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.

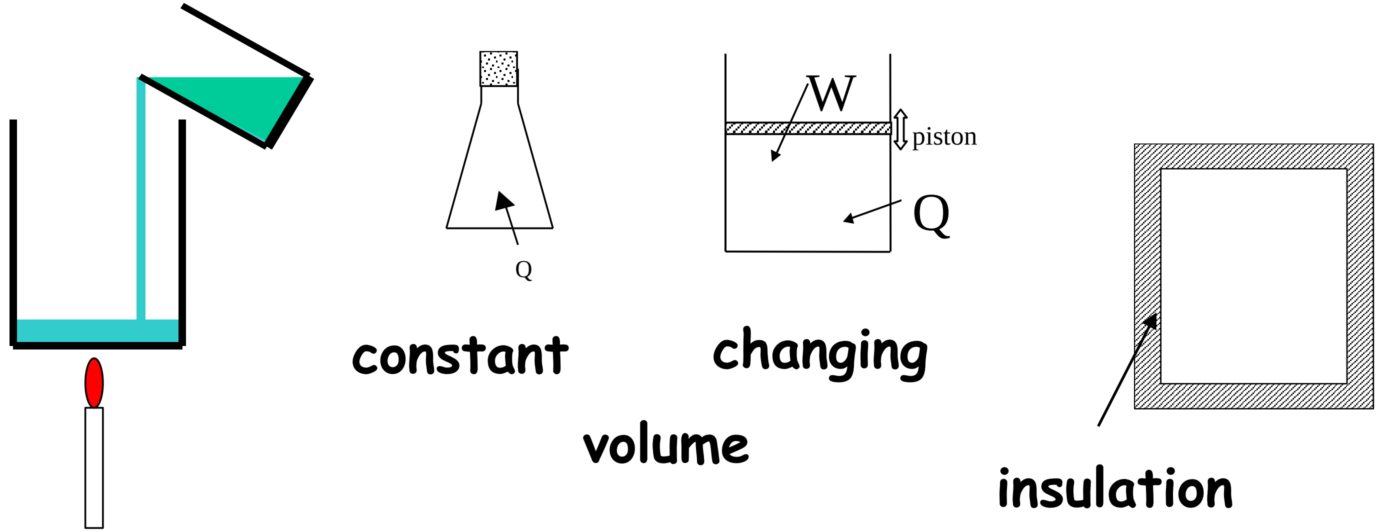
Surroundings: everything outside the system.

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

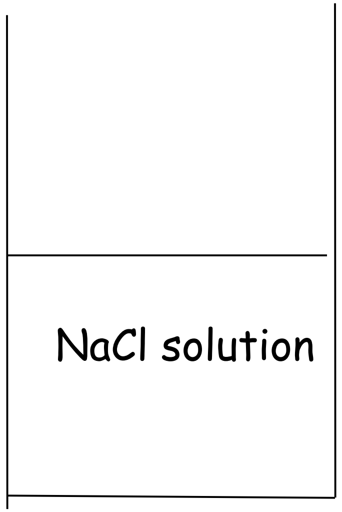


	OPEN	CLOSED	ISOLATED
Energy transport	✓	✓	☒
Material transport	✓	☒	☒

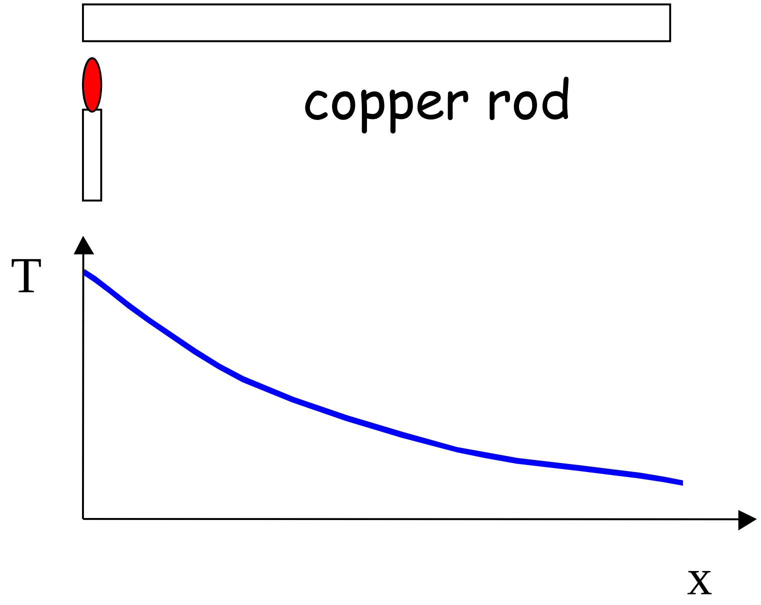
Q: heat
W: work

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

E.g.

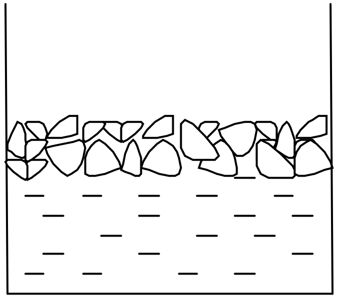


Inhomogeneous: certain macroscopic properties change from place to place; their distribution is described by continuous function.



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 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 = const.)
isobaric (p = const.)
isochoric (V = 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 change: Δ, d; joule, J; kJ

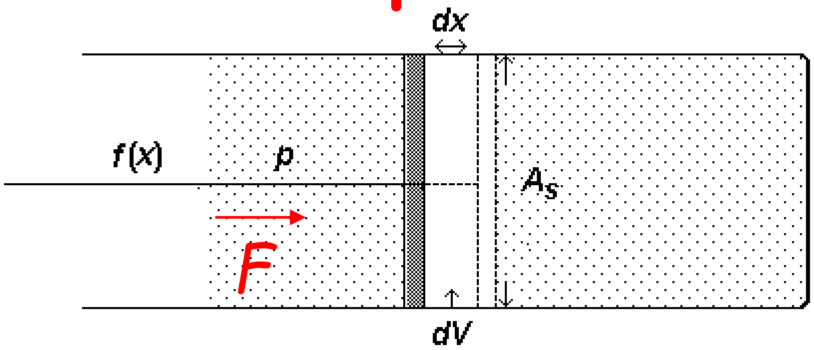
S J/K

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

W, Q δW, δQ; joule, J; kJ

Work as a process function

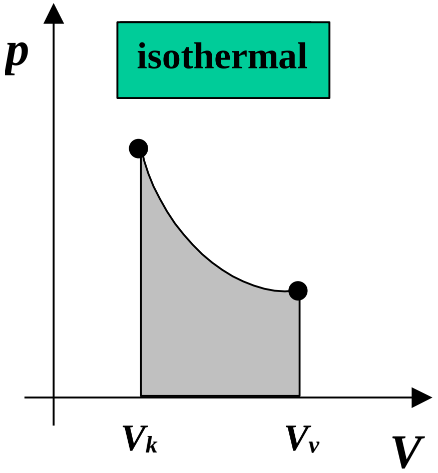
$$W_{mech} = \vec{F} \cdot \vec{\ell}$$

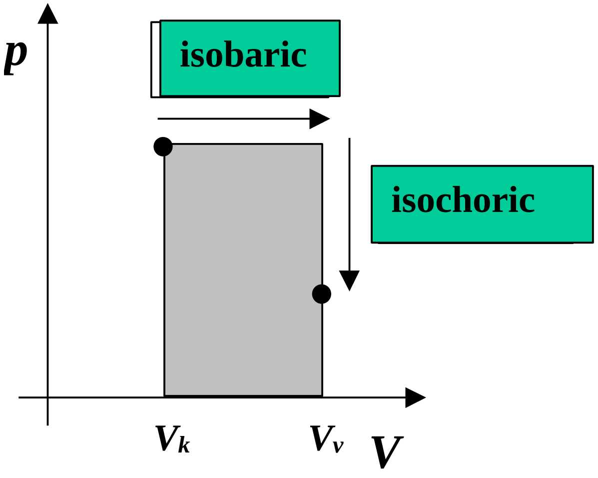


$$\delta W_{vol} = -pA_s dx = -pdV$$

sign convention

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





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

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

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

isothermal work

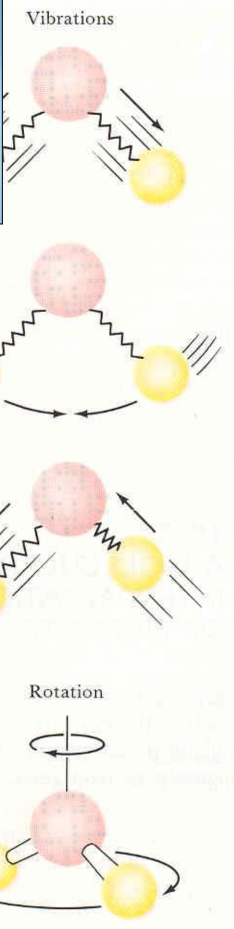
$$W_{vol} = W_{vol,ibar} + W_{vol,ichor} =$$

