.3.

***Homogeneous**: macroscopic properties are the same everywhere in the system, see example, Fig. 1.4.*

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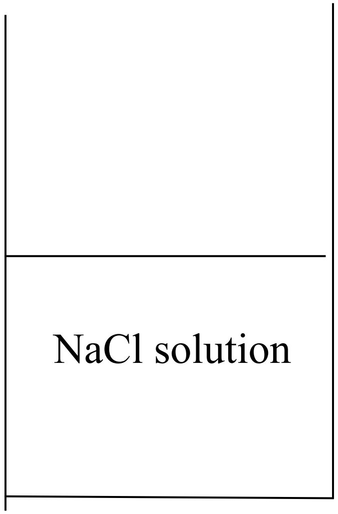


Fig. 1.4.

__Inhomogeneous:__ certain macroscopic properties change from place to place; their distribution is described by continuous function.

Example: a copper rod is heated at one end, the temperature (T) changes along the rod.

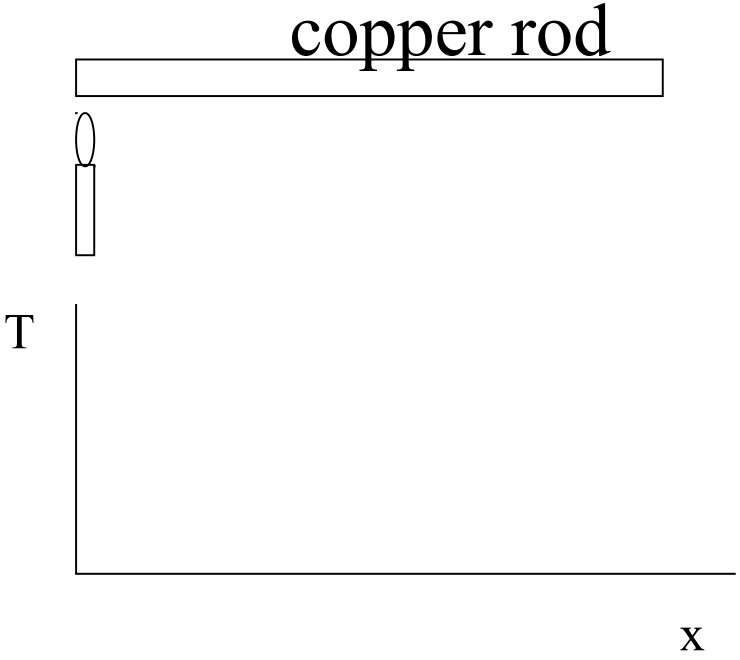
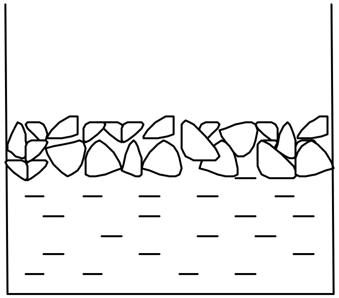


Fig. 1.5.

***Heterogeneous**: discontinuous changes of macroscopic properties.*
Example: water-ice system, Fig. 1.6.

Fig. 1.6.



One component
Two phases

***Phase:** a well defined part of the system which is uniform throughout both in chemical composition and in physical state.*

*The phase may be **dispersed**, in this case the parts with the same composition belong to the same phase.*

***Components**: chemical constituents (see later).*

1.2. The state of the thermodynamic system

*The **state** of a thermodynamic system is characterized by the collection of the measurable physical properties.*

The basic measurable properties (MP):

- *amount of substance: mass (m), chemical mass (n)*
- *volume (V)*
- *pressure (p)*
- *temperature (T)*
- *concentration (c)*

A system is in thermodynamic ***equilibrium*** *if none of the MPs are changing. In equilibrium no macroscopic processes take place.*

In a ***non-equilibrium*** *system the MPs change in time, the system tends to be in equilibrium.* ***Meta-stable state****: the state is not of minimal energy, energy is necessary for crossing an energy barrier.*

A ***reversible change*** *is one that can be reversed by an infinitesimal modification of one variable.*

A ***reversible process*** *is performed through the same equilibrium positions from the initial state to the final state as from the final state to the initial state.*

Example: reversible compression of a gas means that the external pressure is just infinitesimally larger than the pressure of the gas, i.e. the system is in mechanical equilibrium with its environment.

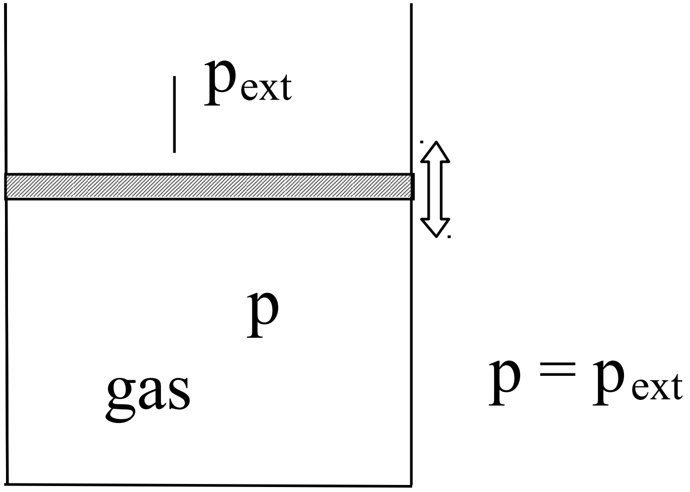


Fig. 1.7.

***Real processes** are sometimes very close to the reversible processes.*

The following processes are frequently studied:

isothermal *(T = const.)*

isobaric *(p = const.)*

isochoric *(V = const.)*

adiabatic *(Q = 0, Q: heat)*

The change of a state function depends only on the initial and the final state of the system.

*It is **independent of the path** between the two states (e.g. potential energy in the gravitation field).*

*Important **state functions** in thermodynamics*:

- ***U – internal energy***
- ***H – enthalpy***
- ***S – entropy***
- ***A – Helmholtz free energy***
- ***G – Gibbs free energy***

***Change**, example*: ΔU

***Infinitesimal change**, dU (exact differential).*

Work *and* ***heat are not state functions****. They depend on the path between the initial and final state. They are* ***path functions****.*

For example, an object is moved from A to B along two different paths on a horizontal frictious surface:

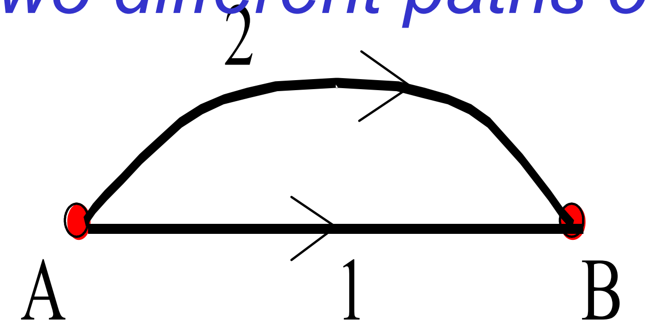


Fig. 1.8.

$$W_2 \neq W_1$$

We do not use the expression „change" for work and heat (change is labelled by „d" like dH).

Infinitesimal values of work and heat are labelled by **„δ":** δW, δQ, *since they are not exact differentials. Further parameters have to be given for their integration*.

Another type of classification of thermodynamic terms:

Extensive quantities: *depend on the extent of the system and are additive :* ***mass*** *(m)*
volume *(V)*
internal energy *(U)*

Intensive quantities: *do not depend on the extent of the system and are not additive :* ***temperature*** *(T)*
pressure *(p)*
concentration *(c)*

Extensive quantities can be converted to intensive quantities, if they are related to unit mass, volume, etc.

Density $\rho = m/V$

Molar volume: $V_m = V/n$ *(subscript m refer to molar)*

Molar internal energy: $U_m = U/n$

Equation of state*: is a relationship among the state variables of the system in equilibrium .*

Equation of state of an ***ideal gas****:*

$R = 8.314\ \mathrm{J mol^{-1} K^{-1}}$ *(gas constant)*

its ***definition:***

$$pV = nRT \qquad (1.1)$$

$V\ [\mathrm{m^3}]$

$T\ [\mathrm{K}]$

$p\ [\mathrm{Pa}]$

$n\ [\mathrm{mol}]$

The equations of states of real materials are given in forms of power series, diagrams and tables.

Temperature

The temperature scale used at present in every day life was defined by Anders Celsius in 1742.

Two basic points: *melting ice*: 0 °C
boiling water (at 1.013 bar): 100 °C

What property of what material should be used for measuring temperature?

Example: volume of liquids (mercury or ethanol)

They cannot be used in wide temperature range.

If the same thermometer is filled with different liquids, they show slightly different values at the same temperature. Reason: thermal expansion is different for the different liquids. For example: with Hg 28.7 ℃, with ethanol 28.8 ℃ is measured.

The pV_m product of an ideal gas has been selected for the basis of temperature measurement. ***All real gases behave ideally if the pressure approaches zero.***

The temperature on the ***Celsius scale:***

$$t = \frac{(p \cdot V_m)_t - (p \cdot V_m)_0}{(p \cdot V_m)_{100} - (p \cdot V_m)_0} \cdot 100 \qquad (1.2)$$

Substituting the ***exact values:***

$$t = \frac{(p \cdot V_m)_t}{8.314} - 273.15 \qquad (1.3)$$

On the ***absolute temperature scale***: $(T = 273.15 + t)$

$$pV_m = RT, \quad pV = nRT \qquad R = 8.314\ \mathrm{Jmol}^{-1}\ \mathrm{K}^{-1}$$

*For the definition of **thermodynamic temperature scale the triple point of water** is used (at the triple point the gas, liquid and the solid states are in equilibrium), 0.01°C. One Kelvin (K) is equal to 1/273.16 times the temperature of the triple point of water.*

The triple point of water is exactly 273.16 K on the thermodynamic temperature scale.

1.3. Internal energy, the first law of thermodynamics

*The **energy of a system**:*

$$E = E_{kin} + E_{pot} + U \qquad (1.4)$$

***Internal energy**, **U is the sum of the kinetic and potential energies of the particles relative to the center mass point of the system**. Therefore it does not include the kinetic and potential energy of the system, i.e. it is assumed in the definiton of U that the system itself does neither move, nor rotate.*

Parts of the internal energy:

***Thermal energy** is connected to the **motion** of atoms, molecules and ions (translation, rotation, vibration)*

***Intermolecular energy** is connected to the **forces** between molecules.*

***Chemical energy** is connected to chemical **bonds**.*

***Nuclear energy** (nuclear reactions)*

*Einstein: **$E = mc^2$**, the mass is equivalent to energy.*

We cannot determine the absolute value of U, only the change, ΔU

The first law of thermodynamics expresses the conservation of energy.

Isolated system: $\Delta U = 0$ (1.5.)

Closed system: $\Delta U = W + Q$ *W: work* (1.6)

Q: heat

Infinitesimal change: $dU = \delta W + \delta Q$ (1.7)

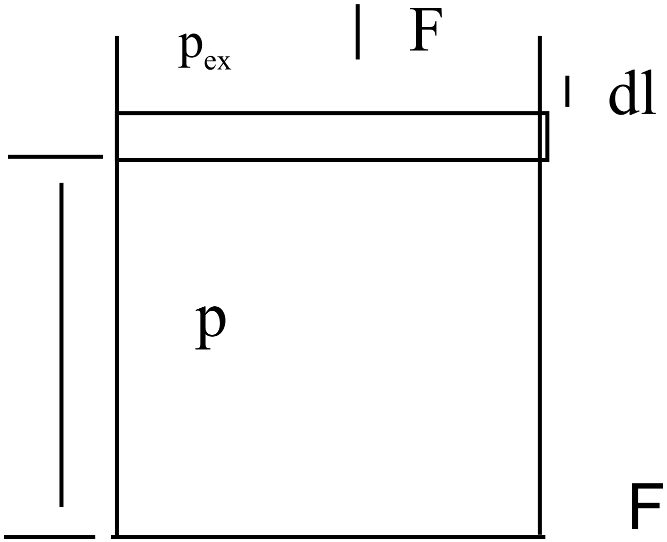
Open system, *see Fig. 1.3 and subsection 1.12.*

Work

*The **mechanical work** is the scalar product of force and displacement*

$$\ln(W) \qquad (1.8)$$

Work in changes of volume, expansion work (pV work): p_{ex} acts on surface A, reversible process:



$$\delta W = \vec{F} \cdot \vec{dl} = p_{ex} \cdot A \cdot (-dl)$$

$$\delta W = -p_{ex} \cdot dV$$

$$W = -\int_{V_1}^{V_2} p_{ex}\, dV \qquad (1.9)$$

Fig. 1.9.

Remarks:

a) The change in energy is considered always from the point of view of the system.

b) The external pressure (p_{ex}) is used

reversible change: $\boldsymbol{p = p_{ex}}$

c) ***If the volume increases, the work is negative***

If the volume decreases, the work is positive

d) ***If p = constant****, it is easy to integrate (temperature is changed) :*

$$W = -p \cdot \int_{V_1}^{V_2} dV = -p \cdot \Delta V \qquad (1.10)$$

Work in changes of volume in p-V diagram

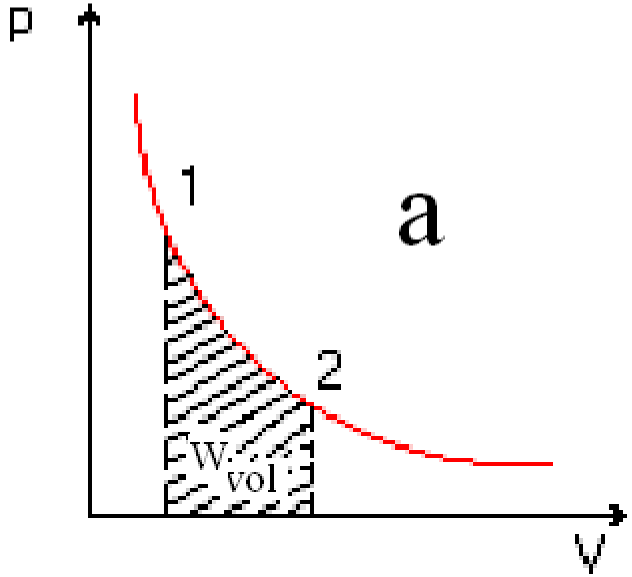


Fig. 1.10a

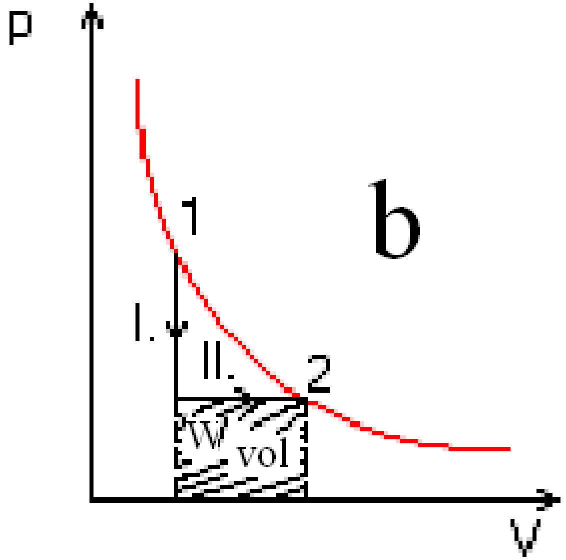


Fig. 1.10b.

