

Physical chemistry:

Description of the chemical phenomena
with the help of the physical laws.

THERMODYNAMICS

It is able to explain/predict

- direction
- equilibrium
- factors influencing the way to equilibrium

Follow the interactions during the chemical reactions

VOCABULARY (TERMS IN THERMODYNAMICS)



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

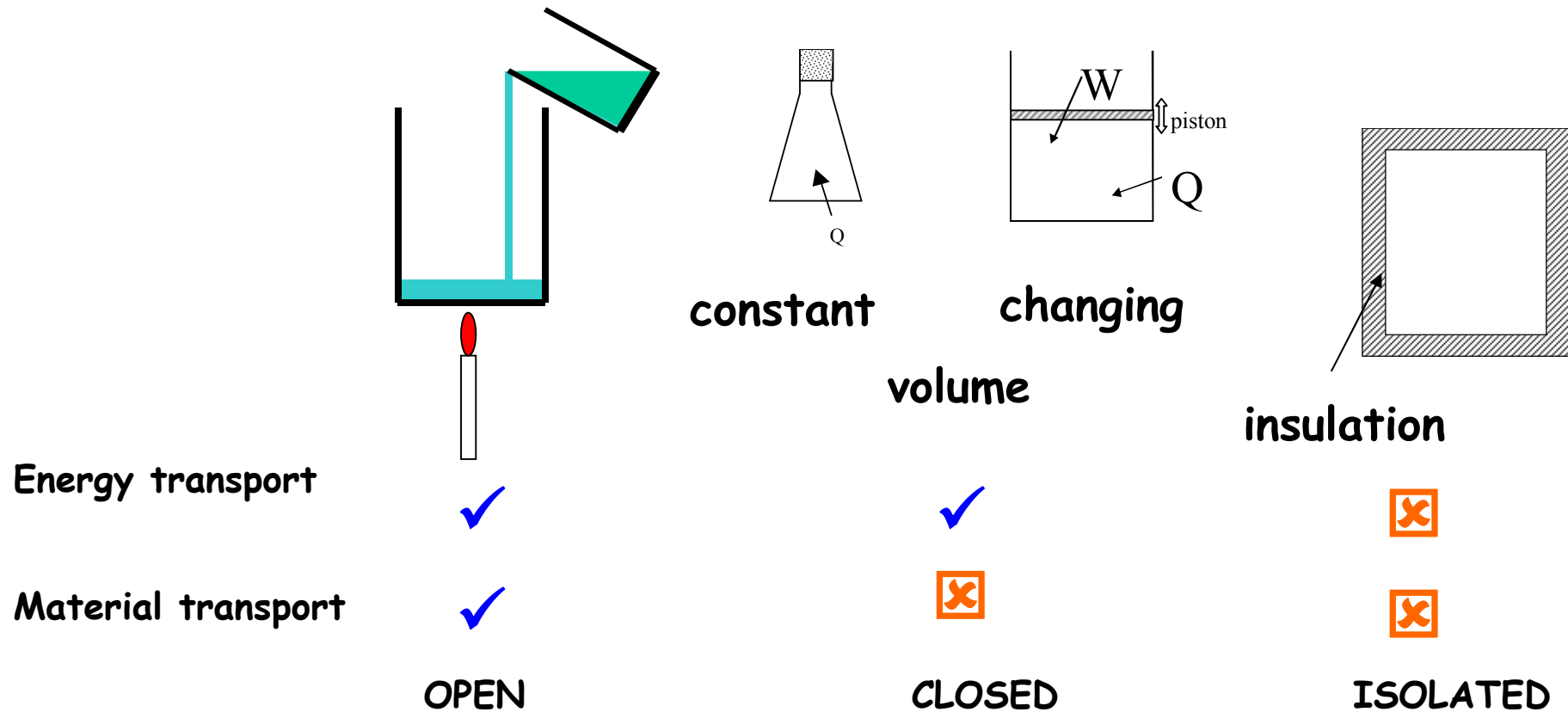
Surroundings: everything outside the system.

There are two points 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*.