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

$$= -p\Delta V$$

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 among particles having charges or electric/magnetic momentum

10^{-2}

Coulomb	80-100 RT
H-bridge	10-15 RT
van der Waals	0.5-20 RT
dispersion	
hydrophobic	

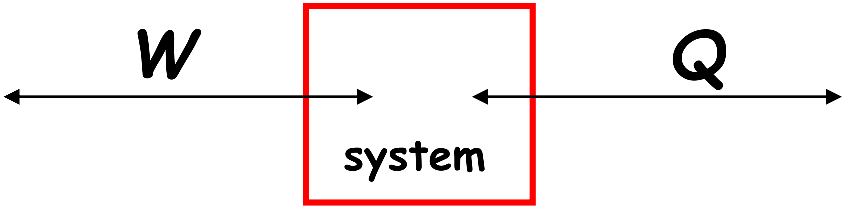
Weak nuclear reaction, thermonuclear fusions

10^{-14}

Gravitational significant in cosmic ranges

10^{-39}

The FIRST LAW OF THERMODYNAMICS expresses the conservation of energy



Isolated system: $dU = 0$

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

If no work: $\boxed{dU = \delta Q}$

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 <u>not</u> a state function.
We have to specify the path.

Processes accompanied by heat transfer:

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

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:

$$\boxed{H \equiv U + pV}$$

enthalpy

THE CHARACTERSITICS 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=const.) if only pV work takes place:

$$\boxed{dH = \delta Q}$$

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:

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

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

The difference is the most significant in case of gases

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

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)

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 polynom:

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

After substituting into the integral expression:

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

2- Phase transition: isobaric+isothermic

e.g.: molar enthalpy (=heat) of vaporisation; symbol: ΔH_m(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 $2H_2 + O_2 = 2H_2O$ 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 = 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:

$$2H_2 + O_2 = 2H_2O$$

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

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

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 **amount**s 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:

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

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

A generalized approach:

A general reaction equation: $\sum \nu_A M_A = \sum \nu_B M_B$

ν : stoichiometric coefficient,
M: molecules,
A: for reactants, B for products.

The standard heat of reaction (enthalpy of reaction):

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

H^0_m is the standard molar enthalpy of the substances

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, the state of the compounds and the temperature

Reaction	Standard reaction enthalpy at 25 °C
$2\ H_2(g) + O_2\ (g) = 2\ H_2O(l)$	-571.6 kJ
$H_2(g) + \frac{1}{2}\ O_2\ (g) = H_2O(l)$	-285.8 kJ
$H_2(g) + \frac{1}{2}\ O_2\ (g) = H_2O(g)$	-241.9 kJ

As enthalpy is a state function its change depends on the initial and final states only. This stateÍment 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.**

Example: C(graphite) + O_2 = CO_2 (1)

The reaction enthalpy of this reaction 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)

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

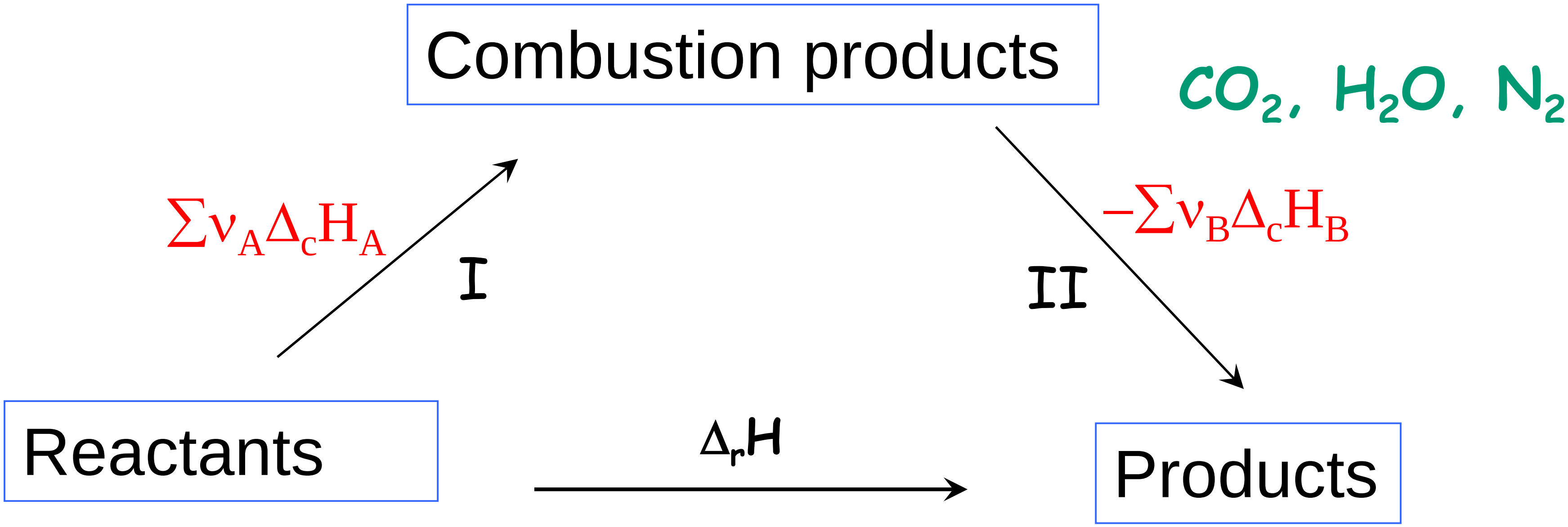
So if we know two of the three reaction enthalpies,the third one can be calculated.

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



$$\Delta_r H = \Delta_r H(I) + \Delta_r H(II) = \sum \nu_A \Delta_c H_A - \sum \nu_B \Delta_c H_B = -\Delta_r(\Delta_c H)$$

$$3C_2H_2 = C_6H_6$$

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

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.

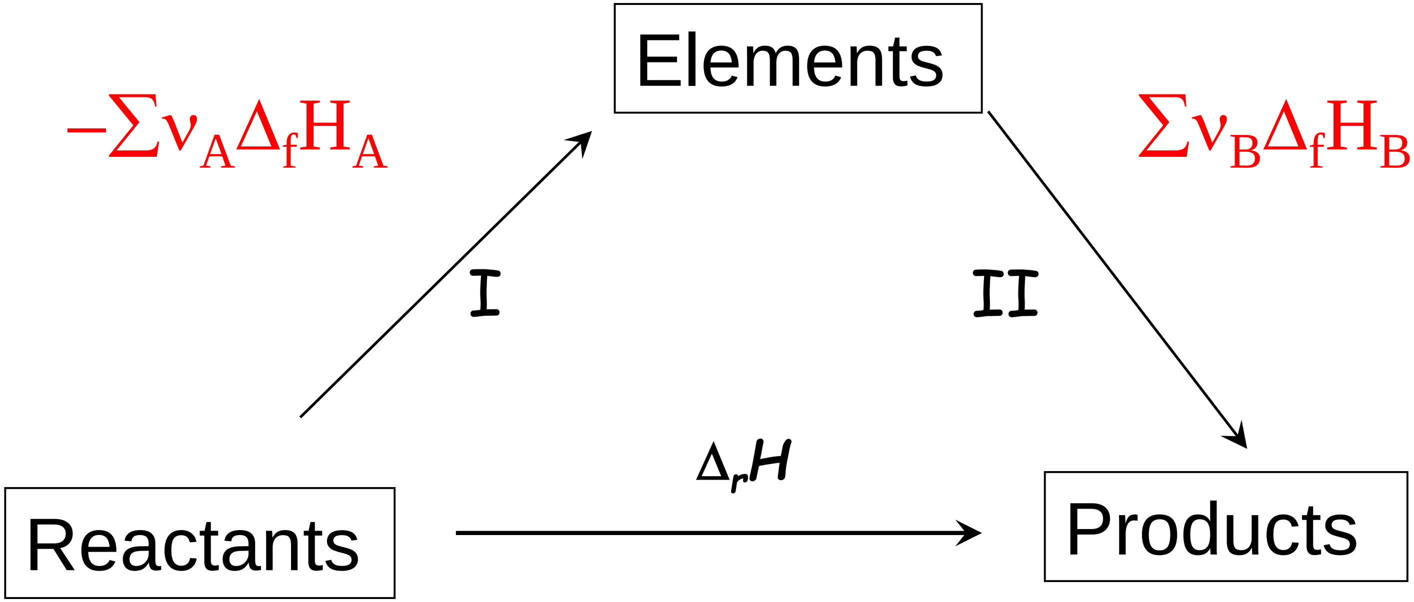
Example: The heat of formation of SO_3 is the heat of the following reaction

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

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

Heat of reaction from heat of formation data

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



Elements

$-\sum \nu_A \Delta_f H_A$

$\sum \nu_B \Delta_f H_B$

I

II

$\Delta_r H$

Reactants

Products

$$\Delta_r H = \Delta_r H(I) + \Delta_r H(II) = \sum \nu_B \Delta_f H_B - \sum \nu_A \Delta_f H_A = \Delta_r(\Delta_f H)$$

$$3C_2H_2 \rightarrow C_6H_6$$

$$\Delta_r H = \Delta_f H_{C6H6} - 3 \cdot \Delta_f H_{C2H2}$$

THE DIRECTION OF PROCESSES IN NATURE

(spontaneity)

- $H_2+O_2 \rightarrow H_2O$ and not the reverse
- gases uniformly fill the space available (expand)
- a hot object cools down to the temperature of its environment (heat is dissipated)

Ordered ⟶ Disordered

In the processes occurring spontaneously energy is dissipating.