***Expansion** of the gas at constant temperature*

*I. **cooling** at constant volume to the final pressure*

*II. **heating** at constant pressure*

$$W_a \neq W_b$$

The pV work is not a state function!

There are other types of work. In general the work can be expressed as the product of an intensive quantity and the change of an extensive quantity.

Work	*Intensive quantity*	*Extensive quantity*	*Elementary work*
pV	*Pressure (-p)*	*Volume V*	$\delta W = -pdV$
Surface	*Surface tension* (γ)	*Surface (A)*	$\delta W = \gamma dA$
Electric	*Potential* (φ)	*Charge (q)*	$\delta W = \varphi dq$

The work is an energy transport through the boundary of the system.

The ***driving force*** *is the gradient of the intensive parameter (of the potencial)belonging to the process. The themperature drive process is handled in thermodynamics otherwise (see heat).*

Heat

The heat is the transport of energy (without material transport) through the boundary of a system.
The driving force is the gradient of the temperature.

Processes accompanied by heat transfer:

A) Warming, cooling
B) Phase change
C) Chemical reaction

A) *Warming, cooling:*

$$Q = c \cdot m \cdot \Delta T \quad (1.11)$$

c = *specific heat [J/kg·K]*

Water c = 4.18 kJ/kg·K

$$Q = C_m \cdot n \cdot \Delta T \quad (1.12)$$

C_m = molar heat capacity [J/mol·K]

The above equations are approximations.

The heat capacities are functions of temperature.

$$Q = n\int_{T_1}^{T_2} C_m(T)\,dT \quad (1.13)$$

$$C_m(T) = \frac{1}{n}\cdot\frac{\delta Q}{dT} \quad (1.14)$$

The heat (like the work) is not a state function.
We have to specify the path.

Most frequently heating and cooling are performed either at constant pressure or at constant volume.

$$Q_p = n \int_{T_1}^{T_2} C_{mp} dT \quad (1.15)$$

$$Q_v = n \int_{T_1}^{T_2} C_{mv} dT \quad (1.16)$$

$C_{mp} > C_{mV}$ *because heating at constant pressure is accompanied by pV work.*

B) *Phase change*

In isobaric systems phase changes are isotermal processes (and in isothermal systems the phase changes are isobaric processes).

In case of pure substances either the temperature or the pressure can be freely selected.

As it was already mentioned, at 1.013 bar the boiling point of water is 100 °C.

Heat of fusion and heat of vaporization are called latent heat.

C) *Chemical reaction (see later)*

Enthalpy

The first law: $\Delta U = W + Q$ (1.17)

If there is no pV work done (W=0, ΔV=0), the change of internal energy is equal to the heat.

$\Delta U = Q_V$

1. constant volume
2. no other work

(1.18)

Processes at constant volume are well characterized by the internal energy.

In chemistry constant pressure is more frequent than constant volume. Therefore we define a state function which is suitable for describing processes at constant pressure.

Enthalpy $H = U + pV$ *Unit: Joule* (1.19)

The differential form (1.20a):

$$dH = dU + pdV + Vdp$$

If only pV work is done and the process is reversible:

$$dU = -pdV + \delta Q \quad (1.21a)$$

Then $dH = \delta Q + Vdp$

(1.22)

For final change:

$\Delta H = \Delta U + \Delta(pV)$ (1.20b)

At constant pressure:

$\Delta H = \Delta U + p\Delta V$ (1.20c)

$\Delta U = W + Q$ (1.21b)

Only pV work: $W = -p\Delta V$

$\Delta H = -p\Delta V + Q + p\Delta V$

If the pressure is constant

$$dH = \delta Q_p \qquad \Delta H = Q_p \qquad (1.23)$$

In an isobaric process (if no other than pV work is done) the change of enthalpy is equal to the heat.

Calculation of enthalpy change in case of isobaric warming or cooling:

$$\Delta H = n\int_{T_1}^{T_2} C_{mp}\,dT \qquad (1.24)$$

C_{mp} *is expressed in form of power series:*

$$C_{mp} = a + bT + cT^{-2} + d\cdot T^2 \qquad (1.25)$$

$$\Delta H = n\left[a\left(T_2 - T_1\right) + \frac{b}{2}\left(T_2^2 - T_1^2\right) - c\left(T_2^{-1} - T_1^{-1}\right) + \frac{d}{3}\left(T_2^3 - T_1^3\right)\right]$$

(1.26)

Phase changes (isothermal and isobaric processes):

ΔH_m (vap): - *molar heat of vaporization*

ΔH_m (fus): - *molar heat of fusion*

1.4. Ideal gas (perfect gas)

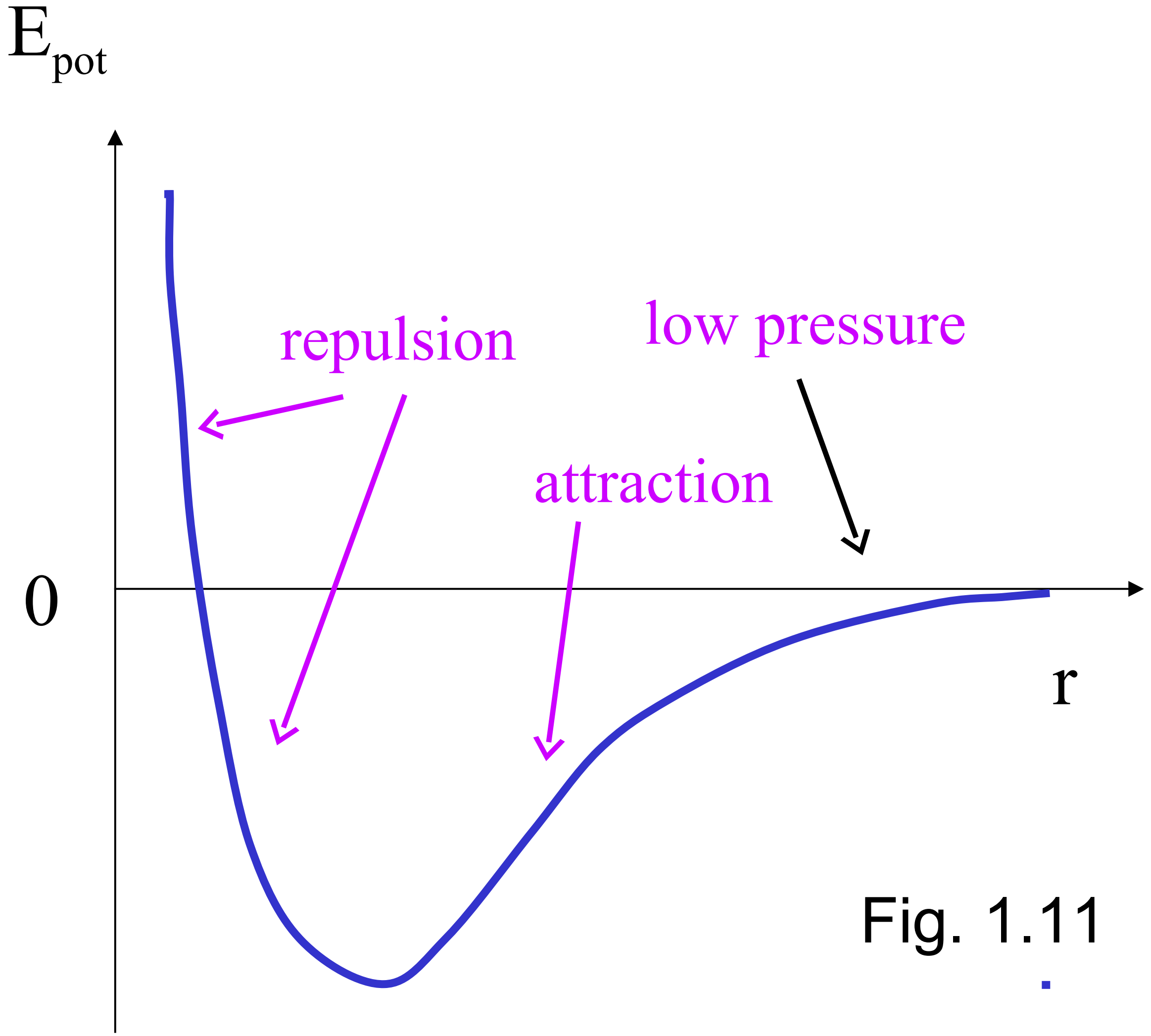
Properties of an ideal gas:

1. *There is no interaction among molecules*
2. *The size of molecule is negligible.*

*The **ideal gas law** (see equation 1.1)*

$$pV = nRT \qquad (1.27)$$

The potential energy between the atoms of a diatomic molecule as a function of their distance



repulsion

low pressure

attraction

Fig. 1.11

minimum, force=0

At low pressures real gases approach the ideal gas behaviour.

In an ideal gas there is no potential energy between molecules. It means that the internal energy does not depend on pressure (or volume).

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad (1.28a)$$

$$\left(\frac{\partial U}{\partial p}\right)_T = 0 \qquad (1.28b)$$

The internal energy of an ideal gas depends on temperature only.

Enthalpy: $\mathrm{H = U + pV}$

$\uparrow$

depends on temperature only

$(\mathrm{pV=nRT})$

and also U depends only on the temperature

Therefore enthalpy of an ideal gas depends on temperature only.

$$\left(\frac{\partial H}{\partial V}\right)_T = 0 \qquad (1.29a)$$

$$\left(\frac{\partial H}{\partial p}\right)_T = 0 \qquad (1.29b)$$

1.5.Relation between C_{mp} and C_{mv} (ideal gas)

$C_{mp} > C_{mv}$ because the gas expands when heated at constant pressure - pV work is done.

$$\delta Q_v = dU \qquad \delta Q_p = dH$$

$$C_{mv} = \frac{1}{n}\frac{\delta Q_v}{dT} = \frac{1}{n}\cdot\frac{dU}{dT} \qquad (1.30a)$$

$$C_{m\,p} = \frac{1}{n}\frac{\delta Q_p}{dT} = \frac{1}{n}\cdot\frac{dH}{dT} \qquad (1.30b)$$

$$\mathrm{H = U + pV = U + nRT} \qquad (1.31)$$

$$\mathrm{C_{mp} = \frac{1}{n} \cdot \frac{d}{dT}\left(U + nRT\right) = \frac{1}{n}\left(\frac{dU}{dT} + nR\right)}$$

$$C_{mp} = C_{mv} + R$$

ideal gas: $$C_{mp} - C_{mv} = R \qquad (1.32)$$

1.6. Reversible changes of ideal gases (isobaric, isochor, isothermal)

In case of gases reversible processes are good approximations for real (irreversible) processes (this approach is less applicable at high pressures).

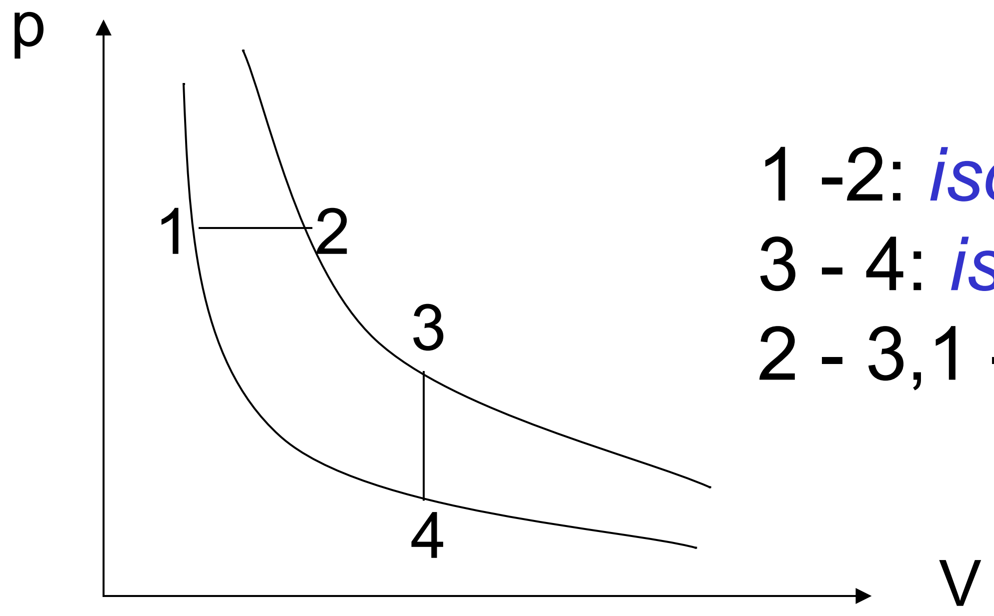


Fig. 1.12

1 -2: *isobaric*
3 - 4: *isochor*
2 - 3,1 - 4: *isothermal*

Isobaric

pV work: (1.33a)

$$W = -\int p dV = -p \int_{V_1}^{V_2} dV = -p\left(V_2 - V_1\right) = -nR\left(T_2 - T_1\right)$$

$$pdV = nRdT$$

Heat (change of enthalpy):

$$Q_p = \Delta H = n \int_{T_1}^{T_2} C_{mp} dT \qquad (1.33b)$$

Change of internal energy: (1.33c)

$$\Delta U = W + Q = -nR \int_{T_1}^{T_2} dT + n \int_{T_1}^{T_2} C_{mp} dT = n \int_{T_1}^{T_2} \left(C_{mp} - R\right) dT = n \int_{T_1}^{T_2} C_{mv} dT$$

Isochor

pV work: $W = 0$ (1.34a)

Heat (change of internal energy)

$$Q_v = \Delta U = n \int_{T_1}^{T_2} C_{mv} dT \qquad (1.34b)$$

Change of enthalpy: (1.34c)

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR \int_{T_1}^{T_2} dT = n \int_{T_1}^{T_2} (C_{mv} + R) dT = n \int_{T_1}^{T_2} C_{mp} dT$$

Isothermal $\Delta U = 0$ $Q = -W$ $\Delta H = 0$

pV work:

$$W = \int_{V_1}^{V_2} - p\,dV \qquad p = \frac{nRT}{V}$$

$$W = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{V_1}{V_2} \qquad \text{(1.35a)}$$

Boyle`s law: $\longrightarrow$ $p_1 V_1 = p_2 V_2$ $\quad \frac{V_2}{V_1} = \frac{p_1}{p_2}$

$$W = -nRT \ln \frac{p_1}{p_2} = nRT \ln \frac{p_2}{p_1} \qquad \text{(1.35b)}$$

Heat

$$Q = -W = -nRT\ln\frac{p_2}{p_1} \qquad (1.35c)$$

For ideal gases in any process:
$$\Delta U = n\int_{T_1}^{T_2} C_{mV}\cdot dT \qquad (1.36a)$$