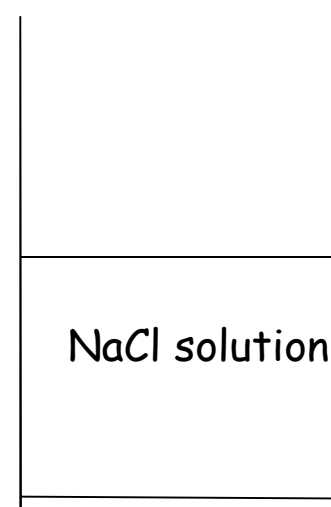
Classification based on the interactions between the system and its surrounding



Q: heat
W: work

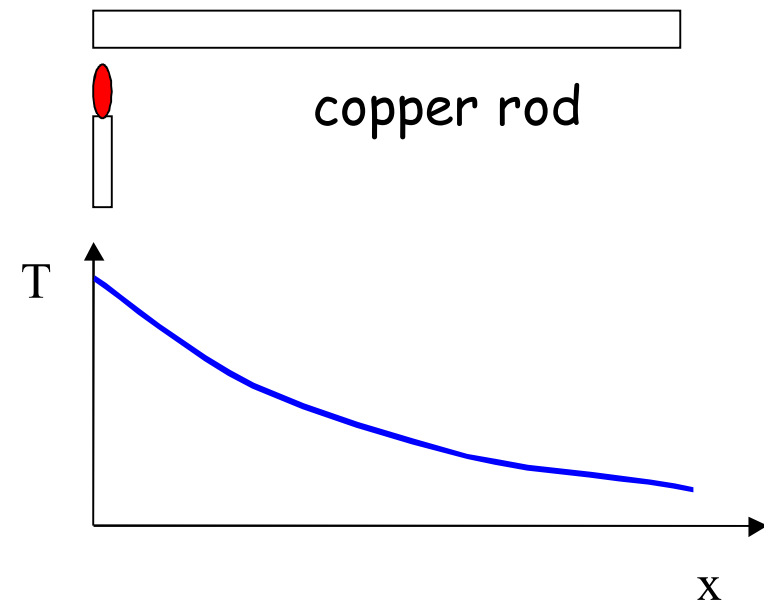
Homogeneous: macroscopic properties are the same everywhere in the system.

E.g.

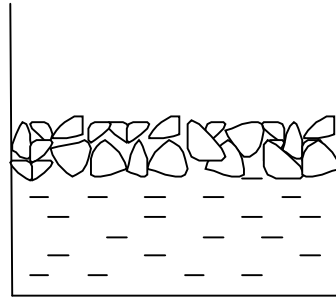


Inhomogeneous: certain macroscopic properties change from place to place; their distribution is described by continuous function.

E.g. a copper rod is heated at one end, the temperature changes along the rod.



Heterogeneous: discontinuous changes of macroscopic properties.



E.g. water-ice system

One component

Two phases

Phase: 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.

Component: chemical compound

Characterisation of the **macroscopic** state of the system

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

amount of substance: mass (m, g), chemical mass (n, mol)

- volume (V, m^3)
- pressure (p, Pa)
- temperature (T, K)
- concentration ($c, mol/L; x, -$)

State equation: relationship between the characteristics

e.g.: $pV = nRT$

$$R = 8.314 \text{ J/molK}$$

also diagrams

Classification of thermodynamic quantities:

Extensive quantities:

depend on the extent of the system and are additive:

mass (m)

volume (V)

internal energy (U), etc.

Intensive quantities:

do not depend on the extent of the system and are not additive :

temperature (T)

pressure (p)

concentration (c)

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

In a **non-equilibrium** system the state functions 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.

The following processes are frequently studied:

isothermal ($T = \text{const.}$)

isobaric ($p = \text{const.}$)

isochoric ($V = \text{const.}$)

adiabatic ($Q = 0$)

State function: a property of a system that depends only on the current state of the system, not on the way in which the system acquired that state (independent of path). A state function describes the equilibrium state of a system.

Important state functions in thermodynamics:

U - internal energy

H - enthalpy

S - entropy

A - Helmholtz free energy

G - Gibbs free energy

U, H, A, G
 S

change: Δ, d ; joule, J; kJ
J/K

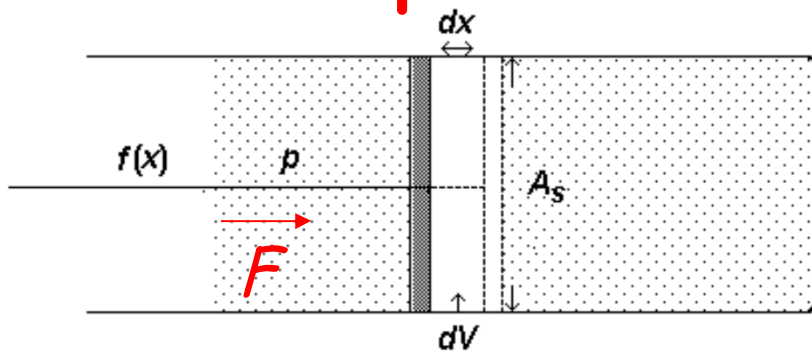
Process quantities: their values depend on the specific *transition* (or path) between two equilibrium states.