We introduce a new state function, which can be used as the measure of the disorder. In *spontaneous* processes in *isolated* systems its change should be *positive*:

S: entropy, the measure of disorder

$$Q_{rev} = T \cdot S \qquad [S] = J/K$$

Heat input: the motion becomes more disordered

Work input: makes the system more ordered

Any changes can be characterized by an entropy change.

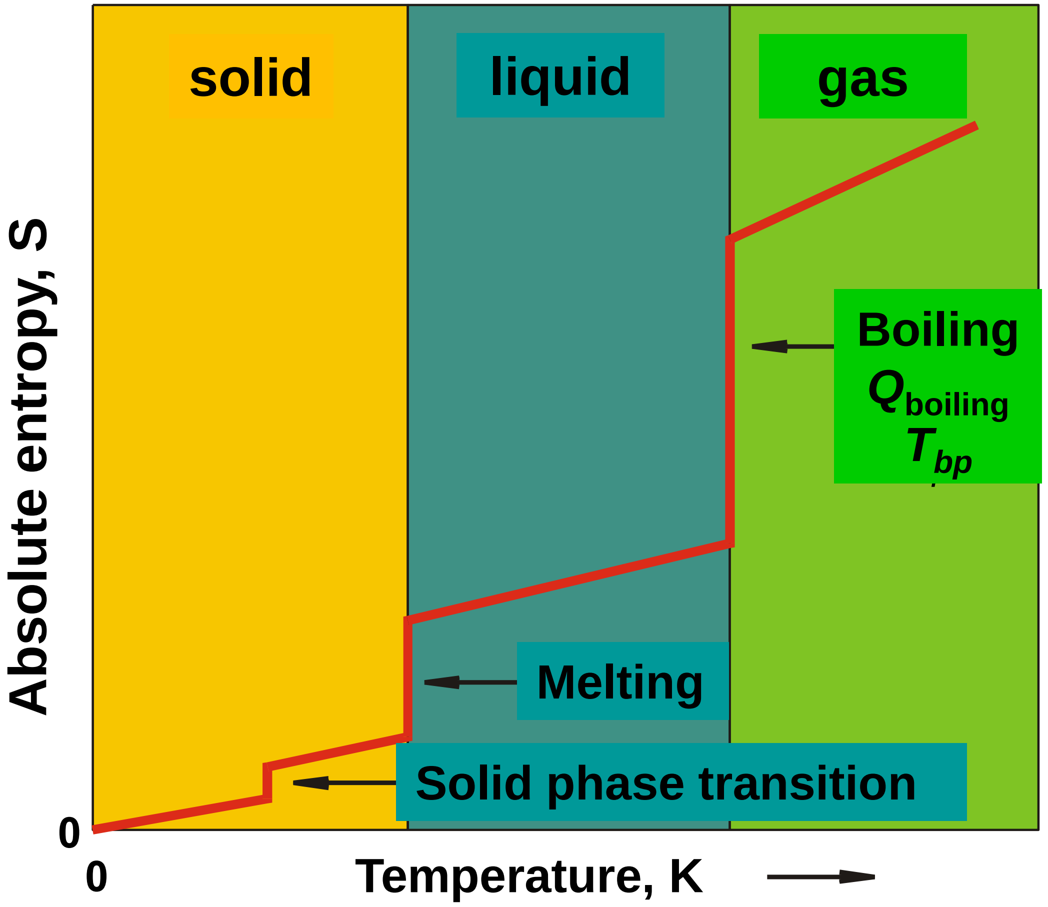
State function, extensive property (depends of the amount)

$S = nS_m$ **molar entropy**

Spontaneous macroscopic processes in isolated systems always increase the entropy. The system gets into equilibrium when its entropy reaches its maximum value.

(This is the 2nd law of thermodynamics.)

T dependence of entropy:



$$\Delta S(phase\ tr.) = \frac{Q_{phase\ tr.}}{T_{phase\ tr.}}$$

at T=0 K

- No motion: $S_{thermal}=0$
- Organisation (configuration) of the atoms might be disordered: $S_{configurationl}>0$

For pure and perfect crystals at $T \equiv 0$ K S = 0. (This is the 3rd law of thermodynamics.)

→ Unlike *U* and *H*, the absolute value of entropy is known!

Entropy at phase transitions (isothermal-isobaric processes)

e.g.

$$\Delta S(melting) = \frac{\Delta H(melting)}{T_{melting}}$$

$$\Delta S(evap) = \frac{\Delta H(evap)}{T_{boiling}}$$

S increases	S decreases
heating	cooling
melting	freezing
evaporation	condensation
expansion	compression
Disorder increases	Disorder decreases

Entropy of evaporation at the normal boiling point (p=1 atm)

chemical	ΔS(evap), $JK^{-1}mol^{-1}$
bromine	88.6
benzene	87.2
carbon tetrachloride	85.9
cyclohexane	85.1
H_2S	87.9
ammonia	97.4
water	109.1
mercury	94.2

EXERCISE 1

Problem:

The entropy of evaporation of cyclohexane at its normal boiling point (1 atm, 197.3 °C) is 85.1 J/(molK). Calculate its heat of evaporation at this temperature.

Solution:

EXERCISE 2

Problem:

The melting point of nitrogen is -196 °C.
What will be the change of entropy if 15 liter of liquid nitrogen is evaporated at atmospheric pressure ? The density of the liquid nitrogen is 0.81 g/cm^3 ?
What will be the sign of the change and explain why.

Solution:

EXERCISE 3

Problem:

How much heat should be removed from the system if we intend to cool 5 m^3 ethane gas from 140 °C to 30 °C ? The temperature dependence of the molar heat can be neglected.

Solution:

EXERCISE 4

Problem:

The mass of a single cube of sugar ($C_{12}H_{22}O_{11}$) is ca. 1.5 g. How much heat is evolved when a cube is completely burned in excess oxygen?

Solution:

In spontaneous macroscopic processes the entropy always increases.

In isolated system $\Delta S_{system} \geq 0$

If not isolated

$$\Delta S_{system} + \Delta S_{surrounding} \geq 0$$

The entropy change of an arbitrary process:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} \qquad \Delta S = \frac{Q_{rev}}{T} = \frac{\Delta H}{T}$$

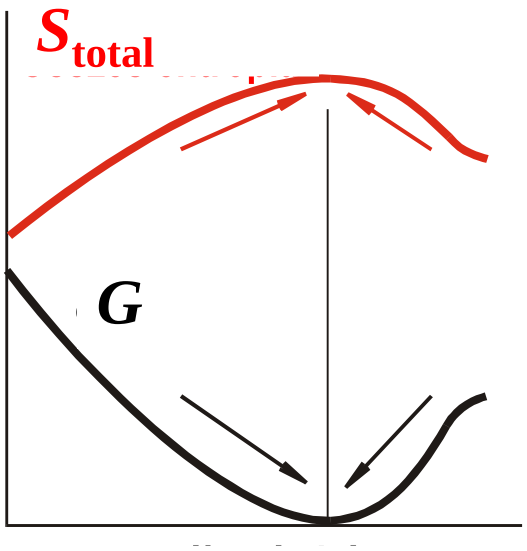
if p and T are constant

$$\Delta S_{surrounding} = -\frac{\Delta H_{system}}{T}$$

endothermic
exothermic

$$\Delta S_{total} = -\frac{\Delta H_{system}}{T} + \Delta S_{system} \qquad /\cdot T$$

$$T\Delta S_{total} = -\Delta H_{system} + T\Delta S_{system}$$



Direction of changes

$G \equiv H - TS$ Gibbs free energy

$$-T\Delta S_{total} = \Delta H - T\Delta S \equiv \Delta G$$

In a closed system at constant T and p in spontaneous processes G decreases. When equilibrium is reached, it has a minimum (if no work occurs).