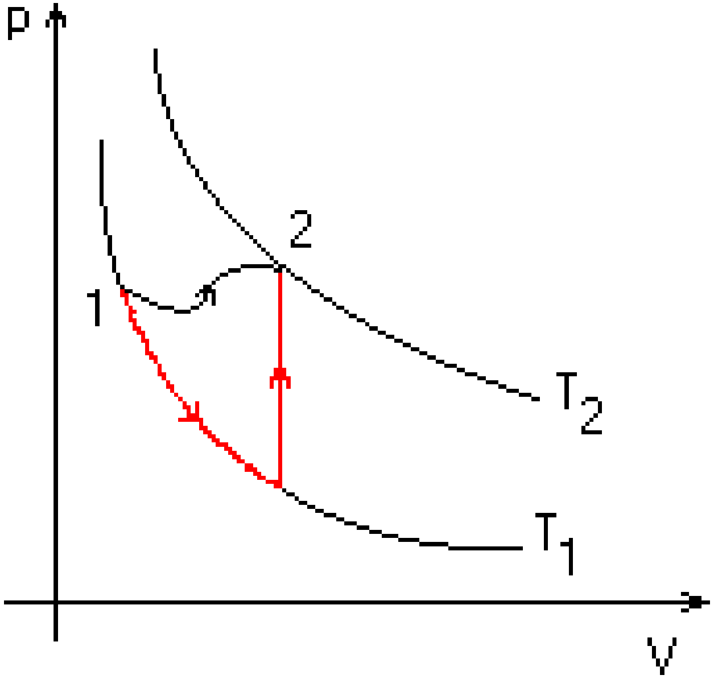


Fig. 1.13

U is a state function. Let us perform the process in two steps (position 1: V_1, T_1, p_1)

I. isothermal (expansion to V_2)

II. isochor (warming to T_2)

$\Delta U = \Delta U_I + \Delta U_{II}$

$\Delta U_I = 0$

$$\Delta U_{II.} = n\int_{T_1}^{T_2} C_{mV}\cdot dT$$

Similarly, in an ideal gas for any process:

$$\Delta H = n \int_{T_2}^{T_1} C_{mp} dT$$

(1.36e)

Reversible changes of ideal gases (See Table 1)

Table 1.1. Reversible changes in ideal gases

	W	Q	ΔU	ΔH
Isobaric	-nR(T_2-T_1)	$n\int_{T_1}^{T_2} C_{mp}\,dT$	$n\int_{T_1}^{T_2} C_{mv}\,dT$	$n\int_{T_1}^{T_2} C_{mp}\,dT$
Isochor	0	$n\int_{T_1}^{T_2} C_{mv}\,dT$	$n\int_{T_1}^{T_2} C_{mv}\,dT$	$n\int_{T_1}^{T_2} C_{mp}\,dT$
Isothermal	nRTln $\frac{p_2}{p_1}$	-nRTln $\frac{p_2}{p_1}$	0	0
Ad.rev.	$n\int_{T_1}^{T_2} C_{mv}\,dT$	0	$n\int_{T_1}^{T_2} C_{mv}\,dT$	$n\int_{T_1}^{T_2} C_{mp}\,dT$

1.7. Adiabatic reversible changes of ideal gases

Adiabatic:

$Q = 0$ (1.37a) $\Delta U = W$ (1.37b)

Compression, the work done on the system increases the internal energy → T increases

Expansion, some of the internal energy is used up for doing work → T decreases

In adiabatic processes all the three state functions (T, p and V) change.

In a p - V diagram adiabats are steeper than isotherms.

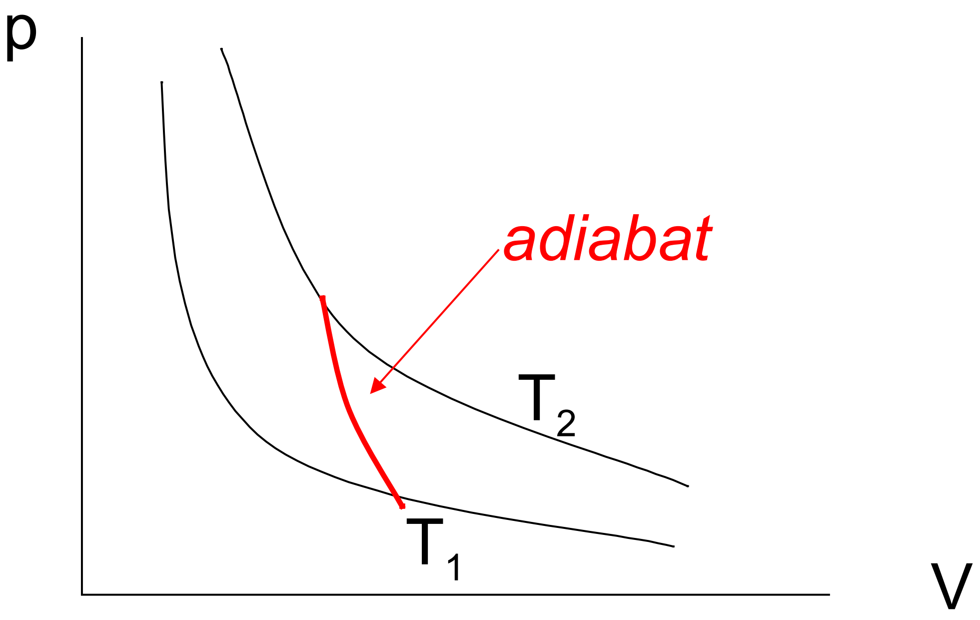


Fig. 1.14.

Derivation of adiabats

a) Relation of V and T

Reversibility is introduced here

$$dU = \delta W$$

$$dU = nC_{mv}\,dT \qquad dW = -p\,dV$$

$$nC_{mv}\,dT = -p\,dV \qquad p = \frac{nRT}{V}$$

(ideal gas)

$$nC_{mv}\,dT = -\frac{nRT}{V}\,dV$$

$$C_{mv}\frac{dT}{T} = -R\frac{dV}{V}$$

Integrate between initial (1) and final (2) state.

We neglect the T-dependence of C_{mv} (and C_{mp}).

$$C_{mv} \int_{T_1}^{T_2} \frac{dT}{T} = - R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_{mv} \ln \frac{T_2}{T_1} = - R \ln \frac{V_2}{V_1}$$

$$R = C_{mp} - C_{mv} \qquad - R = C_{mv} - C_{mp}$$

$$C_{mv} \ln \frac{T_2}{T_1} = \left(C_{mv} - C_{mp}\right) \ln \frac{V_2}{V_1}$$

divided by C_{mv}

$$\ln\frac{T_2}{T_1}=\left(1-\frac{C_{mp}}{C_{mv}}\right)\ln\frac{V_2}{V_1} \qquad \frac{C_{mp}}{C_{mv}}=\kappa$$

Poisson constant

(1.37c)

$$\ln\frac{T_2}{T_1}=(1-\kappa)\ln\frac{V_2}{V_1}=(\kappa-1)\ln\frac{V_1}{V_2}$$

$$\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\kappa-1} \qquad T_1V_1^{\kappa-1}=T_2V_2^{\kappa-1}$$

$$TV^{\kappa-1}=const.$$

(1.37d)

To find the relationship between p and V and between p and T we use the ideal gas law ($pV = nRT$).

b) Relation of p and V

$$T_1 V_1^{\kappa-1} = T_2 V_2^{\kappa-1} \quad T_1 = \frac{p_1 V_1}{nR} \quad T_2 = \frac{p_2 V_2}{nR}$$

$$\frac{p_1 V_1}{nR} \cdot V_1^{\kappa-1} = \frac{p_2 V_2}{nR} \cdot V_2^{\kappa-1}$$

$$p_1 V_1^{\kappa} = p_2 V_2^{\kappa}$$

$$pV^{\kappa} = const. \qquad (1.37e)$$

c) Relation of p and T

$$p_1 V_1^{\kappa} = p_2 V_2^{\kappa} \qquad V_1 = \frac{nRT_1}{p_1} \quad V_2 = \frac{nRT_2}{p_2}$$

$$p_1 \left(\frac{nRT_1}{p_1} \right)^{\kappa} = p_2 \left(\frac{nRT_2}{p_2} \right)^{\kappa}$$

$$p_1^{1-\kappa} \cdot T_1^{\kappa} = p_2^{1-\kappa} \cdot T_2^{\kappa}$$

$$T_1 p_1^{\frac{1-\kappa}{\kappa}} = T_2 p_2^{\frac{1-\kappa}{\kappa}}$$

$$T p^{\frac{1-\kappa}{\kappa}} = const. \qquad (1.37f)$$

1.8. The standard reaction enthalpy

In a chemical reaction the molecular energies change during the breaking of old and forming of new chemical bonds.

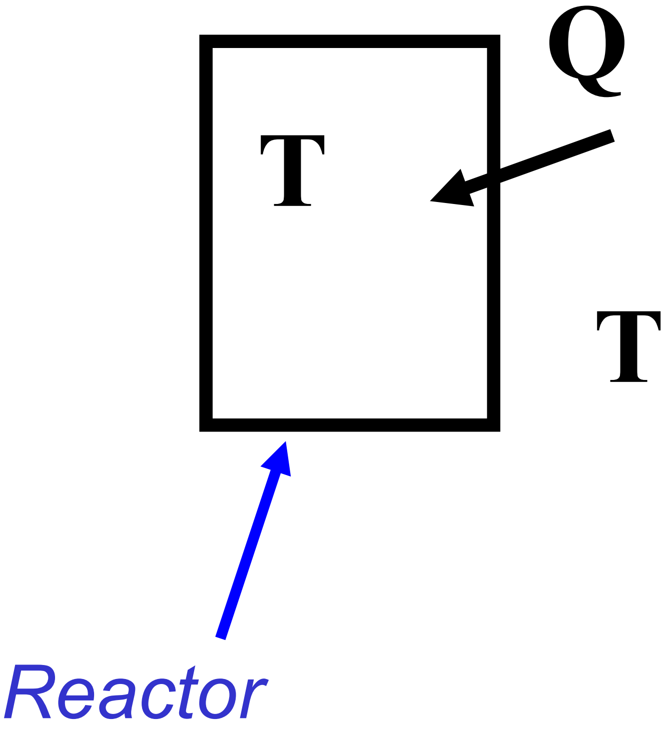
Example: in the reaction $2H_2 + O_2 = 2H_2O$ the H-H and O-O bonds break and O-H bonds are formed.

Exothermic: *energy is liberated.*
Endothermic: *energy is needed to perform the reaction at constant temperature.*

Table 1.2. Comparison of the adiabatic and isothermal processes

	adiabatic (Q= 0)	isothermal (T = const.)
exothermic	T rises	Heat exits
endothermic	T falls	Heat enters

Heat of isothermal reaction



Exothermic: **$Q < 0$**

Endothermic: **$Q > 0$**

Fig. 1.15.

Heat of reaction *is the heat entering the reactor (or exiting from the reactor) if the amounts of substances expressed in the reaction equation react at constant temperature.*

At constant volume: $\Delta_r U$, at constant pressure: $\Delta_r H$

E.g.: $2H_2 + O_2 = 2H_2O$

$$\Delta_r U = 2U_m(H_2O) - 2U_m(H_2) - U_m(O_2)$$

$$\Delta_r H = 2H_m(H_2O) - 2H_m(H_2) - H_m(O_2)$$

The heat of reaction defined this way depends on T, p and the concentrations of the reactants and products.

Standardization*: the pressure and the concentrations are fixed but not the temperature*.

Standard heat of reaction*: is the heat entering the reactor (or exiting from the reactor) if the amounts of substances expressed in the reaction equation react* ***at constant temperature,*** *and both the reactants and the products are pure substances at* p^o *pressure.*

Standardization means : pure substances

p^o pressure (10^5 *Pa)*

Temperature is not fixed but most data are available at 25 °C

The standard state will always be denoted by a superscript ***0***

Standard pressure:

$$p^0 \ (= 10^5 \, \mathrm{Pa} = 1 \, \mathrm{bar})$$

It follows from the definition of enthalpy ($\Delta H = Q_p$) that the standard heat of reaction is a change of enthalpy.

A general reaction: $\Sigma\, \nu_A M_A = \Sigma\, \nu_B M_B$ (1.38)

ν: *stoichiometric coefficient,*

M: *molecules,*

A-s are for reactants, B-s are for products.

The standard heat of reaction (enthalpy of reaction):

$$\Delta_r H^0 = \sum_B \nu_B H^0_{mB} - \sum_A \nu_A H^0_{mA} \qquad (1.39)$$

H^0_m *is the standard molar enthalpy*

Example: $2H_2 + O_2 = 2H_2O$

$$\Delta_r H^0 = 2H_m^0(H_2O) - 2H_m^0(H_2) - H_m^0(O_2)$$

We have to specify the reaction equation (very important, see the examples), the state of the participants and the temperature.

Example reactions	*Standard reaction enthalpy at 25 °C*
$2H_2(g) + O_2(g) = 2H_2O(l)$	-571,6 kJ
$H_2(g) + 1/2O_2(g) = H_2O(l)$	-285,8 kJ
$H_2(g) + 1/2O_2(g) = H_2O(g)$	-241,9 kJ

1.9.Measurement of heat of reaction

Calorimeters are used for measuring heats of reaction

Bomb calorimeter is suitable for measuring heat of combustion. The substance is burned in excess of oxygen under pressure.