W, Q

$\delta W, \delta Q$; joule, J; kJ

Work as a process function

$$W_{mech} = \vec{F} \cdot \vec{\ell}$$

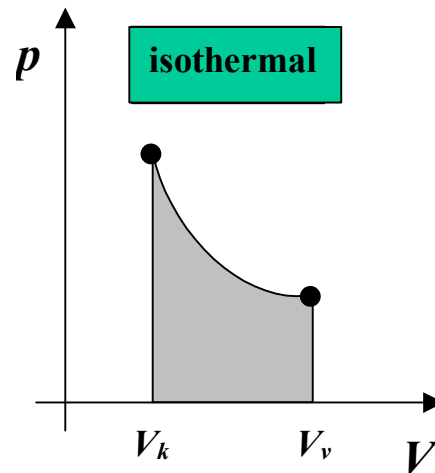


$$\delta W_{vol} = -pA_s dx = -pdV$$

sign convention

$$\delta W_{vol} = -pdV$$

$$W_{vol} = -\int_{V_i}^{V_f} pdV$$



$$\int \frac{1}{x} dx = \ln|x| + c$$

$$W_{vol} = -\int_{V_i}^{V_f} pdV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV =$$

$$= -nRT \ln \frac{V_f}{V_i}$$

isothermal work

$$W_{vol} = W_{vol,ibar} + W_{vol,ichor} =$$

$$= -p(V_f - V_i) + 0 =$$

$$= -p\Delta V$$

isobaric work

THE INTERNAL ENERGY

The energy of the system

$$E = E_{pot} + E_{kin} + U$$

$$E_{pot} = m \cdot g \cdot h$$

$$E_{kin} = \frac{1}{2} m \cdot v^2$$

The internal energy

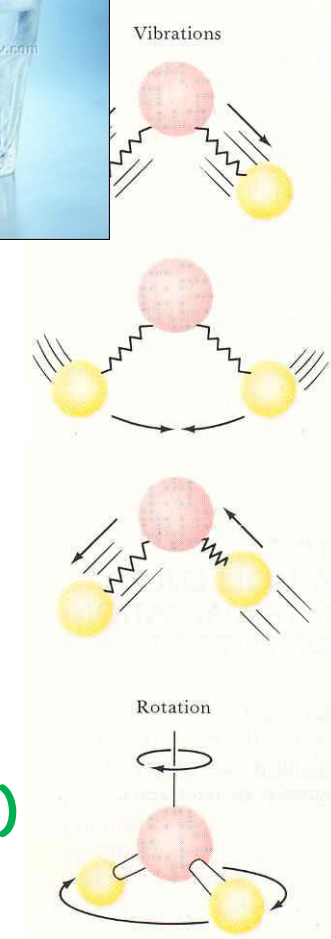
$$U = U_0 + U_{trans} + U_{rot} + U_{vibr} + U_{inter}$$

chemical structure

(e.g. nucleus, chem. bonds)

thermal energy

intermolecular interactions



The absolute value of the internal energy U cannot be determined
only its change ΔU

Interactions among particles

Strong

nuclear energy

1

Electromagnetic

10^{-2}

among particles having charges or electric/magnetic momentum

Coulomb 80-100 RT

H-bridge 10-15 RT

van der Waals 0.5-20 RT

dispersion

hydrophobic

Weak

10^{-14}

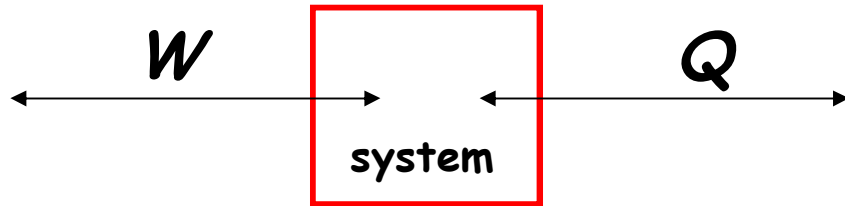
nuclear reaction, thermonuclear fusions

Gravitational

10^{-39}

significant in cosmic ranges

The FIRST LAW OF THERMODYNAMICS expresses the conservation of energy



Isolated system: $dU = 0$

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

If no work:

$$dU = \delta Q$$

WORK: in general the work can be expressed as the product of an intensive quantity and the change of an extensive quantity:

Type of 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 (or potential function) is the gradient of the intensive parameter belonging to the process.