Spontaneity ⇔ rate

$$G_{m,graphite} - G_{m,diamond} = -3\,\frac{kJ}{mol}$$

Most important properties of *G*:

1. State function
2. Extensive quantity $G = nG_m$
3. $G = H - TS$

Total energy stored in the system

Energy stored by the thermal motion of the atoms/molecules

The spontaneity of a process depends on the sign of ΔG during the transition:

e.g., in phase transition (no chemical changes)

$$\text{PHASE 1} \longrightarrow \text{PHASE 2}$$

$$G = n \cdot G_m$$

$$n \cdot G_m(2) - n \cdot G_m(1) = n\,[G_m(2) - G_m(1)] < 0 \quad ?$$

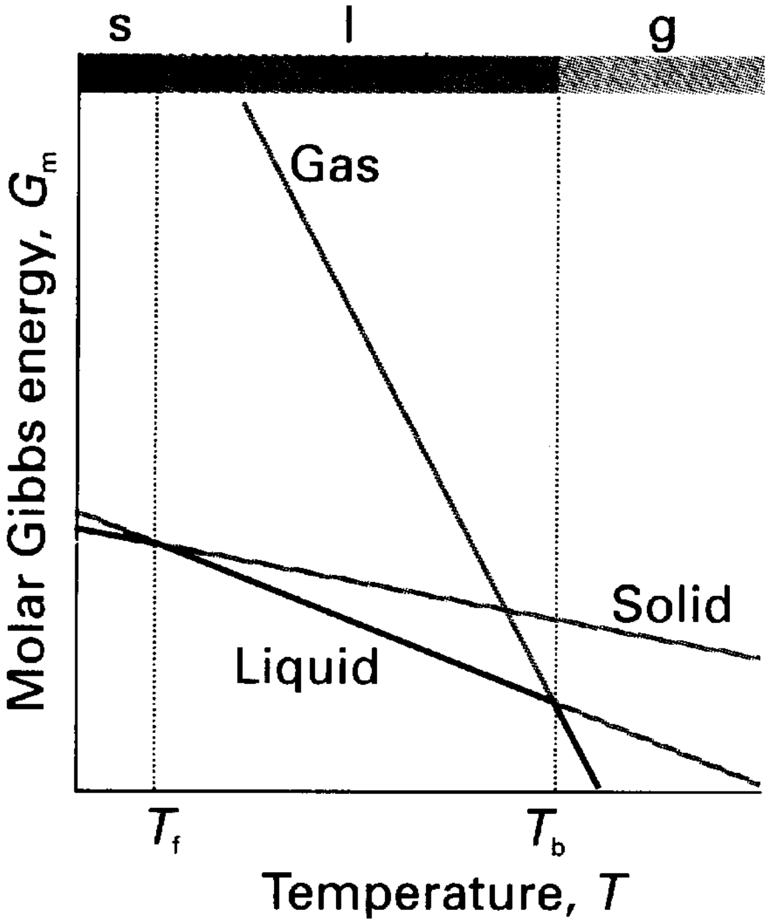
G(T) p = const.

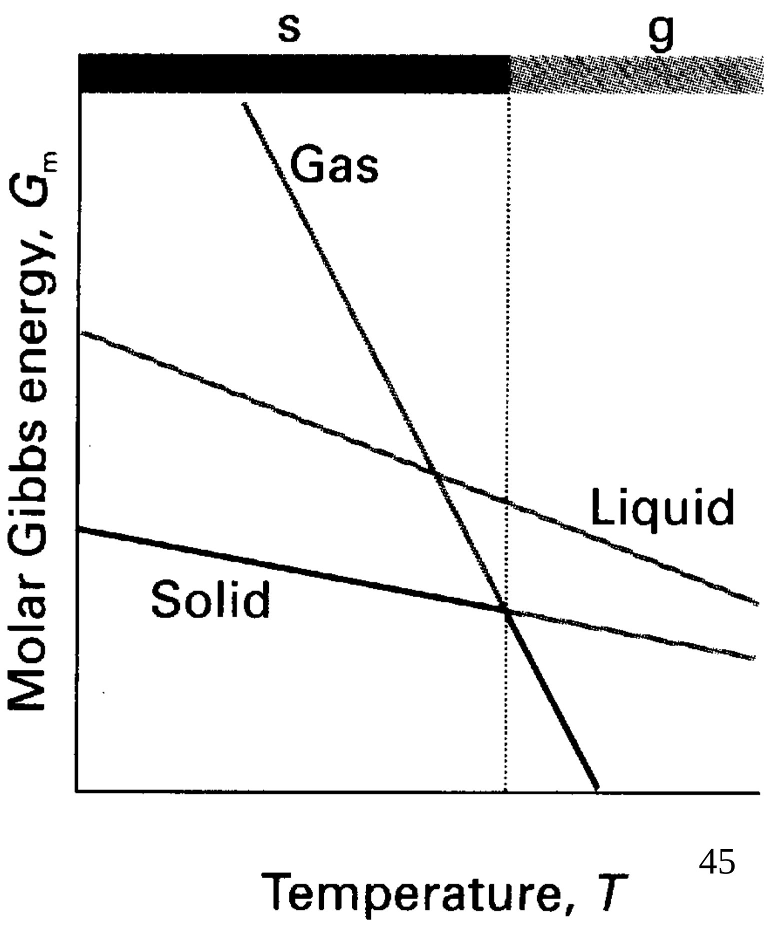
$dG = -SdT$

$G = H - TS$

$H \equiv U + pV$

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



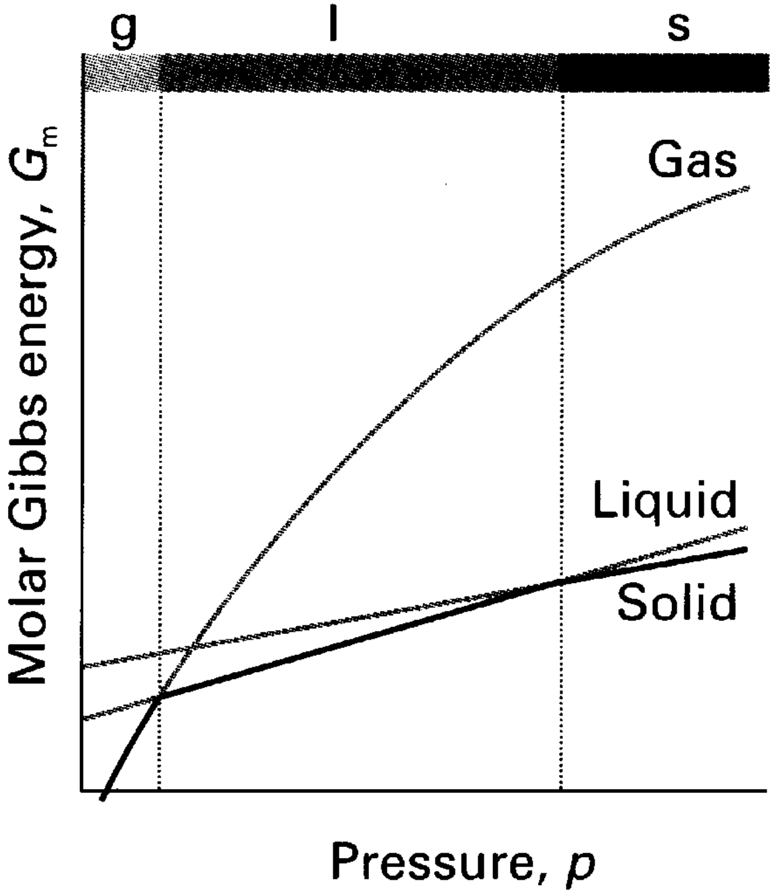


$G(p)$ T = const.