Bomb calorimeter

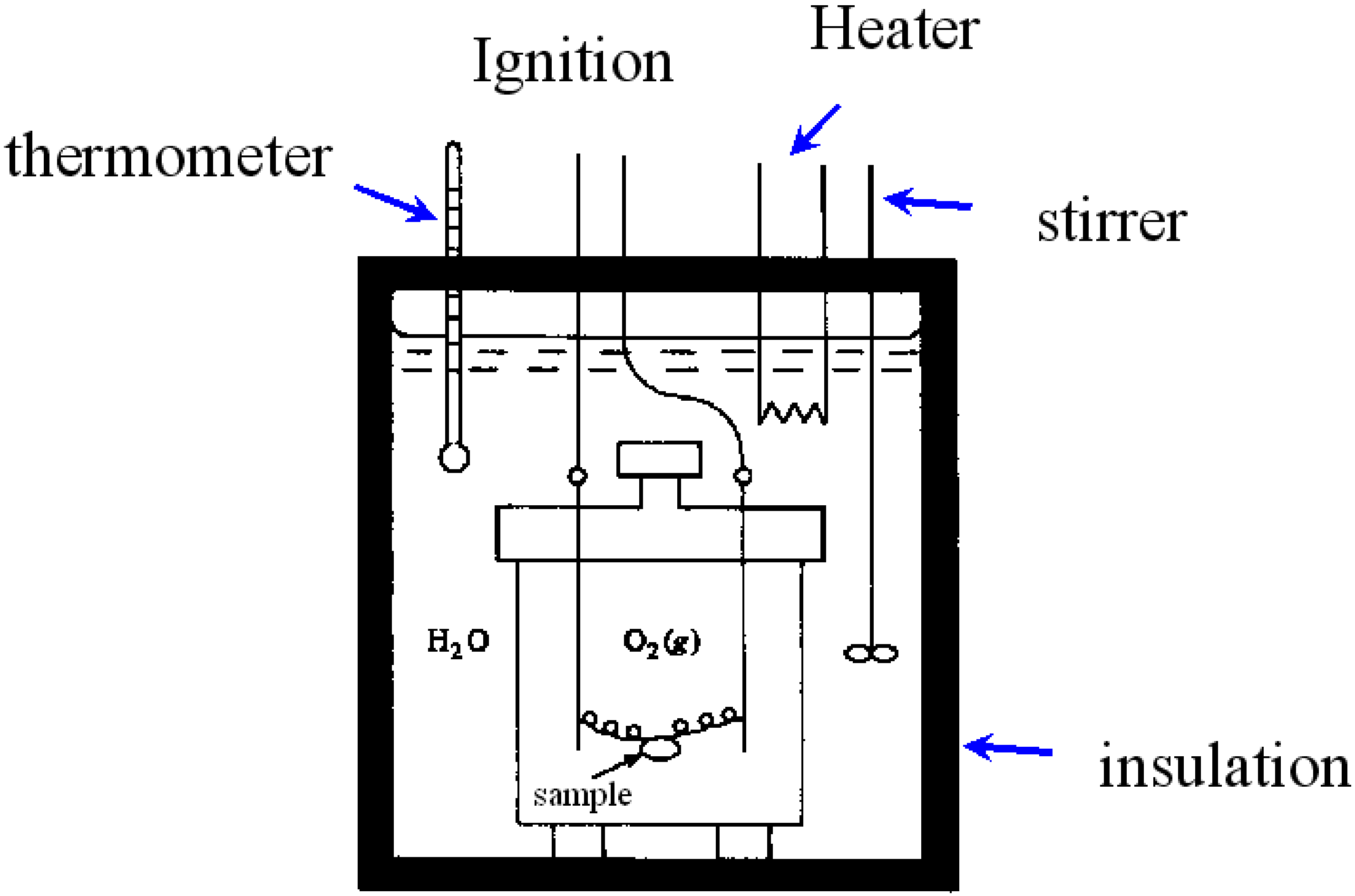


Fig. 1.16.

The heat of reaction can be determined from (ΔT):

$$q = -C \cdot \Delta T \qquad (1.40)$$

C is the heat capacity of the calorimeter (including everything inside the insulation, wall of the vessel, water, bomb, etc.).

Determination of C with known amount of electrical energy, which causes $\Delta T'$ temperature rise

$$U \cdot I \cdot \Delta t = C \cdot \Delta T' \qquad (1.41)$$

where U is the electric potential, I is the current and Δt is the time of heating.

In a bomb calorimeter $\Delta_r U$ is measured because the volume is constant.

$$H = U + pV$$
$$\Delta_r H = \Delta_r U + \Delta_r(pV) \qquad (1.42)$$

The pV product changes because the number of molecules of the ***gas phase components*** *changes.*

Ideal gas approximation: $pV = nRT$.

$$\Delta_r(pV) = \Delta_r \nu_g RT \qquad (1.43)$$

where $\Delta_r \nu_g$ is the change of the stochiometric coefficients for gaseous components:

$$\Delta_r \nu_g = \Sigma \nu_g(\textit{products}) - \Sigma \nu_g(\textit{reactants}) \qquad (1.44)$$

Example:

$$C_6H_5COOH(s) + 7{,}5O_2(g) = 7CO_2(g) + 3H_2O(l)$$

$$\Delta_r\nu_g = 7 - 7{,}5 = -0.5$$

The difference of $\Delta_r U$ and $\Delta_r H$ is usually small.

1.10. Hess`s law

Enthalpy is a state function. *Its change depends on the initial and final states only*. *(It is independent of the intermediate states.)*

This statement can be applied for the reaction enthalpy.

The reaction enthalpy is independent of the intermediate states, it only depends on the initial and the final states.

Example: *The reaction enthalpy of the reaction*

$C(graphite) + O_2 = CO_2$ (1)

is equal to the sum of reaction enthalpies of the following two reactions:

$C(graphite) + 1/2O_2 = CO$ (2)

$CO + 1/2\ O_2 = CO_2$ (3)

$$\Delta_r H(1) = \Delta_r H(2) + \Delta_r H(3)$$

So if we know two of the three reaction enthalpies, the third one can be calculated.

Hess discovered this law in 1840.

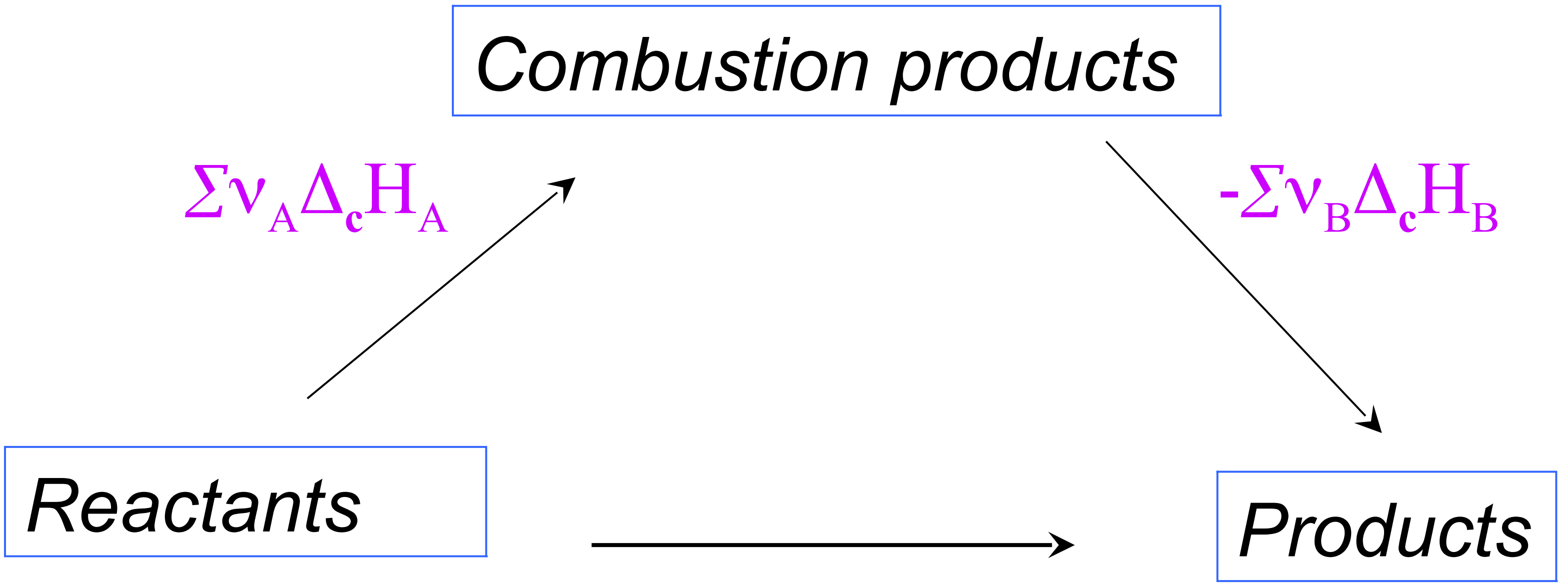
The significance of Hess`s law is that reaction enthalpies, which are difficult to measure, can be determined by calculation.

The reaction enthalpies can be calculated from heats of combustion or heats of formation.

Calculation of heat of reaction from heats of combustions:

Suppose we burn the reactants and then we perform a reverse combustion in order to make the products.

$\Delta_c H$: *heat of combustion (enthalpy of combustion)*



Combustion products

$\Sigma\nu_A\Delta_c H_A$

$-\Sigma\nu_B\Delta_c H_B$

Reactants

Products

The heat of reaction is obtained if we subtract the sum of the heats of combustion of the products from the sum of the heats of combustion of reactants.

$$\Delta_r H = - \Delta_r(\Delta_c H) \qquad (1.45)$$

Example: $3C_2H_2 = C_6H_6$

$$\Delta_r H = -(\Delta_c H(C_6H_6) - 3\Delta_c H(C_2H_2))$$

$$= 3\Delta_c H(C_2H_2) - \Delta_c H(C_6H_6)$$

The heat of formation (enthalpy of formation) of a compound is the enthalpy change of the reaction, in which the compound is formed from (the most stable forms of) its elements.

It is denoted by $\Delta_f H$.

Example: The heat of formation of SO_3 is the heat of the following reaction

$$S + 3/2 O_2 = SO_3$$

It follows from the definition that the heat of formation of an element is zero (at standard temperature).

Calculation of heat of reaction from heats of formations:

Suppose we first decompose the reactants to their elements (reverse of the formation reaction), then we compose the products from the elements.

$$\begin{tikzcd}
 & \textit{Elements} \arrow[dr, "\sum\nu_B\Delta_f H_B"] & \\
\textit{Reactants} \arrow[ur, "-\sum\nu_A\Delta_f H_A"] \arrow[rr] & & \textit{Products}
\end{tikzcd}$$

The heat of reaction is obtained if we subtract the sum of the heats of formation of the reactants from the sum of the heats of formation of the products.

$$\Delta_r H = \Delta_r(\Delta_f H) \qquad (1.46)$$

Example: $3C_2H_2 = C_6H_6$

$$\Delta_r H = \Delta_f H(C_6H_6) - 3\Delta_f H(C_2H_2)$$

1.11.Standard enthalpies

We do not try to determine the absolute values of internal energy (remember, it has not absolute value).

The standard enthalpies of compounds and elements are determined by international convention.

1. At 298,15 K (25 °C) and $p^o = 10^5$ Pa the enthalpies of the stable forms of the elements are taken zero:

$$H_m^0(298) = 0 \quad \text{(elements)} \qquad (1.47)$$

At temperatures different from 25 °C the enthalpy is not zero.

E.g. the standard molar enthalpy of an element which is solid at 25 °C but gaseous at T can be calculated as follows:

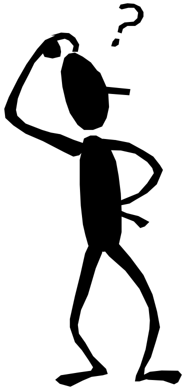
$$H_m^0(T)=\int_{298}^{\overset{\text{melting point}}{T_m}}\underbrace{C_{mp}^{s}}_{\text{Molar heat capacity of solid}}dT+\underbrace{\Delta H_m^0(fus)}_{\text{Enthalpy of fusion of solid}}+\int_{T_m}^{\overset{\text{boiling point}}{T_b}}\underbrace{C_{mp}^{l}}_{\text{Molar heat capacity of liquid}}dT+\underbrace{\Delta H_m^0(vap)}_{\text{Heat of vaporization of liquid}}+\int_{T_b}^{T}\underbrace{C_{mp}^{g}}_{\text{Molar heat capacity of gas}}dT \tag{1.48}$$

2. The standard enthalpy of a compound at 298.15 K is taken equal to its heat of formation since that of the elements is zero.

$$H_m^0(298) = \Delta_f H^0$$ **at 298 K only!** (1.49)

At any other temperature the enthalpy differs from the heat of formation.

In tables: standard molar enthalpies at 298 K and molar heat capacity (C_{mp}) functions are given.



***Question**: How can we calculate the enthalpy of reaction at temperature T?*

***Answer:** The simplest way is to calculate the enthalpy of each component at T then take the difference.*

If there is no phase change from 298 K to T,

$$H_m^0(T) = H_m^0(298) + \int_{298}^{T} C_{mp}\, dT \qquad (1.50)$$

In case of phase change(s) of elements we use the formula (1.48).

For compounds we use a formula similar to Eq. 1.48.

If the compound is solid at 25 °C but gaseous at T.

$$H^{0}_{m}(T) = H^{0}_{m}(298) + \int_{298}^{T_m} C^{s}_{mp}\,dT + \Delta H^{0}_{m}(\text{fus}) +$$

$$+ \int_{T_m}^{T_b} C^{l}_{mp}\,dT + \Delta H^{0}_{m}(\text{vap}) + \int_{T_b}^{T} C^{g}_{mp}\,dT \qquad (1.51)$$

1.12.The first law for open systems, steady state systems

In an open system (see Fig. 1.3) both material and energy exchange with the surroundings are allowed.

Technological processes are usually performed in open systems.

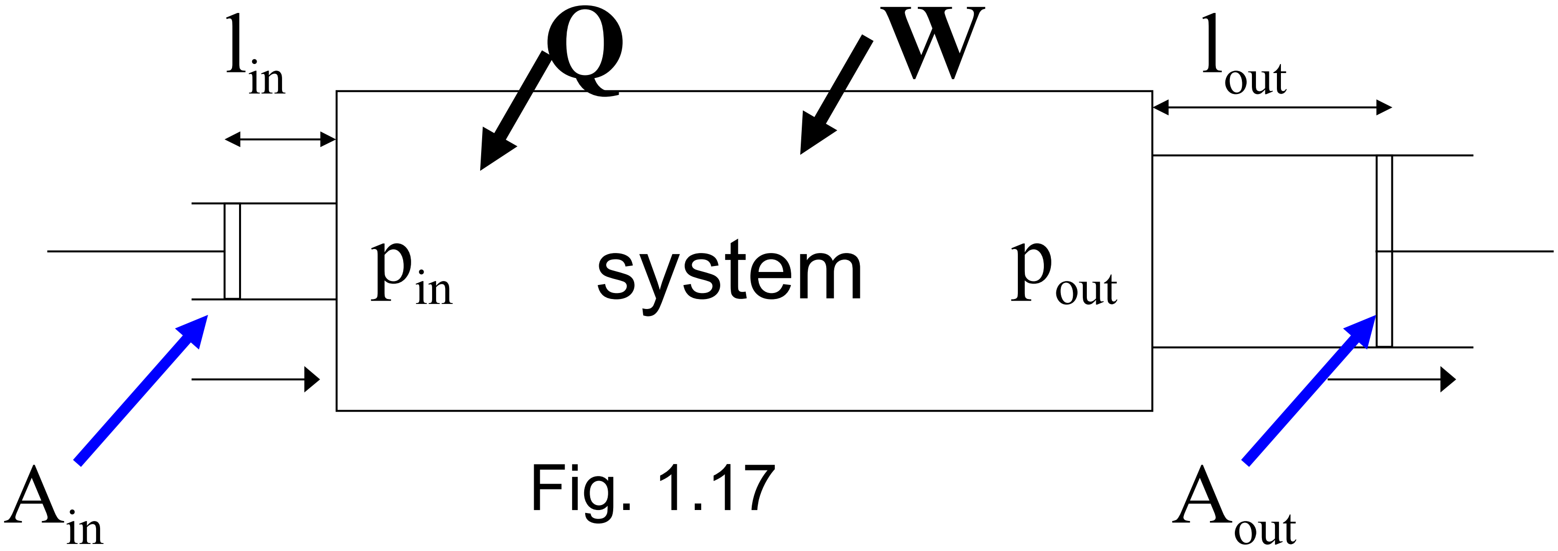


Fig. 1.17

The substances entering and leaving the system carry energy. Their transport also needs energy.

$$\Delta U = Q + W + U_{in} - U_{out} + p_{in}\overset{\mathbf{-\Delta V_{in}}}{\boxed{A_{in} l_{in}}} - p_{out}\overset{\mathbf{\Delta V_{out}}}{\boxed{A_{out} l_{out}}}$$

$$\boxed{\Delta U = Q + W + H_{in} - H_{out}} \qquad (1.52)$$

This is the first law for open systems

A ***steady state system*** *is an open system where the density of state functions change in space but* ***do not change in time****.*

Energy does not come into being and does not disappear:

$$\Delta U = 0 \qquad (1.53a)$$

$$\underset{\substack{\uparrow \\ \text{Total} \\ \text{exiting} \\ \text{enthalpy}}}{H_{out}} - \underset{\substack{\uparrow \\ \text{Total} \\ \text{entering} \\ \text{enthalpy}}}{H_{in}} = \underset{\substack{\uparrow \\ \text{Heat}}}{Q} + \underset{\substack{\uparrow \\ \text{Work}}}{W} \qquad (1.53b)$$

(balance of enthalpy)

*If there is **no chemical reaction**, H_{out} - H_{in} is the enthalpy change of the substance going through the system*

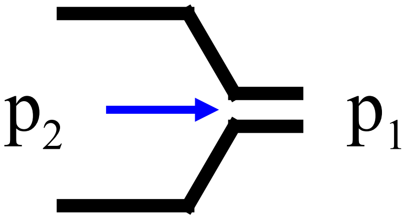
$$\Delta H = Q + W \qquad (1.54)$$

We will discuss three examples important in industry:

1) *Expansion of gases through throttle*
2) *Adiabatic compressor*
3) *Steady state chemical reaction*

1) Expansion of gases through throttle

The purpose is to reduce the pressure of the gas.