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*.

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

Processes accompanied by heat transfer:

- A) Heating, cooling
- B) Phase change
- C) Chemical reaction

A) Heating, cooling

$$Q = n \cdot \int_{T_1}^{T_2} C_m dT$$

C_m : molar heat capacity

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

$$Q_p = n \int_{T_1}^{T_2} C_{mp} dT \quad Q_v = n \int_{T_1}^{T_2} C_{mv} dT$$

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

The difference is the most significant in case of gases

If $C_m \neq f(T)$ $Q = n \cdot C_m \cdot \Delta T$

B) Phase transition

Phase changes are isothermal **and** isobaric processes.

Heat of.... (latent heat)
evaporation - condensation
melting - freezing
sublimation - condensation

Molar heat of...

C) Chemical reaction (see later)

Processes at constant volume are well characterized by the internal energy. In chemistry (and in the environment) constant pressure is more frequent than constant volume. Therefore we define a state function which is suitable for describing processes at constant pressure:

$$H \equiv U + pV \quad \text{enthalpy}$$

THE CHARACTERISTICS OF THE ENTHALPY FUNCTION

Extensive quantity (depends on the amount of the material)

State function: similarly to the internal energy U only its change ΔH is known, not the absolute value

$$\Delta H = H_f - H_i = \int_f^i dH$$

It can be deduced that in isobaric conditions ($p=\text{const.}$)
if only pV work takes place:

$$dH = \delta Q$$

thus the change of enthalpy during

1- Isobaric heating/cooling

$$\Delta H = Q_p = n \int C_{m,p}(T) \cdot dT$$

The molar heat capacity is generally expressed as a polynomial:

$$C_{m,p} = a + bT + cT^{-2} + d \cdot T^2$$

After substituting into the integral expression:

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

2- Phase transition: isobaric+isothermic

e.g.: molar enthalpy (=heat) of vaporisation; symbol: $\Delta H_m(\text{vap})$

3- Chemical reactions

$\Delta_r H$ enthalpy (=heat) of reaction

Chemical reaction: the electron energies connected to chemical bonds change.

E.g. in the reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ the H-H and O-O bonds break and O-H bonds are formed.

The **heat of reaction** is the heat entering the system (or released from the system) if the amounts of substances expressed in the reaction equation react at constant temperature.

Exothermic: energy is released

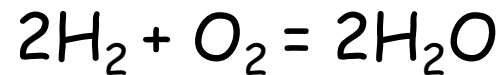
Endothermic: energy is needed to perform the reaction at constant temperature

When a chemical reaction is performed, according to the heat involved (exo, endo) and the conditions set (eg., adiabatic, isothermal):

	adiabatic ($Q = 0$)	isothermal ($T = \text{const.}$)
exothermic	T increases	Heat is released
endothermic	T decreases	Heat is absorbed

The heat of the reaction can be expressed by the enthalpy $\Delta_r H$ (at constant pressure).

Each component has an enthalpy. For a reaction to obtain the enthalpy change during the reaction we have to calculate the Δ between the final and the initial state:



$$\Delta_r H = 2H_m(\text{H}_2\text{O}) - 2H_m(\text{H}_2) - H_m(\text{O}_2)$$

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

To avoid the confusion standardisation of the database is needed.

Standard heat of reaction: is the heat entering the reactor (or leaving 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° pressure.

The standard state will always be denoted by a superscript 0

Standard pressure:

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

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

A generalized approach:

A general reaction equation: $\sum v_A M_A = \sum v_B M_B$

v : stoichiometric coefficient,

M : molecules,

A : for reactants, B for products.

The standard heat of reaction (enthalpy of reaction):

$$\Delta_r H^0 = \sum_B v_B H_{mB}^0 - \sum_A v_A H_{mA}^0$$

H_m^0 is the standard molar enthalpy of the substances



$$\Delta_r H^0 = 2H_m^0(\text{H}_2\text{O}) - 2H_m^0(\text{H}_2) - H_m^0(\text{O}_2)$$

We have to specify the reaction equation, the state of the compounds and the temperature

Reaction	Standard reaction enthalpy at 25 °C
$2 \text{H}_2(\text{g}) + \text{O}_2 (\text{g}) = 2 \text{H}_2\text{O}(\text{l})$	-571.6 kJ
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{H}_2\text{O}(\text{l})$	-285.8 kJ
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2 (\text{g}) = \text{H}_2\text{O}(\text{g})$	-241.9 kJ