$G = H - TS$

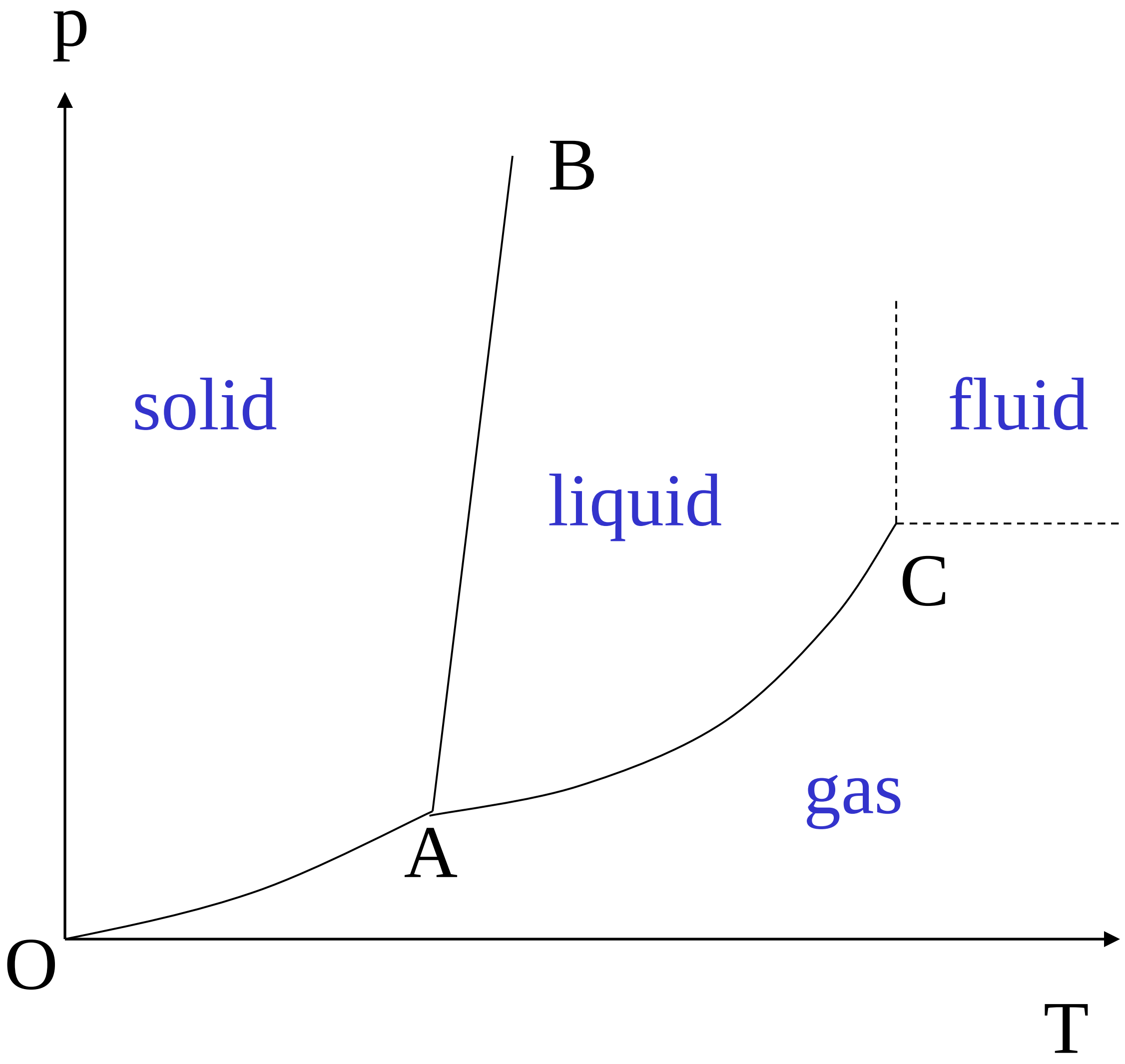
$H \equiv U + pV$

$dG = Vdp$



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

p-T phase diagram



OA: subl. curve

AB: melting curve

AC: vapor pressure curve

A: triple point

C: critical point

Solid → liquid melting positive slope (except for water)

Solid →gas sublimation

Liquid → gas boiling

Equilibrium of two phases, p and T are not independent

A: triple point, three phases are in equilibrium. Its temperature and pressure are characteristic of the substance.

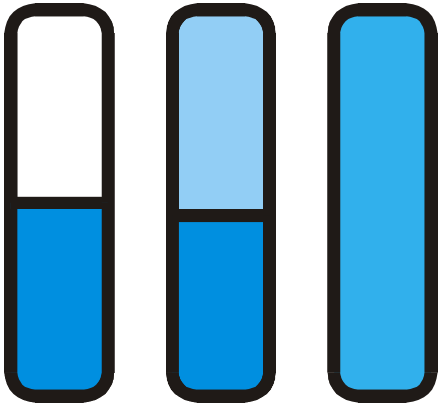
E.g. Water: 6,11 mbar, 273,16 K

CO_2: 5,11 bar, 216,8 K

At atmospheric pressure CO_2 does not exist in liquid state.

C: critical point: The difference between liquid and vapor phase diminishes.

At greater temperatures and pressures only one phase exists: fluid (supercritical) state.



Let us heat a liquid-vapor system in a vessel of an appropriate volume. (We are going from left to right on the vapor pressure curve.) It can be observed:

The density of the liquid decreases.
The density of the vapor increases.

Other physical properties (e.g. refractive index) also approach each other. Finally we reach to a point where the difference between the two phases diminishes → critical point.

Critical temperature: above which a gas cannot be liquified

Critical pressure: necessary to liquify the gas at its critical temperature.

Critical volume: occupied by 1 mol gas occupies at its critical pressure and temperature

The critical data are characteristic of the substance

E.g. Water: T_C = 647,4 K, p_C = 221,2 bar

CO_2: T_C = 304,2 K, p_C = 73,9 bar

T_C below room temperature: O_2, N_2, CO, CH_4

These gases cannot be liquified at room temperature.

T_C above room temperature : CO_2, NH_3, Cl_2, C_3H_8

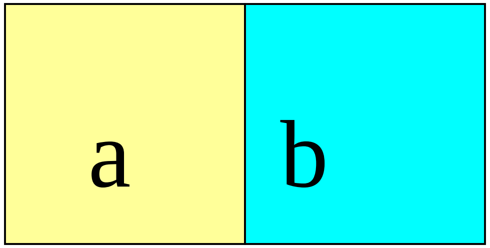
These gases can be liquified at room temperature

Thermodynamic interpretation of the p-T diagram (the Clapeyron equation)

PHASE EQUILIBRIUM

At given T and p the condition of equilibrium is the minimum of G.

One component, two phases (a and b)



At equilibrium the molar Gibbs free energy of the component must be equal in the two phases. (Otherwise there is a flow of the substance from the phase where G_m is higher to the phase where G_m is lower.)

Three cases:

1. $G_m^a > G_m^b$: substance goes from a to b

2. $G_m^a < G_m^b$: substance goes from b to a

Macroscopic process takes place

3. $G_m^a = G_m^b$:
equilibrium

No macroscopic process

On the molecular level there are changes. The rates of the processes in opposite direction are the same (e.g. in liquid vapor equilibrium the macroscopic rates of evaporation and of condensation are equal).

The equilibrium is **dynamic** (and not static), **fluctuation** occurs.

$$G_m(1) = G_m(2)$$

$$G_m(1) + dG_m(1) = G_m(2) + dG_m(2)$$

$$dG_m(1) = dG_m(2)$$

$$dG_m = V_m dp - S_m dT$$

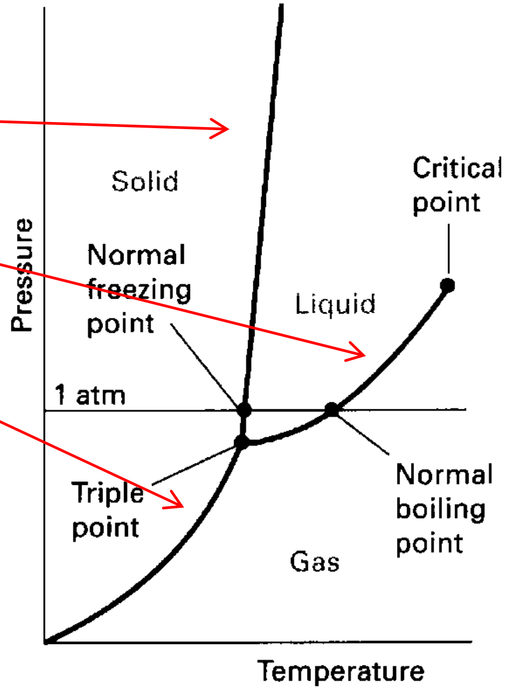
$$dG_m(1) = V_m(1)dp - S_m(1)dT$$

$$dG_m(2) = V_m(2)dp - S_m(2)dT$$

$$V_m(1)dp - S_m(1)dT = V_m(2)dp - S_m(2)dT$$

$$\left[S_m(2) - S_m(1)\right]dT = \left[V_m(2) - V_m(1)\right]dp$$

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$



The phase transition is an isothermal and isobaric process:

$$\Delta S_m = \frac{\Delta H_m}{T} \qquad \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\,\Delta V_m}$$

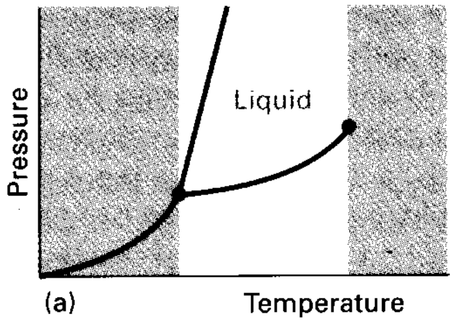
Clapeyron

$$\boxed{\frac{dp}{dT} = \frac{\Delta H_m}{T \cdot \Delta V_m}}$$

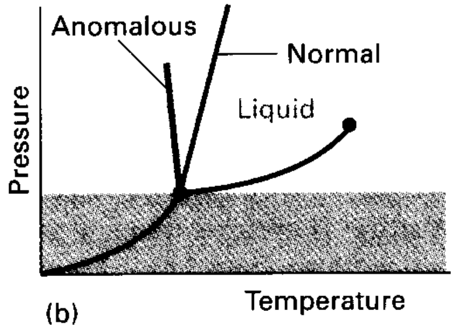
Clapeyron equation (the equation of one component phase equilibrium).