$p_2 > p_1$

Fig. 1.18

The operation is continuous, the state functions of the gas do not change in time (steady state).

Adiabatic process: $\mathbf{Q = 0}$ (1.55a)

No work done: $\mathbf{W = 0}$. (1.55b)

Applying Eq. 1.54:

$$\Delta H = 0 \qquad (1.56)$$

2) Continuous adiabatic compressor

$$Q = 0 \tag{1.57}$$

according to Eq. 1.52:

$$\Delta H = W \tag{1.58}$$

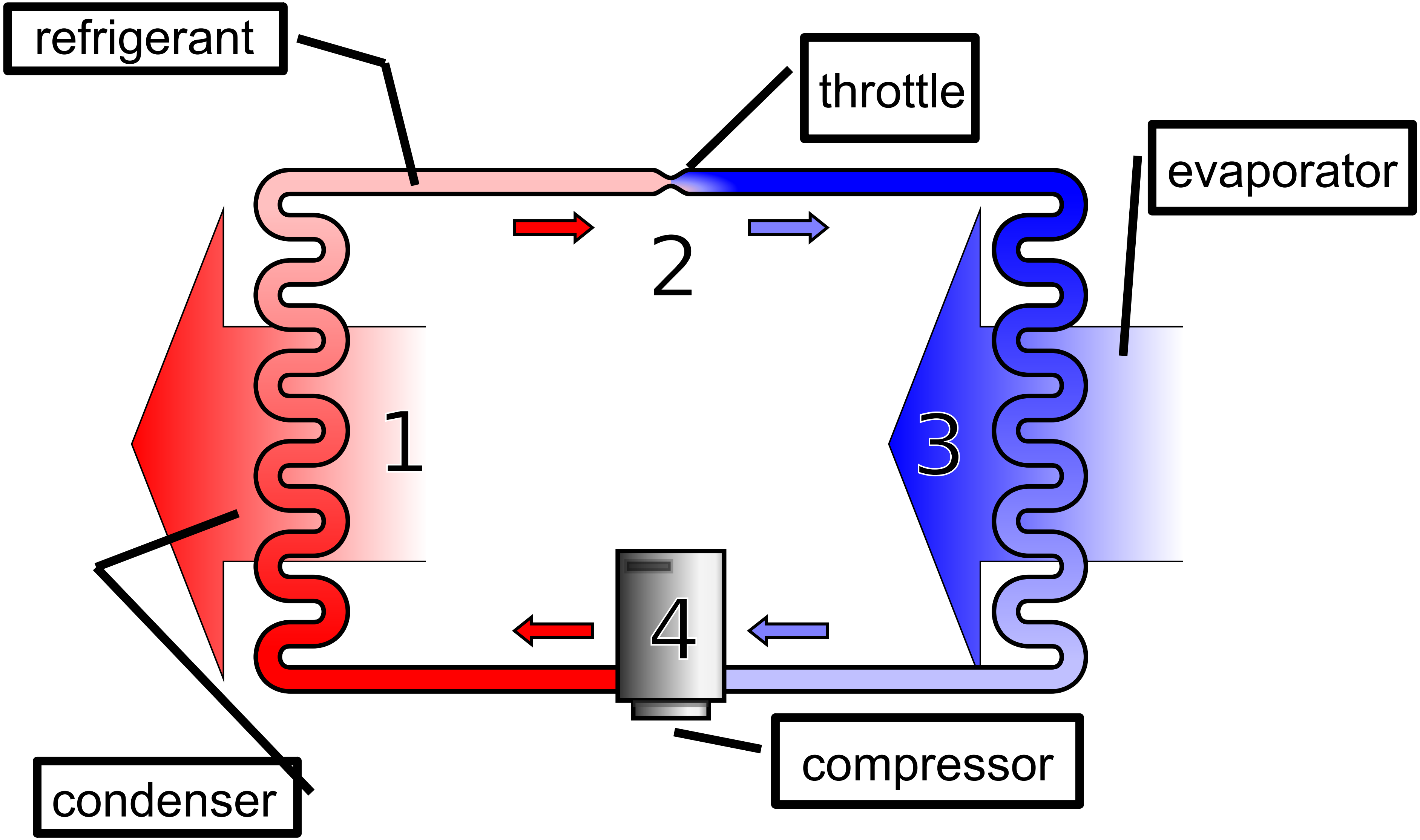
W *: the work of the compressor*

3) Steady state reactor

Applying Eq. 1.54: (1.59)

$$(H_{out} - H_{in} =) \ \Sigma n_{out} H_{m,out} - \Sigma n_{in} H_{m,in} = Q + W$$

Examples: airconditioner, refrigerator, geothermal heat pump



1.13. The second law of thermodynamics

New idea:
*Thermodynamic definition of **entropy***

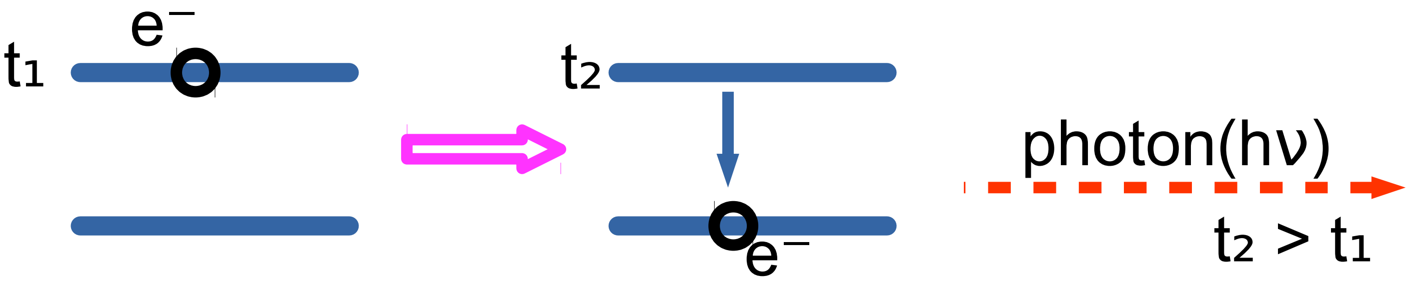
1. *law: conservation of energy. It does not say anything about the direction of processes.*

II. law: it gives information about the direction of processes in nature.

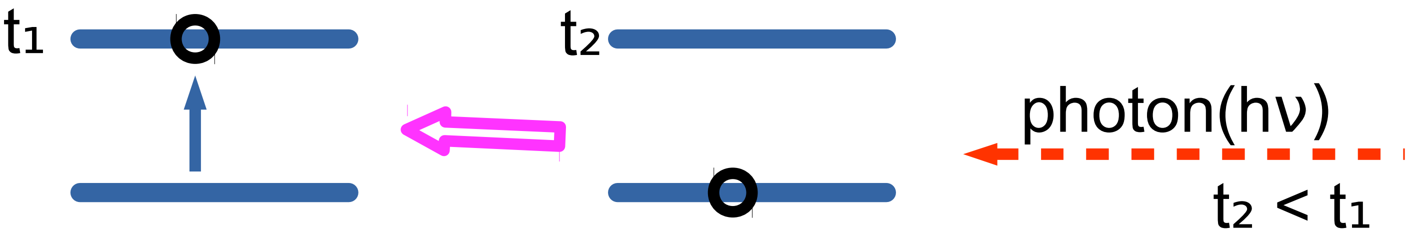
Time reversibility

At microscopic level the equations of physics are invariant to the change of time. (More precisely the CPT symmetry is the exact symmetry of nature at the fundamental level.) E.g.,

t_1



The time reversal of the above process is also possible:



Imagine the following phenomenon:

Heat transfers from the cold table to the hot water

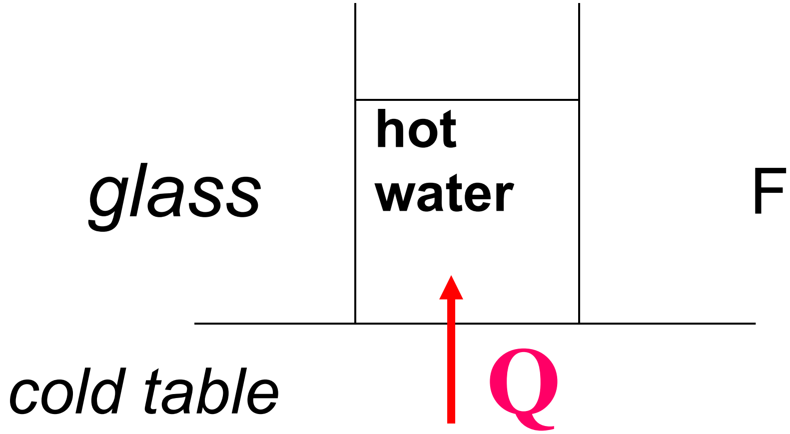


Fig. 1.19

Is that possible? **NO!**

In ***spontaneous processes*** *heat always goes from bodies of higher temperature to bodies of lower temperature.*

Processes in nature → <u>dissipation of energy</u>

Ordered → *Disordered*

We are going to define a function that expresses the extent of disorder.

We will call it **entropy**: **S**

Most important property: ***In spontaneous processes (in isolated system) it always increases.***

For definition of entropy consider the first law (Eq. 1.7):

$$dU = \delta W + \delta Q$$

It is valid both for reversible and for irreversible processes.

For a reversible process: $dU = \delta W_{rev} + \delta Q_{rev}$ (1.60)

$$\text{PV work: } \delta W_{rev} = -p \cdot dV \qquad (1.61)$$

(see Eq. 1.10)

intensive extensive

Let us express the heat, too, as a product of an intensive function of state and the infinitesimal change of an extensive function of state.

It is straightforward that the intensive parameter is the temperature. Let us denote the extensive one by S and call it entropy:

$$\delta Q_{rev} = T \cdot dS \qquad (1.62)$$

From this expression dS is

$$dS = \frac{\delta Q_{rev}}{T} \qquad (1.63)$$

This is the thermodynamic definition of entropy.

Its unit is J/K. The finite change of entropy if the system goes from state "A" to state "B"

$$\Delta S = \int_A^B \frac{\delta Q_{rev}}{T} \qquad (1.64)$$

In isothermal processes (T is constant)

$$\Delta S = \frac{1}{T}\int_A^B \delta Q_{rev} = \frac{Q_{rev}}{T} \qquad (1.65)$$

Applying the expession of the elementary heat (Equ. 1.62) and the expression of the elementary pV work (1.61) the equation 1.60 ($dU=\delta W+\delta Q$) has the form

$$\mathbf{dU = -pdV + TdS} \qquad (1.66)$$

Fundamental equation of a closed system.

*(This is the exact differential of **U** in closed systems).*

1.14. Change of entropy in closed systems

$$\Delta S = \int_A^B \frac{\delta Q_{rev}}{T}$$

We start from this expression (Eq. 1.64).

Isobaric process:

$$\delta Q_{rev} = nC_{mp}dT \qquad (1.67)$$

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_{mp}}{T} dT = n\int_{T_1}^{T_2} C_{mp} d\ln T \qquad (1.68)$$

increases at heating, decreases at cooling

Isochor process:

$$\delta Q_{rev} = nC_{mv}dT \qquad (1.69)$$

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_{mv}}{T} dT = n\int_{T_1}^{T_2} C_{mv} d\ln T \qquad (1.70)$$

increases at heating, decreases at cooling

Isothermal process: (1.65) $\longrightarrow$ $\Delta S = \frac{1}{T}\int_A^B \delta Q_{rev} = \frac{Q_{rev}}{T}$

Isothermal reversible process in an ideal gas:

$$\Delta U = 0, \quad Q = -W, \qquad W = nRT\ln\frac{p_2}{p_1} \qquad Q = -nRT\ln\frac{p_2}{p_1}$$

$$\Delta S = -nR\ln\frac{p_2}{p_1} = nR\ln\frac{V_2}{V_1}$$ (1.71) *increases at expansion, decreases at contraction*

because $\frac{p_2}{p_1} = \frac{V_1}{V_2}$

Phase transition (isothermal, isobaric processes)

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_m}$$ (1.72a)

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$ (1.72b)

increases at melting and evaporation, decreases at freezing and condensation

Change of S in closed systems

S increases	*S decreases*
warming	*cooling*
melting	*freezing*
evaporation	*condensation*
expansion	*contraction*
(mixing)	*(separation)*
(dissolving)	*(precipitation)*
DISORDER INCREASES	***DISORDER DECREASES***

1.15. The second law and entropy

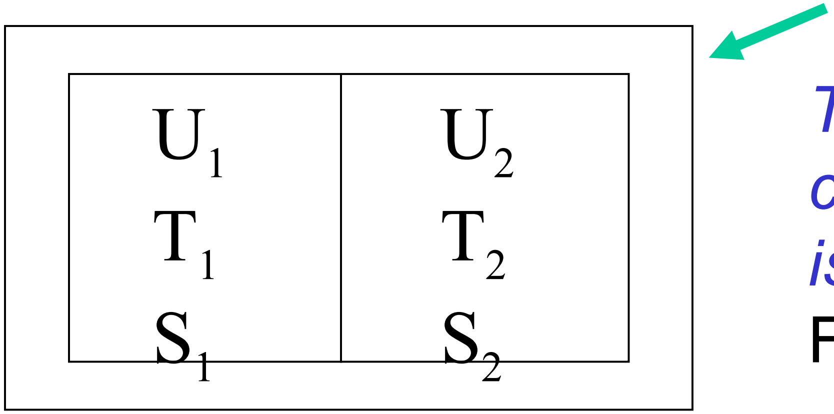
We examine how entropy changes in real (irreversible) processes.