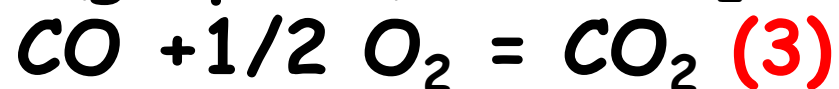
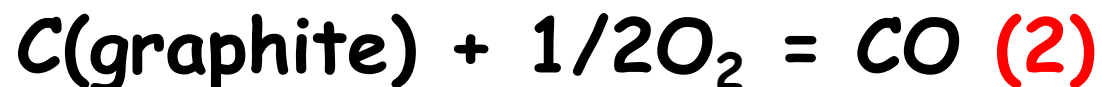
As enthalpy is a state function its change depends on the initial and final states only. This statement is also valid for the reaction enthalpy.

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

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



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



$$\Delta_rH(1) = \Delta_rH(2) + \Delta_rH(3)$$

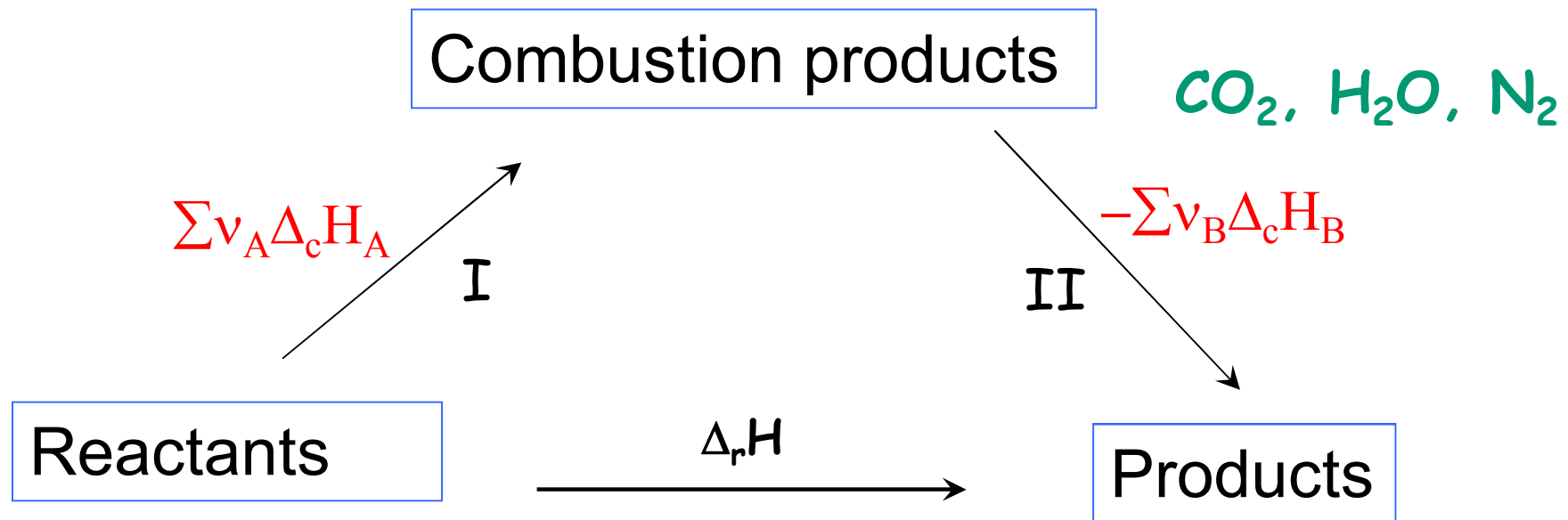
So if we know two of the three reaction enthalpies, the third one can be calculated.

Most data available are heats of combustion or heats of formation. Let's see how these data can be used to calculate the heat of a reaction

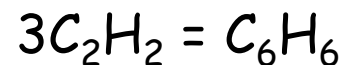
Heat of reaction from heat of combustion data

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

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



$$\Delta_r H = \Delta_r H(I) + \Delta_r H(II) = \sum v_A \Delta_c H_A - \sum v_B \Delta_c H_B = -\Delta_r(\Delta_c H)$$



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

Heat of formation

The heat (enthalpy) of formation ($\Delta_f H$) of a compound is the enthalpy change occurring when the compound is built up from (the most stable forms of) its elements.

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



It follows from the definition that the heat of formation of an element is zero (at 298 K).