Nothing was neglected in the derivation.

It is valid for: liquid-vapor
solid-liquid
solid-vapor
solid-solid equilibrium



$$\frac{dp}{dT}=\frac{\Delta S_m}{\Delta V_m}$$

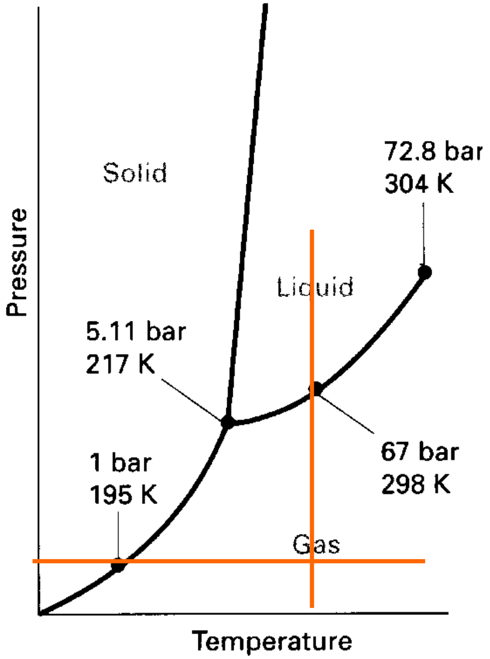


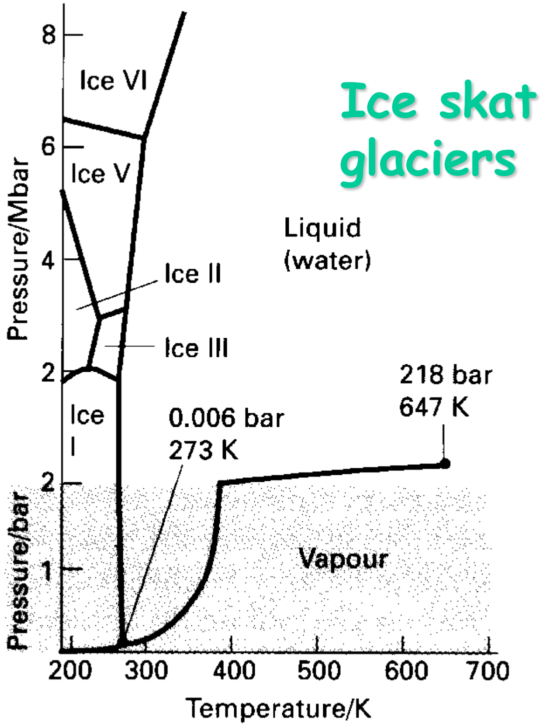
S/L reaction to increasing p $(V_m\,dp)_S \overset{?}{=} (V_m\,dp)_L$

Water

CO_2

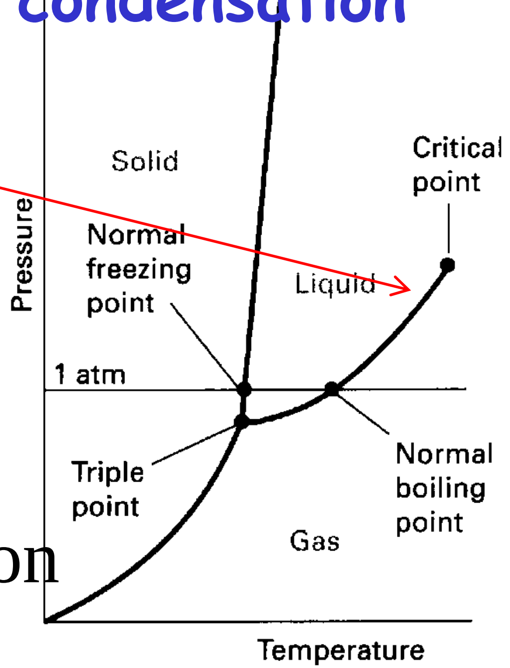
ice: 19,7 cm^3/mol water: 18,0 cm^3/mol





Ice skating glaciers

The liquid – gas transition: evaporation and condensation



Let's apply the Clapeyron equation for liquid-vapor equilibrium:

$$\frac{dp}{dT} = \frac{\Delta_{evap} H_m}{T \, \Delta V_m}$$

molar heat of vaporization

change of molar volume at vaporization

1. We neglect the molar volume of the liquid (compared to vapor).

$$\Delta V = V_m(gas) - V_m(liq) \cong V_m(gas)$$

2. We regard the vapor as ideal gas.

$$V_m(gas) = \frac{RT}{p}$$

$$\frac{dp}{dT} = \frac{p \Delta_{evap} H_m^{'}}{RT^2}$$

Clausius-Clapeyron

$$\frac{dp}{p} = \frac{p\Delta_{evap}H_m'}{RT^2}dT$$

The saturation pressure

of a pure liquid only depends on *T*.

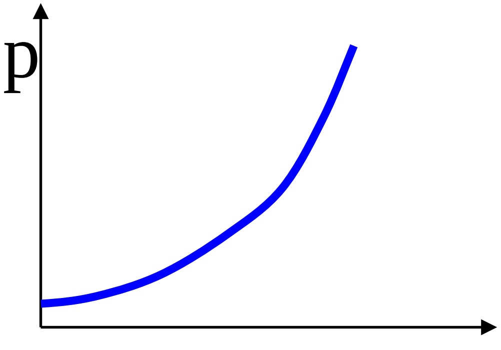
$$\frac{dp}{p} = d\ln p \qquad \frac{dT}{T^2} = -d\frac{1}{T}$$

d(1/T)/dT = -1/T²

$$\int_{p_k}^{p_V} d\ln p = \int_{T_k}^{T_V} \frac{\Delta_{evap}H'}{RT^2}dT$$

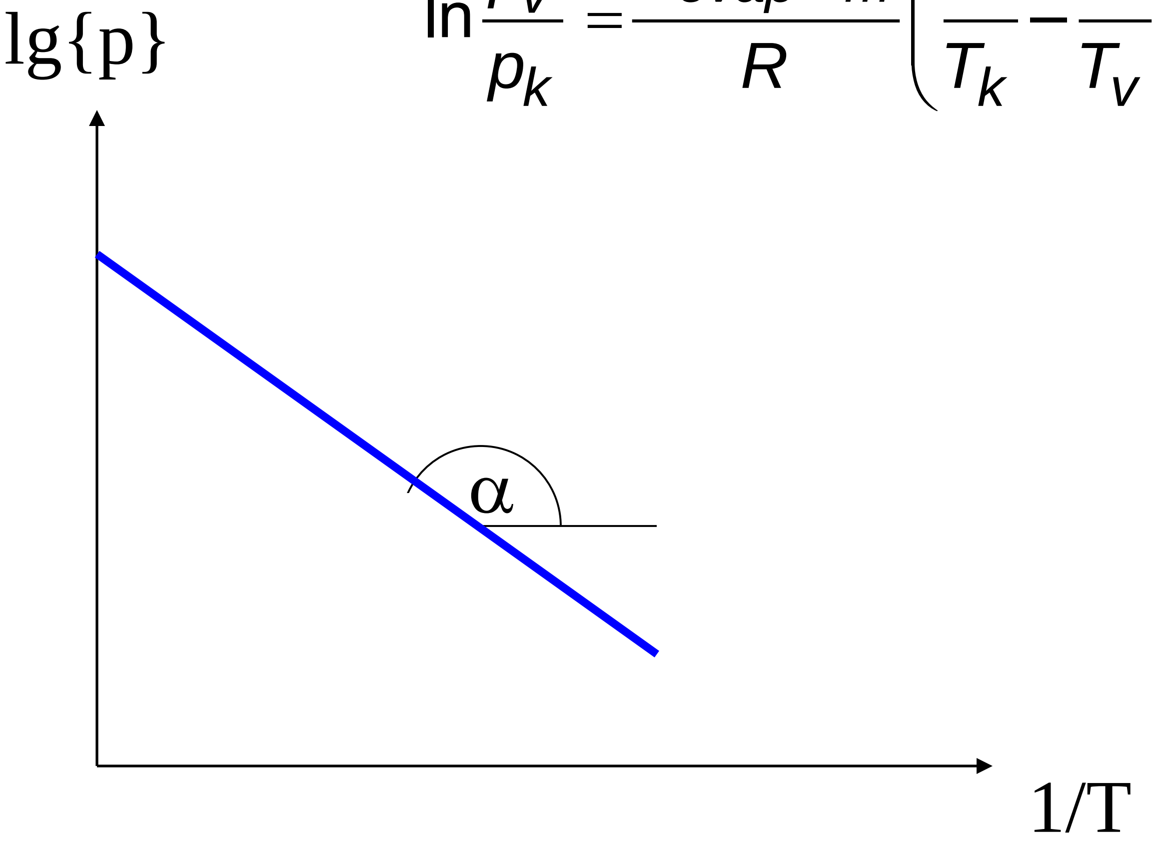
$$\ln p = -\frac{\Delta_{evap}H_m'}{R}\cdot\frac{1}{T} + C$$