Two examples (in isolated systems)

1. *Two bodies of different temperature are in contact. Heat goes from the body of higher temperature to the body of lower temperature.*

2. *The temperatures in the two sub-systems are equal, but the pressures are initially different*

1.



The two bodies are in thermal contact but together they are isolated from the surroundings: Fig. 1.20.

Ignore the change of volume: $dV_1 = dV_2 = 0$

First law: $dU = dU_1 + dU_2 = 0$ $\quad dU_2 = -dU_1$

$dU_1 = T_1 dS_1 \quad dU_2 = T_2 dS_2$

The overall entropy change:

$$dS = dS_1 + dS_2 = \frac{dU_1}{T_1} + \frac{dU_2}{T_2} = \frac{dU_1}{T_1} - \frac{dU_1}{T_2} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \cdot dU_1$$

$$dS = \frac{T_2 - T_1}{T_1 \cdot T_2} \cdot dU_1 \qquad (1.73)$$

$$dS = \frac{T_2 - T_1}{T_1 \cdot T_2} \cdot dU_1$$

Heat goes (spontaneously) from the higher to lower temperature place (experience).

a) If body 2 is the warmer:

$T_2 - T_1 > 0$

$dU_1 > 0$ *(because heat goes* ***to*** *body 1)*

$dS > 0$

b) If body 1 is the warmer:

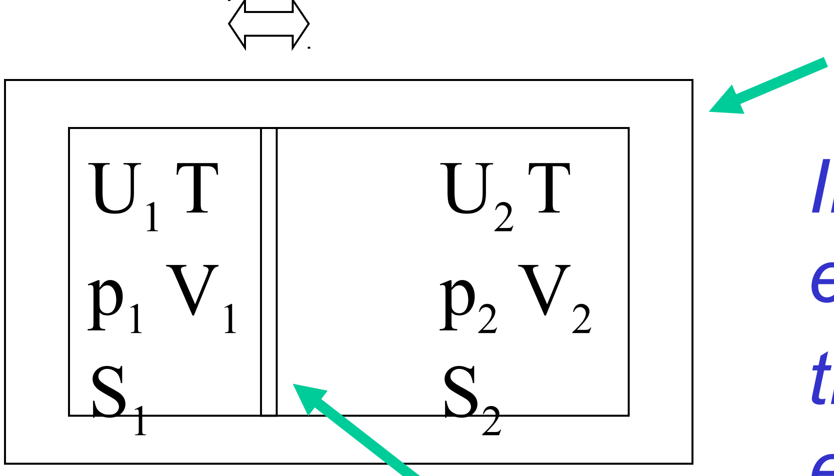
$T_2 - T_1 < 0$

$dU_1 < 0$ *(because heat goes* ***from*** *body 1)*

$dS > 0$

In both cases: $\boxed{\mathbf{dS > 0}}$ (1.74)

2.



insulation

piston

Initially there is thermal equilibrium ($T_2 = T_1$), but there is no mechanical equilibrium ($p_2 \neq p_1$) :

Fig. 1.21

Ideal gas:

$dU_2 = -dU_1$ *(because of isolation)*

$dV_2 = -dV_1$ *(the total volume is constant)*

$$dU_1 = -p_1 dV_1 + TdS_1 \qquad dU_2 = -p_2 dV_2 + TdS_2$$

$$dS_1 = \frac{1}{T} dU_1 + \frac{p_1}{T} dV_1$$

$$dS_2 = \frac{1}{T} dU_2 + \frac{p_2}{T} dV_2 = -\frac{1}{T} dU_1 - \frac{p_2}{T} dV_1$$

The overall entropy change:

$$dS = dS_1 + dS_2 = \frac{1}{T} dU_1 - \frac{1}{T} dU_1 + \left(\frac{p_1}{T} - \frac{p_2}{T} \right) dV_1$$

$$dS = \frac{p_1 - p_2}{T} \cdot dV_1 \qquad (1.75)$$

a) If $p_1 > p_2$ and $dV_1 > 0$ (the gas of higher pressure expands)

b) If $p_1 < p_2$ and $dV_1 < 0$

In both cases: $\boxed{\mathbf{dS > 0}}$ (1.76)

*In general: if a macroscopic process takes place in an isolated system, the **entropy increases**. At **equilibrium the entropy has a maximum value.***

The second law:

$$\boxed{\Delta S \geq 0} \qquad \text{(in an isolated system)} \qquad (1.77)$$

If the system is not isolated, the entropy change of the surroundings must also be taken into account:

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0 \qquad (1.78)$$

Macroscopic processes are always accompanied by the increase of entropy.

1.16. Statistical approach of entropy

S is the measure of disorder (thermodynamic definition, Eq. 1.63)

$$dS = \frac{\delta Q_{rev}}{T}$$

Is the change of S always connected to heat transfer ?

Examine the expansion of an ideal gas into vacuum!

$$Q = 0 \quad W = 0 \quad \Delta U = 0$$

We expect the increase of S. How to calculate it?

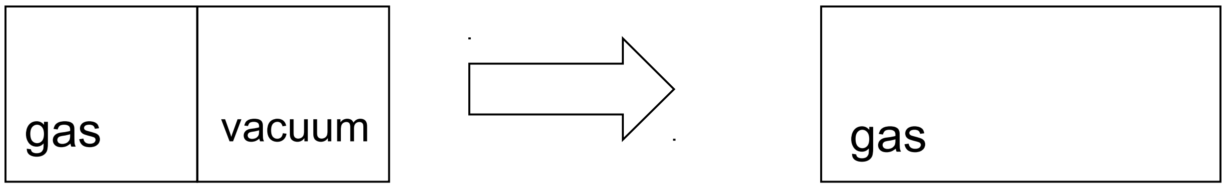


Fig. 1.22

A

The wall is removed

B

To calculate the change of S we choose a reversible path:

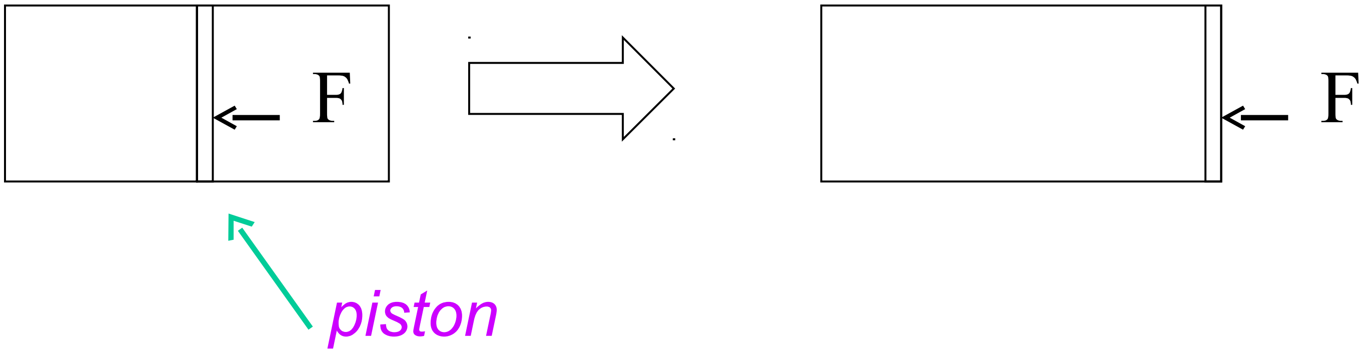


Fig. 1.23

The final state is the same but the process is performed reversibly ($W \neq 0$, $Q \neq 0$)

Isothermal reversible expansion of an ideal gas:

$$W = nRT \ln \frac{p_2}{p_1} \qquad \Delta U = 0, \quad Q = -W, \qquad Q = -\ nRT \ln \frac{p_2}{p_1}$$

$$\Delta S = -\ nR \ln \frac{p_2}{p_1} = nR \ln \frac{V_2}{V_1} \qquad (1.79)$$

Entropy increases.

The process ***A*** *→* ***B*** *goes spontaneously*

The process ***B*** *→* ***A*** *never goes spontaneously*

Why ?

To get the answer we need some ***probability calculations****.*

What is the probability of one molecule being in one half of the vessel?

Answer: 1/2

If there are two molecules, what is the probability of both being in one half of the vessel?

Answer : $(1/2)^2$

If there are N molecules, what is the probability of all being in one half of the vessel?

Answer : $(1/2)^N$

N	**Probability**
10	0.001
20	10^{-6}
100	$8 \cdot 10^{-31}$
300	$5 \cdot 10^{-91}$
$6 \cdot 10^{23}$	~ 0

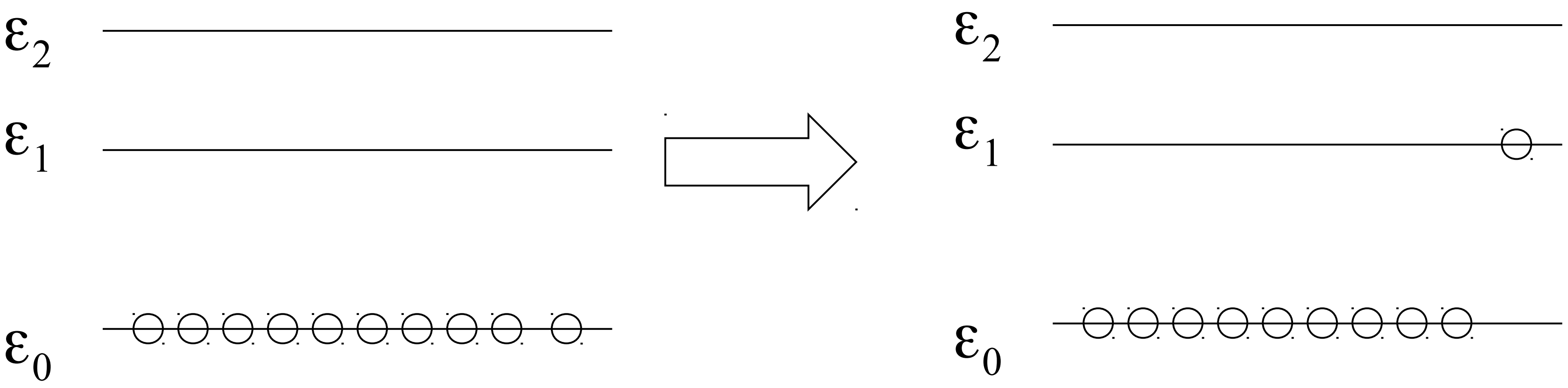
Entropy: measure of disorder.

There are two types of disorder: thermal
spatial (structural)

Thermal disorder

According to quantum theory the energies of particles are quantized.

Example: 10 particles, three energy levels, Fig. 1.25:



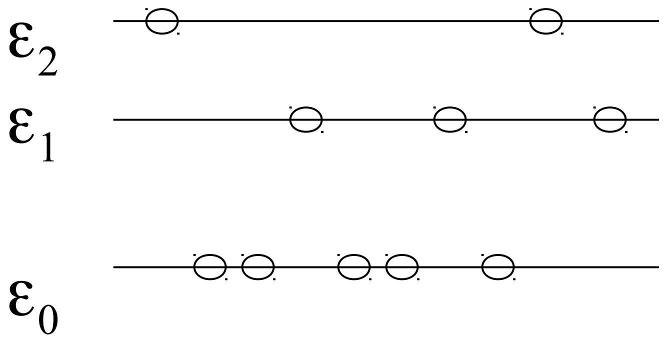
It is a single configuration, W = 1.

If one molecule is on level ε_1, the number of possibilities is 10, W=N.

In case of N molecules the number of possibilities is N.

If 2 molecules are on level ε_2, the number of possibilities is W=N(N-1)/2.

W: Statistical weight of a configuration



How to obtain the statistical weight in general?

Combination: selection of n items from a set of N elements, such that the order of selection does not matter. Number of combinations:

$$\binom{N}{n} = \frac{N!}{(N-n)!\,n!}$$

Number of combinations with repetition

$$W = \binom{N}{N_1}\binom{N-N_0}{N_1}\binom{N-N_0-N_1}{N_2}\ldots = \frac{N!}{N_0!\,N_1!\,N_2!\ldots}$$

Analogous to the number of possibilities of putting N balls in boxes so that we put N_1 in the first box, N_2 in the second one, etc.

$$W = \frac{N!}{N_0! \cdot N_1! \cdot N_2! \ \ldots} \quad (1.81)$$

N_i refers to population of energy level ε_i.

$$N = \sum_{i=0}^{n} N_i \quad (1.82) \qquad E = \sum_{i=0}^{n} N_i \varepsilon_i \quad (1.83)$$

Isolated system!

U(T)=U(0)+E

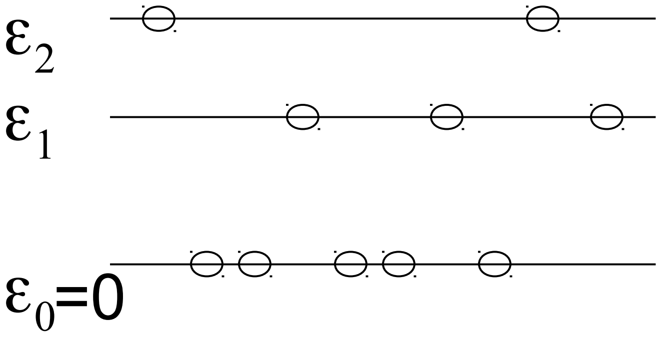


Fig. 1.26

Example: $N_0 = 5$, $N_1 = 3$, $N_2 = 2$, $N = 10$ *(a microstate)*

$$W = \frac{10!}{5! \cdot 3! \cdot 2!} = 2520$$

W is the statistical weight of a given configuration, *therefore characterizes the measure of the disorder.*

Microstate: a possible distribution of particles on the energy levels. (A microstate determines which particles are on which level.)

Macrostate: defined by the measurable properties like p, T, *etc*. It is determined by the populations of energy levels.

The TD system wanders around the possible microscopic states (fixed E and N). It is supposed that there is a state with a weight which overwhelms all the rest in importance. TD system is always found in the macroscopic state with the largest statistical weight.

W: Thermodynamic probability: the number of possible configurations of the given state.

If W is maximal $\Longrightarrow$ $\ln\left(W\right)$ is also maximal

The maxima of ln(W) with conditions $E=\sum_i \varepsilon_i N_i$ and $N=\sum_i N_i$ has to be searched.

To find the extrema of a function subjected to constrains the method of Lagrange multipliers is to use.

The Lagrange function:

$$\Lambda\left(N_0,N_1,N_{2,}\dots,\alpha,\beta\right)=\ln\left(W\left(N_0,N_1,N_{2,}\dots\right)\right)+\alpha\left(\sum_i N_i-N\right)-\beta\left(\sum_i \varepsilon_i N_i-E\right)$$

The necessary condition of the extrema with constrains:

$$\frac{\partial\Lambda}{\partial N_j}=0 \quad \text{for every j}$$

$$\frac{\partial\Lambda}{\partial\alpha}=0,\quad \frac{\partial\Lambda}{\partial\beta}=0$$

$\Longrightarrow$ Constrains are satisfied:

$$\sum_i\left(N_i-N\right)=0,\ \sum_i\left(\varepsilon_i N_i-E\right)=0$$

$$\frac{\partial\ln\left(W\right)}{\partial N_j}+\alpha-\beta\varepsilon_j=0 \qquad (\#)$$

The α Lagrange multiplier obtained from the N=*const.*

The β is obtained from the application to the ideal gas:

$\beta=\frac{1}{kT}$, $\mathrm{k}=1.380656\times10^{-23}\ \mathrm{J/K}$ Boltzmann const.

$k=R/N_A$ ⟵ Avogadro number

After a long derivation (see Atkins, Physical Chemistry) the populations for which $\ln\left(W\left(N_{1,}N_{2,}N_{3,}\ldots\right)\right)$ is maximal:

$$\frac{N_i}{N}=\frac{\exp\left(-\frac{\varepsilon_i}{kT}\right)}{q}$$

Boltzmann distribution

$$q=\sum_i\exp\left(-\frac{\varepsilon_i}{kT}\right)$$

q is the partition function

Energy of the system: $E(T)=\sum_i\varepsilon_i N_i=N\frac{\sum_i\varepsilon_i\exp\left(-\frac{\varepsilon_i}{kT}\right)}{q}$

Boltzmann formula for the entropy

In a reversible isochoric process: $dU_V = TdS$

It is supposed that the heat does not change the energies, only the populations are modified: $dU_V = \sum_i \varepsilon_i dN_i$

$$dS = dU_V/T = k\beta \sum_i \varepsilon_i dN_i =$$

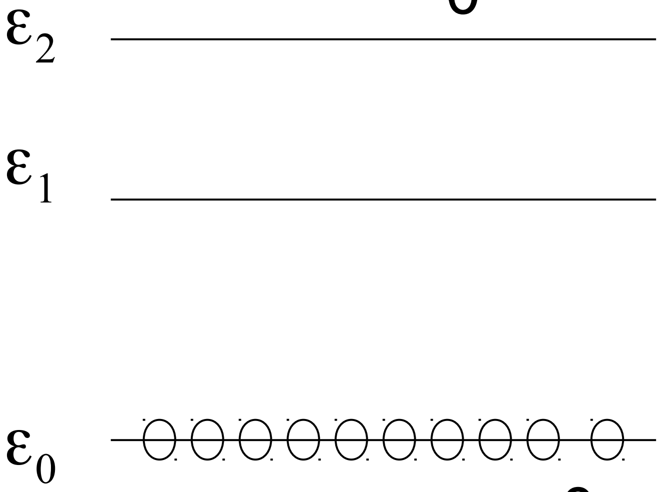
$$= k\underbrace{\boxed{\sum_i \frac{\partial \ln(W)}{\partial N_i} dN_i}}_{d\ln(W)} + \overbrace{k\alpha \sum_i dN_i}^{0\ (N=const.)}$$

(See Eq.#)

$$\Longrightarrow \quad dS = k\, d\ln(W)$$

$$\int_{S(0K)}^{S(T)} dS = k \int_{\ln(W(0K))}^{\ln(W(T))} d\ln(W(T))$$

$$N_i = N\frac{\exp\left(-\frac{\varepsilon_i}{kT}\right)}{q} \xrightarrow[0]{T} \begin{cases} 0, \text{ if } i \neq 0 \\ N, \text{ if } i = 0 \end{cases}$$



At 0 K all molecules are on level ε_0 : W = 1, thermal entropy is 0.

III. law of TD (see later) :
S(T=0K) = 0

$$S(T) - \overset{0}{S(0\,K)} = k\ln(W(T)) - \overset{0}{k\ln(W(0\,K))} \Longrightarrow$$

$$\boxed{\textit{Statistical definition:}\quad S = k\ln W} \qquad (1.80)$$

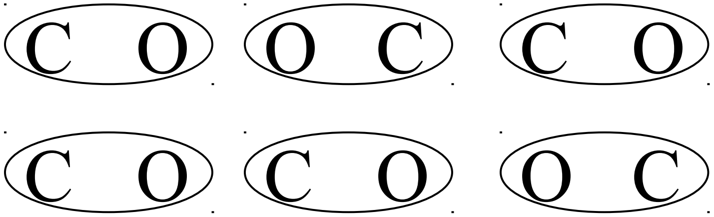
If T increases, more and more molecules get to the higher levels → W increases → S increases.


S = k. log W
LVDWIG
BOLTZMANN
1844 – 1906
DR PHIL. PAULA
BOLTZMANN
GEB. CHIARI
1891 – 1977
ARTHUR

Configuration entropy

Example: Calculate the entropy of 1 mol ***CO*** *at 0 K.*

There is no thermal entropy but there is structural disorder.



The dipole moment is small (Fig. 1.24)

Each molecule can be oriented two ways in the crystal. In 1 mol there are N_A molecules.

$$W = 2^{N_A} \rightarrow \underline{\underline{S}} = k\cdot\ln 2^{N_A} = k\cdot N_A \ln 2 = R\cdot\ln 2 = \underline{\underline{5.76\ J/K}}$$

Example: ***HCl*** *has a large dipole moment. Each molecule is oriented one way.*

At $0\ \mathrm{K}\quad W = 1,\ \ \ln W = 0,\ \underline{S = 0}.$

In case of CO we calculated the entropy arising from structur

1.17. T-S diagram

***p-V** diagram is suitable for illustrating the changes of state of gases.*

In practice we need H or S values.

For pure substances we use tables or diagrams. For describing the state it is enough to give two (properly chosen) intensive state parameters.

In technical diagrams one axis is h (kJ/kg) *or s* (kJ/kgK): **T-s** **h-p** **h-s**

T-S diagram

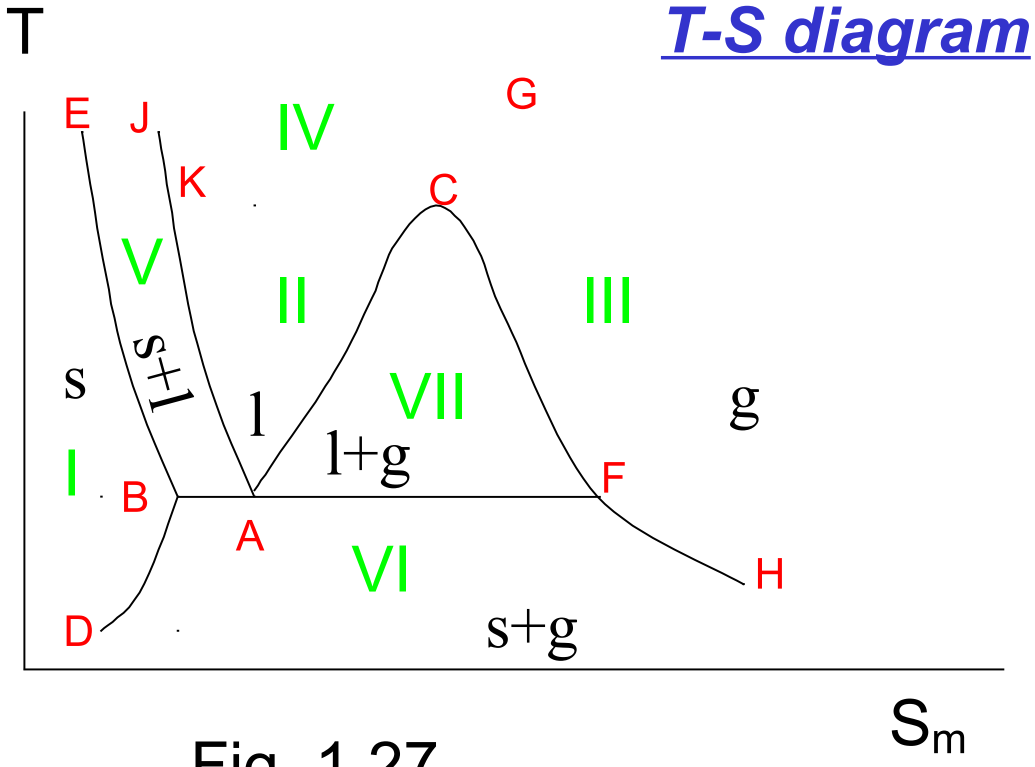


Fig. 1.27

I: solid phase
II: liquid phase
III: gas phase
IV: fluid state
V: solid-liquid
VI: solid-vapor
VII: liquid-vapor

DB: solid (in eq. with vapor)
BAF: triple point
BE: solid (in eq. with liquid)
AJ:liquid (in eq. with solid)
AC: liquid (in eq: with vapor)

CF: vapor (in eq. with liquid)
FH: vapor (in eq. with solid)
C: critical point
KCG: border of fluid state
S_m: molar entropy ($Jmol^{-1}K^{-1}$)

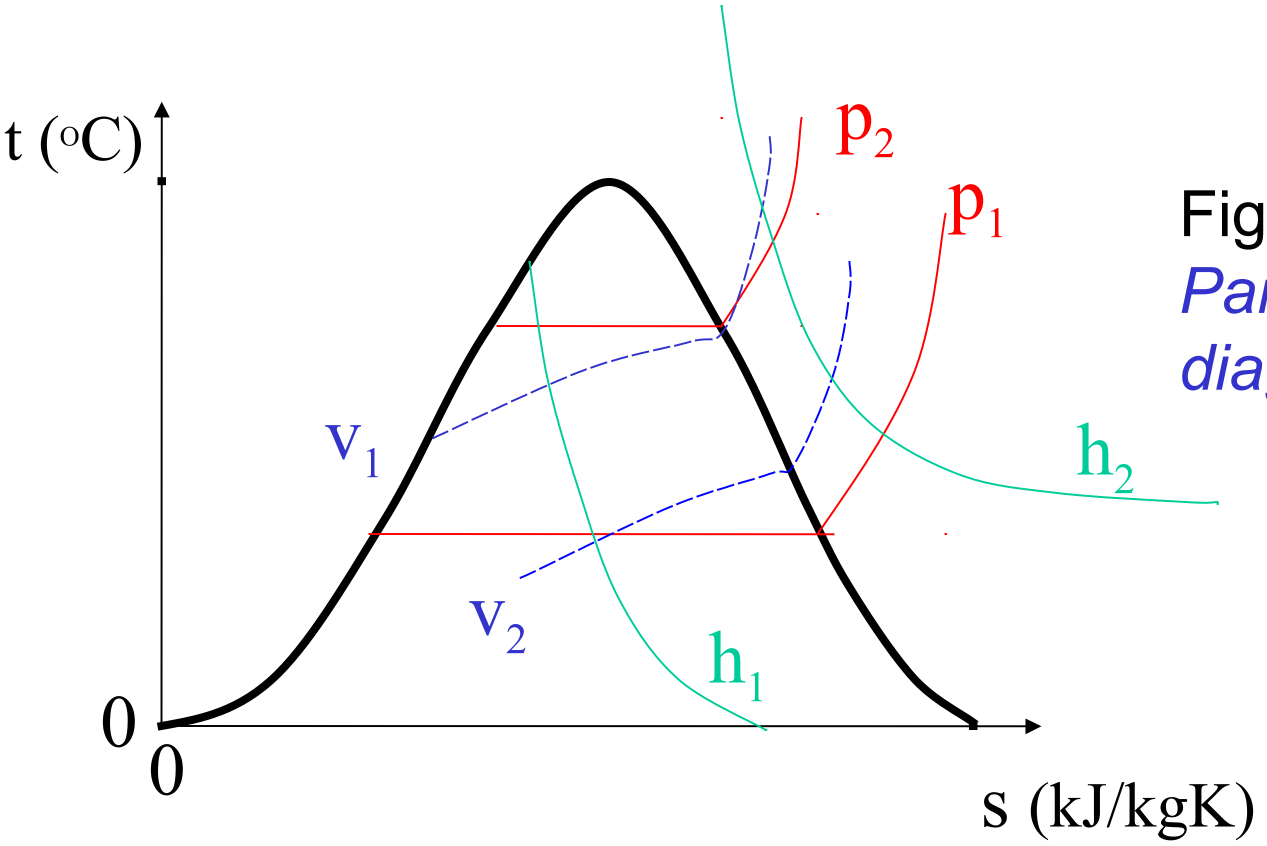


Fig. 1.28. *Part of a t-s diagram*

Isothermal $Q = T \cdot \Delta S$

Isobaric $Q = \Delta H$

Isochor $Q = \Delta U$

Adiabatic reversible $Q = 0$, $s = const.$

Adiabatic throttle $Q = 0$, $h = const.$

Calculation of work: $W = \Delta U - Q = \Delta H - \Delta(pV) - Q$ (1.84)

In steady state process: $W = \Delta H - Q$ (1.85)