$$ln\{p\} = -\frac{A}{T} + B \qquad \{p\} = \frac{p(Pa)}{1Pa}$$



If the logarithm of the vapor pressure is plotted against the reciprocal of temperature, we obtain a straight line:

$$\ln\frac{p_v}{p_k}=\frac{\Delta_{evap}H_m^{'}}{R}\left(\frac{1}{T_k}-\frac{1}{T_v}\right)$$



$$\lg\{p\}=-\frac{A}{T}+B$$

A, B: constants

tanα = -A

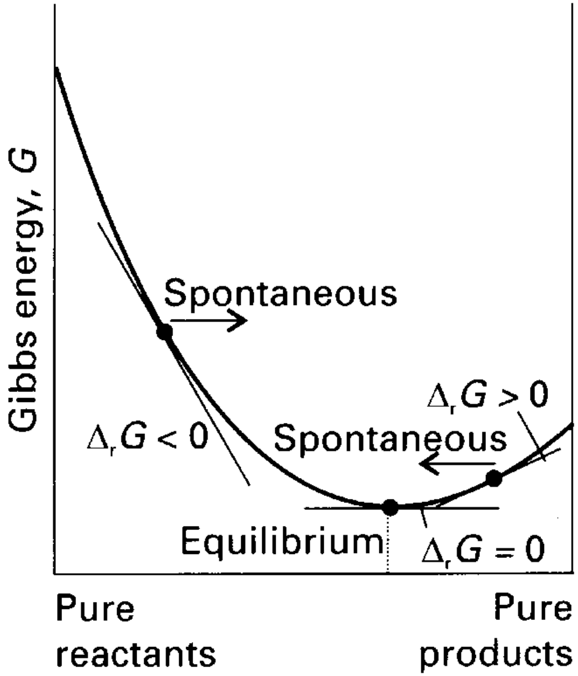
$$\{p\}=\frac{p(Pa)}{1Pa}$$

Equilibrium in chemical reactions

Spontaneity: $\Delta G<0$, p and T are constant

Condition of equilibrium: $\Delta_r G=0$, p and T are constant

$$2H_2 + O_2 \rightarrow 2H_2O$$



General form of the chemical equation:

$$\sum \nu_r M_r = \sum \nu_p M_p$$

$$\Delta_r G = \sum \nu_p G_p - \sum \nu_r G_r$$

$$G_i = \left(\frac{\partial G_{mixture}}{\partial n_i}\right)_{T,p,n_j} = \mu_i$$

μ_i : chemical potential

$$\Delta_r G = \sum \nu_p \mu_p - \sum \nu_r \mu_r$$

standard reaction Gibbs function

$$\mu_i = G_i^{\ominus} + RT\ln a_i = \mu_i^{\ominus} + RT\ln a_i \approx \mu_i^{\ominus} + RT\ln c_i$$

in ideal cases

Quantitative discussion

$$\sum \nu_r M_r = \sum \nu_p M_p$$

$$\Delta_r G = \Sigma \nu_p G_p^\phi - \Sigma \nu_r G_r^\phi + RT(\Sigma \nu_p \ln a_p - \Sigma \nu_r \ln a_r)$$

Sum of logarithms = logarithm of the product
Difference of logarithms = logarithm of the ratio
Constant times logarithm = logarithm of the power

$$\Delta_r G = \Delta_r G^\phi + RT \ln \frac{\Pi (a_p)^{\nu_p}}{\Pi (a_r)^{\nu_r}} = \Delta_r G^\phi + RT \ln Q$$

In equilibrium

$$\boldsymbol{\Delta_r G = \Delta_r G^{\varnothing} + RT \ln Q} = 0$$

$$\Delta_r G^{\varnothing} = -RT \ln K$$ **Thermodynamic equilibrium constant**

The equilibrium constant K only depends on temperature.

e.g. $N_2 + 3H_2 = 2NH_3$ $$K = \frac{a^2_{NH_3}}{a_{N_2} a^3_{H_2}}$$

***K* does not depend on either pressure or concentration. (The concentrations or partial pressures take up values to fulfil the constancy of *K*).**

K defines the composition of the reaction mixture in equilibrium

$$K = \frac{\Pi(a_p)^{\nu_p}}{\Pi(a_r)^{\nu_r}} \approx \frac{\Pi(c_p)^{\nu_p}}{\Pi(c_r)^{\nu_r}}$$

Temperature dependence of the equilibrium constant

$$\Delta_r G^{\varnothing} = \Delta_r H^{\varnothing} - T\Delta_r S^{\varnothing} = -RT\ln K$$

$$\ln K = -\frac{\Delta_r G^{\varnothing}}{RT} = -\frac{\Delta_r H^{\varnothing}}{RT} + \frac{\Delta_r S^{\varnothing}}{R}$$

$$\ln K' = -\frac{\Delta_r G^{\varnothing}{}'}{RT'} = -\frac{\Delta_r H^{\varnothing}}{RT'} + \frac{\Delta_r S^{\varnothing}}{R}$$

$$\ln\frac{K'}{K} = \frac{\Delta_r H^{\varnothing}}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

It is the standard reaction enthalpy that determines the temperature dependence of K

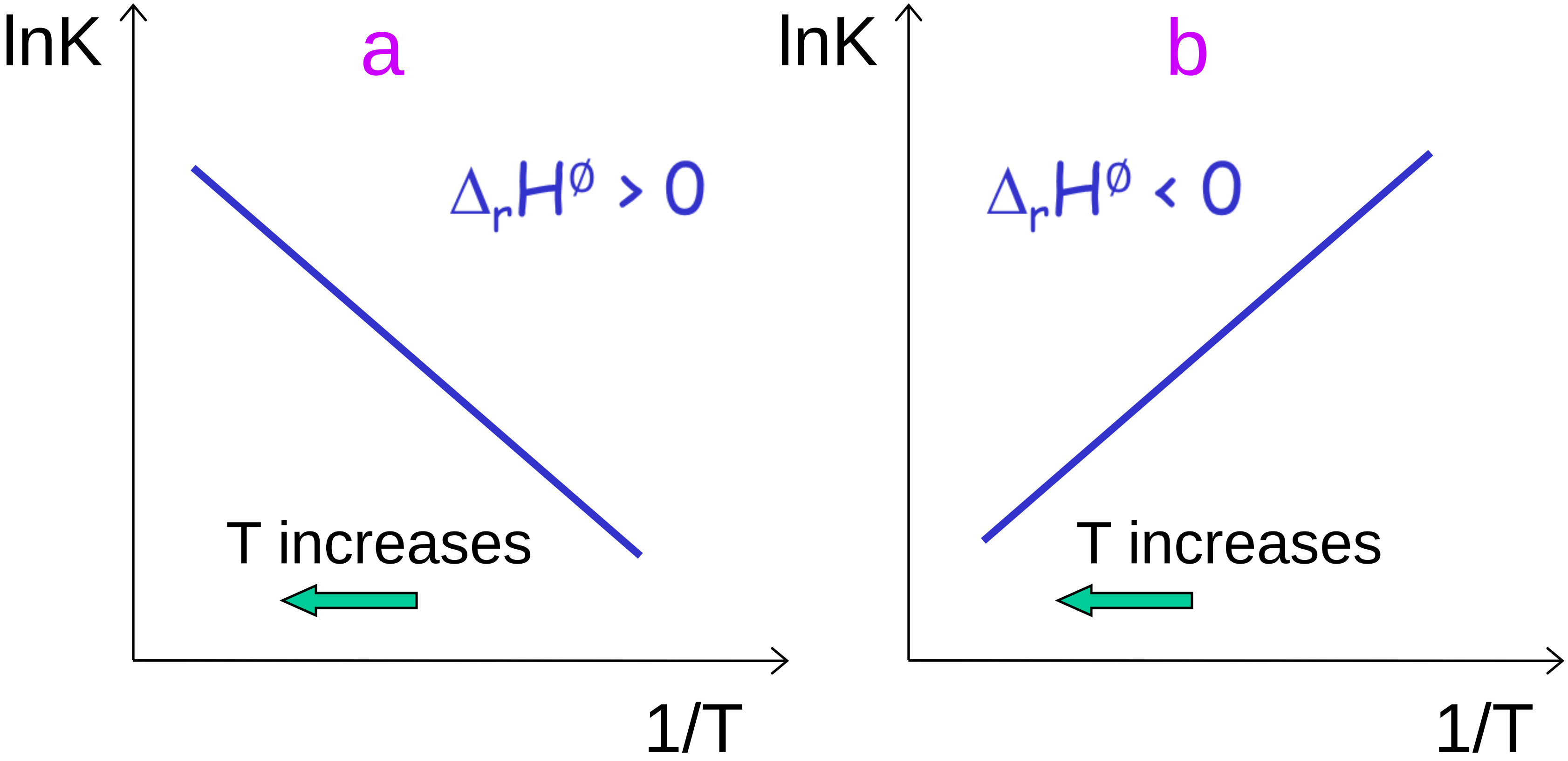
$$\ln \frac{K'}{K} = \frac{\Delta_r H^{\varnothing}}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