Ratio of phases in mixed area: ***lever rule***

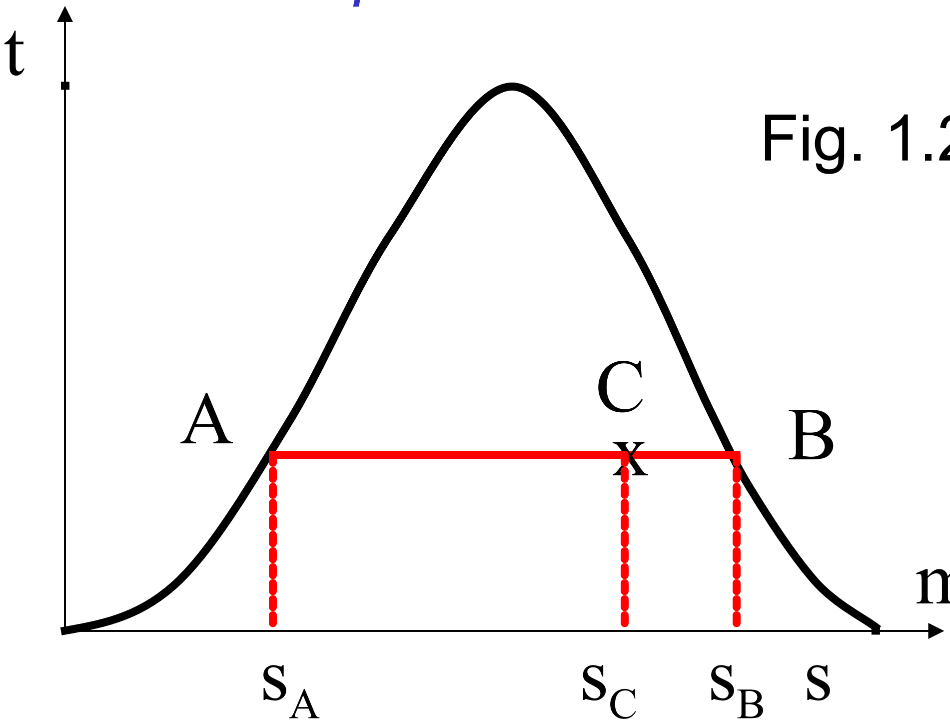


Fig. 1.29

$$m = m_A + m_B$$

$$ms_C = m_A s_A + m_B s_B$$

$$m_A s_C + m_B s_C = m_A s_A + m_B s_B$$

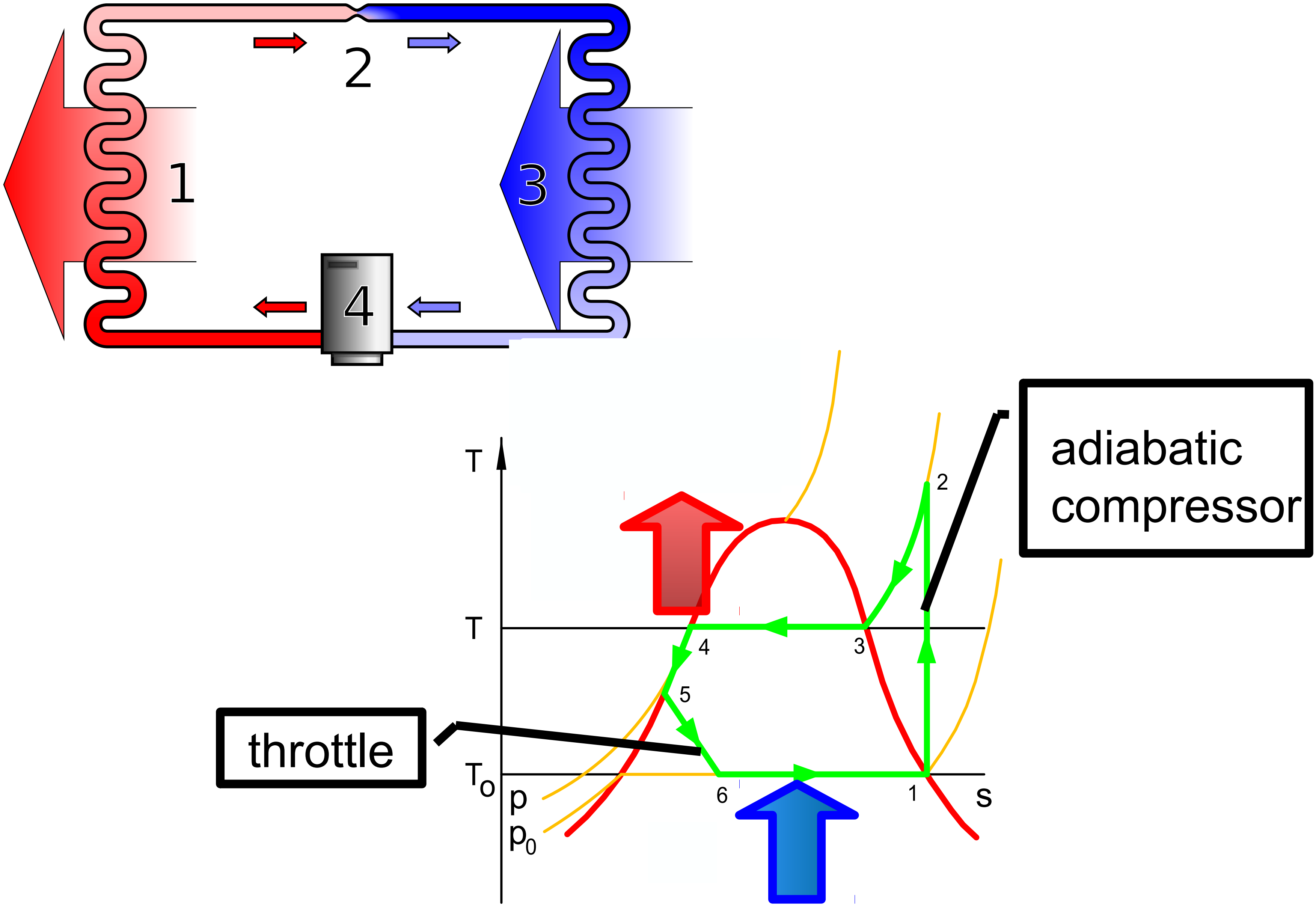
$$m_A(s_C - s_A) = m_B(s_B - s_C)$$

$$m_A \cdot \overline{AC} = m_B \cdot \overline{BC}$$

s_A: *specific entropy of liquid*

s_B: specific entropy of vapor

Example: Heat pump



adiabatic compressor

throttle

1.18. The third law of thermodynamics

Experiments to reach low temperatures

Joule-Thomson effect: gases expanding through a throtle usually cool down

Gas, boiling points at p^o:

Liquefied in the 19th century:	O_2	90 K
	N_2	77 K
	H_2	20 K
In 1908	He	4 K

For reaching lower temperatures:

adiabatic demagnetization

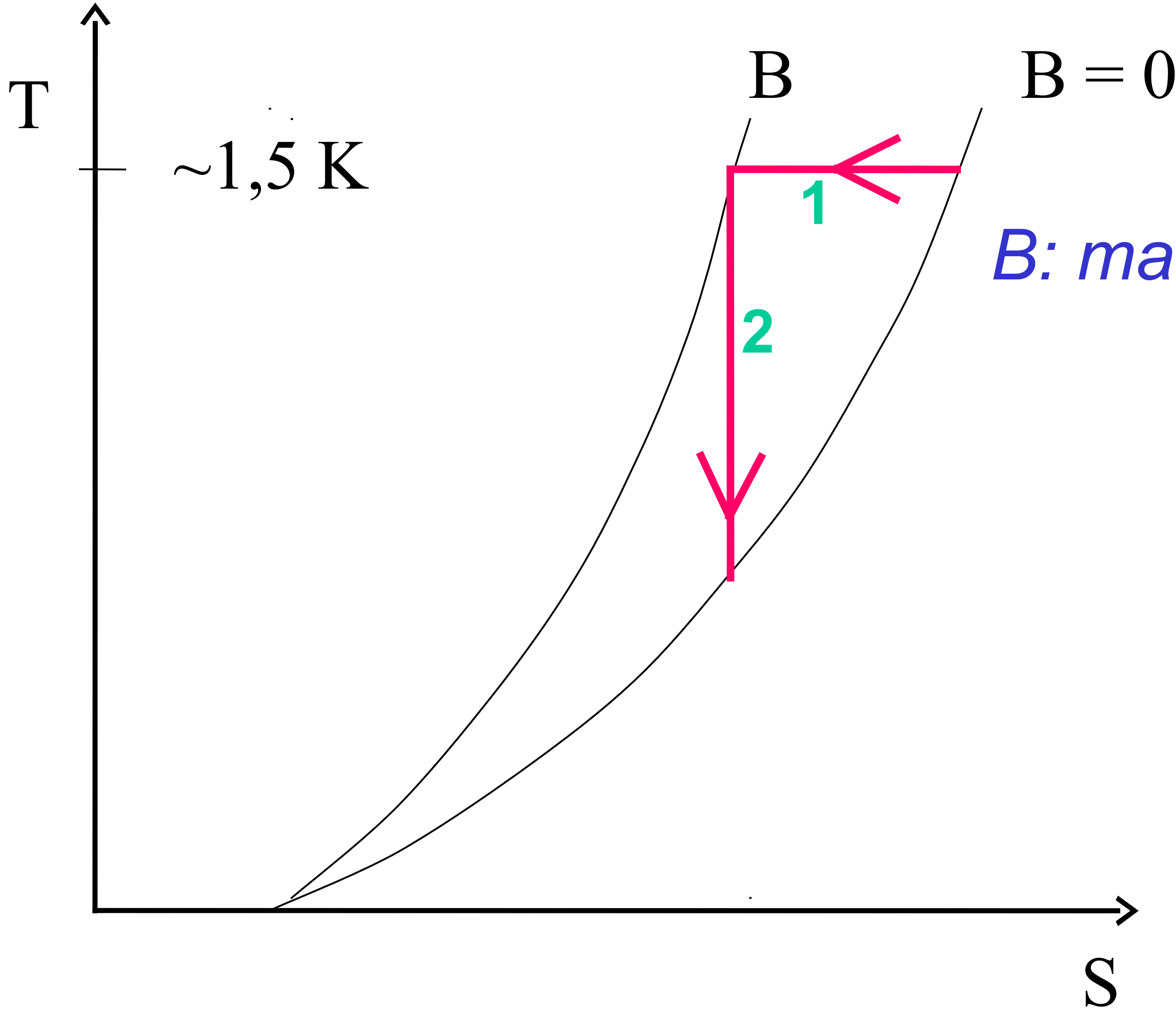
1 *Paramagnetic materials: In a magnetic field the particles act as little magnets, and are oriented in the direction of the field → order*

2 *If the magnetic field is switched off, the alignment of little magnets disappears → T decreases*

Step 1 is isothermal → S decreases

Step 2 is adiabatic → S does not change
(reversible) T decreases

The two steps on a T - S diagram



B: magnetic induction

Fig. 1.30

1. *The cell containing the paramagnetic material (e.g. gadolinium sulphate) is cooled down (by liquid helium) to about 1.5 K. Magnetic field is switched to the system*.

2. *Helium is pumped out, the magnetic field is slowly reduced to zero.*

1933: 0.25 K

1950: 0.0014 K

1995: $4.\ 10^{-8}$ K

1999: $1.0\cdot10^{-10}$ K

Repeat the isothermal and adiabatic steps several times:

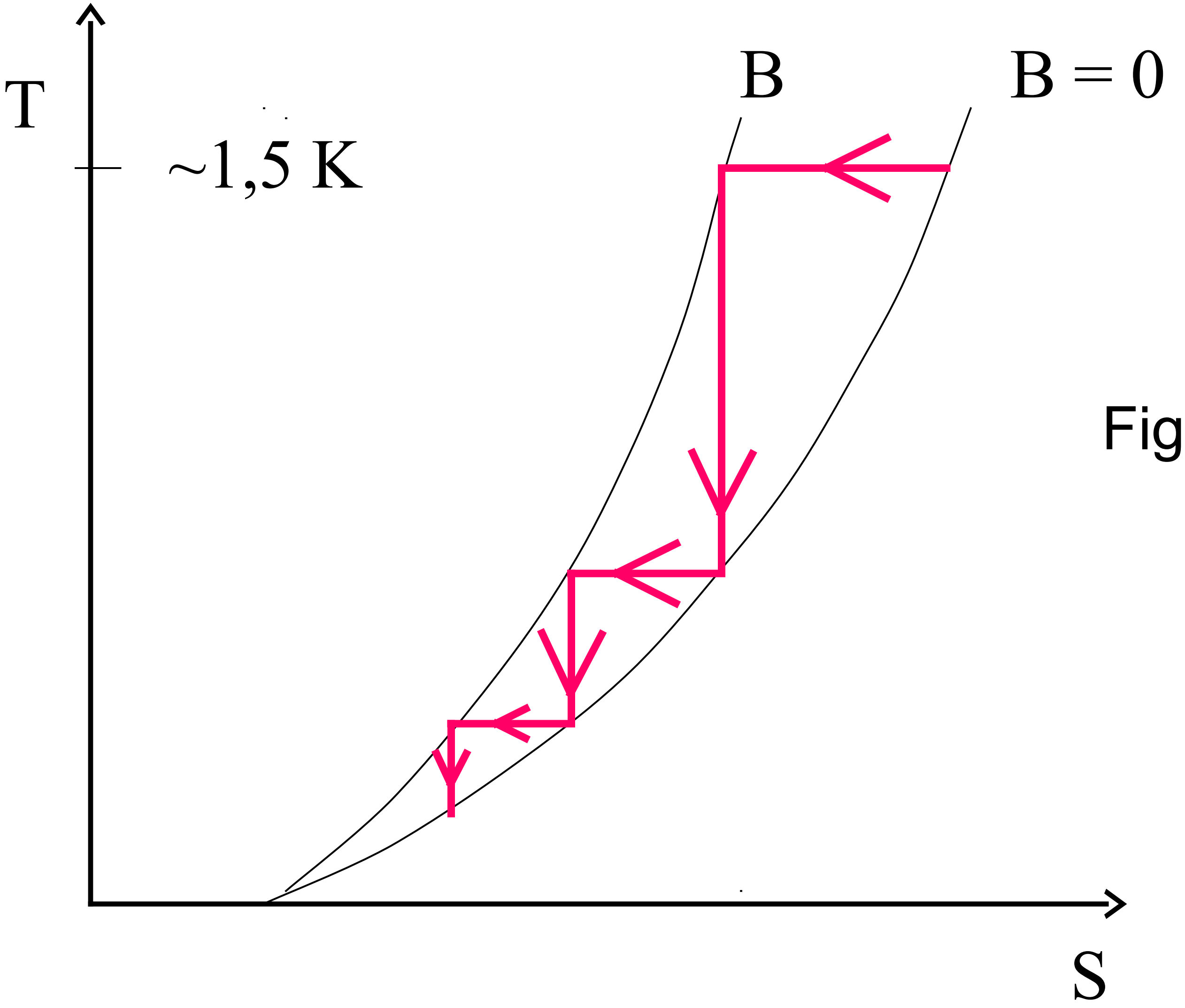
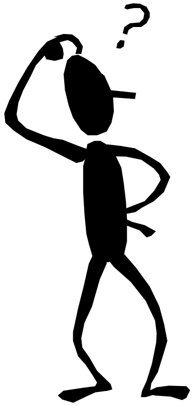


Fig. 1.31



By repeating the isothermal and adiabatic steps can we reach 0 K?

NO

*The conclusion of the experiment is one formulation of **the third law of thermodynamics:** **it is impossible in any procedure to reduce the temperature of any system to the absolute zero in a finite number of operations.***

If we approach 0 K, ΔS approaches 0.

In other isothermal processes (e.g. reactions), too, $\Delta S = 0$, if we approach 0 K.

At 0 K thermal entropy is 0.

The entropy arising from structural disorder may be greater than 0.

Examples: CO

defects in crystals

mixture of isotops (e.g. Cl_2)

An other formulation of the ***third law of thermodynamics: the zero point entropy of pure, perfect crystals is 0.***

In contrast to H and U, S has an absolute value.

Therefore we use the standard molar entropy of a substance, which is in gaseous state at temperature T:

$$S_m^0(T) = S_m^0(0) + \int_0^{T_m} \frac{C_{mp}^s}{T} dT + \frac{\Delta H_{m,fus}}{T_m} + \int_{T_m}^{T_b} \frac{C_{mp}^l}{T} dT + \frac{\Delta H_{m,vap}}{T_b} + \int_{T_b}^{T} \frac{C_{mp}^g}{T} dT \qquad (1.84)$$