endothermic reactions (heat is absorbed form the environment, i.e., $\Delta_r H^{\varnothing} > 0$) the right hand side is positive, so $\ln K' - \ln K > 0$ with increasing temperature.

exothermic reactions (heat is released to the environment, i.e., $\Delta_r H^{\varnothing} < 0$) so $\ln K' - \ln K < 0$ with increasing temperature

Le Chatelier Principle: The equilibrium shifts towards the endothermic direction if the temperature is raised, and in the exothermic direction if the temperature is lowered. For exothermic reactions low temperature favours the equilibrium but at too low temperatures the rate of reaction becomes very low. An optimum temperature has to be found.

lnK - 1/T diagram for an endothermic (a) and for an exothermic (b) reaction



$$\Delta_r G^{\varnothing} = -RT \ln K = \Delta_r H^{\varnothing} - T\Delta_r S^{\varnothing}$$

When is the $\Delta_r G^{\varnothing} < 0$ condition fulfilled ?

$$\Delta_r G^{\varnothing} = \Delta_r H^{\varnothing} - T\Delta_r S^{\varnothing} < 0 \qquad \text{(spontaneity)}$$

$$\frac{\Delta_r H^{\varnothing}}{\Delta_r S^{\varnothing}} < T \qquad \Delta_r G^{\varnothing} = -RT \ln K$$

ΔH	ΔS	ΔG < 0	K > 1
–	+	At any temperature	
+	–	No such temperature	
–	–	when $T < \dfrac{\Delta H}{\Delta S}$	
+	+	when $T > \dfrac{\Delta H}{\Delta S}$	

In practice K>>1, at least K>10^3 is needed

The equilibrium constant is a very important quantity in thermodynamics that characterizes several types of equilibria of chemical reactions

in gas, liquid, and solid-liquid phases;

in different types of reactions between neutral and charged reactants;

Can be expressed using several parameters like pressure, mole fraction, (chemical) concentration, molality.

Chemical equilibrium in gas phase

$$\Delta_r G^0 = -RT \ln K \qquad \boldsymbol{K} = \frac{\Pi \boldsymbol{a}_p^{\nu_p}}{\Pi \boldsymbol{a}_r^{\nu_r}}$$

Ideal gases:

$$a_i = \frac{p_i}{p^0}$$

$$\boldsymbol{K} = \frac{\Pi\left(\frac{\boldsymbol{p}_p}{\boldsymbol{p}^0}\right)^{\nu_p}}{\Pi\left(\frac{\boldsymbol{p}_r}{\boldsymbol{p}^0}\right)^{\nu_r}} \qquad \boldsymbol{K} = \frac{\Pi \boldsymbol{p}_p^{\nu_p}}{\Pi \boldsymbol{p}_r^{\nu_r}} \cdot \left(\boldsymbol{p}^0\right)^{\sum \nu_r - \sum \nu_p}$$

$$K = K_p \left(p^0\right)^{-\Delta\nu}$$

$\Delta\nu$: change in number of molecules

e.g. $SO_2 + ½\, O_2 = SO_3$

$\Delta\nu = 1 – 0,5 – 1 = - 0,5$

Effect of pressure on equilibrium

The equilibrium constant is independent of pressure. On the other hand, the ***equilibrium composition in a gas reaction can be influenced by the pressure***.

Assume that the participants are ideal gases.

$$K = \frac{\Pi\left(\frac{p_p}{p^0}\right)^{\nu_p}}{\Pi\left(\frac{p_r}{p^0}\right)^{\nu_r}}$$

Dalton´s law: $p_i = y_i \cdot p$

$$K = \frac{\Pi\left(\frac{y_p p}{p^0}\right)^{\nu_p}}{\Pi\left(\frac{y_r p}{p^0}\right)^{\nu_r}} = K_y \left(\frac{p}{p^0}\right)^{\Delta\nu}$$

$$K_y = \frac{\Pi y_p^{\nu_p}}{\Pi y_r^{\nu_r}}$$

$$\Delta\nu = \Sigma\nu_p - \Sigma\nu_r$$

$$\boxed{K_y = K \cdot \left(\frac{p}{p^0}\right)^{-\Delta\nu}}$$

The effect of pressure on equilibrium composition depends on the sign of $\Delta\nu$.

If $\Delta\nu > 0$ (the number of molecules increases), increasing the pressure, decreases K_y, i.e., the equilibrium shifts towards the reactants (-$\Delta\nu$ exponent!)

If $\Delta\nu < 0$ (the number of molecules decreases), increasing the pressure, favours the products (K_y increases).

Le Chatelier Principle: a system at equilibrium, when subjected to a perturbation, responds in a way that tends to minimize its effect.

Equilibrium gas reaction: Increasing the pressure, the equilibrium shifts towards the direction where the number of molecules decreases.

Reactions where the volume decreases at constant pressure ($\Delta\nu < 0$) are to be performed at high pressure.

E.g. $N_2 + 3\ H_2 = 2NH_3 \qquad \Delta\nu = -2$
Several hundred bars are used.

Reactions where the volume increases at constant pressure ($\Delta\nu > 0$) are to be performed at low pressure or in presence of an inert gas.

Chemical equilibrium in liquid electrolytes

Even very dilute solutions cannot be regarded ideal (because of the strong electrostatic interaction between ions).

if **chemical concentrations** are used:

$$\mu_i = \mu_i^0 + RT\ln\frac{\gamma_i c_i}{c^0} \qquad \Delta_r\mu^0 = -RT\ln K$$

$$K = \frac{\prod\left(\frac{\gamma_p c_p}{c^0}\right)^{\nu_p}}{\prod\left(\frac{\gamma_r c_r}{c^0}\right)^{\nu_r}} = \frac{\prod\gamma_p^{\nu_p}}{\prod\gamma_r^{\nu_r}}\cdot\frac{\prod c_p^{\nu_p}}{\prod c_r^{\nu_r}}\cdot\left(c^0\right)^{\Sigma\nu_p-\Sigma\nu_r}$$

$$K = K_\gamma \cdot K_c \cdot \left(c^0\right)^{-\Delta\nu} \qquad K_c = \frac{\prod c_p^{\nu_p}}{\prod c_r^{\nu_r}}$$

K_c can be frequently used as equilibrium constant (it is assumed that the activity coefficients are independent of concentration, so K_γ is taken constant).

Dissociation equilibrium

$$KA = K^+ + A^-$$

$$c_0(1-\alpha) \quad c_0 \cdot \alpha \quad c_0 \cdot \alpha$$

$$K_c = \frac{\alpha^2 c_0}{1-\alpha}$$

K^+: cation

A^-: anion

c_0 : initial concentration

α : degree of dissociation

$$0 \leq \alpha \leq 1$$

ACID-BASE EQUILIBRIA

Brönsted-Lowry proton donor / acceptor

$$HA(aq)+H_2O(l) \rightleftarrows H_3O^+(aq) + A^-(aq)$$

hidronium ion + conjugated base of HA

$$K = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA} \cdot a_{H_2O}} = \frac{a_{H_3O^+} \cdot a_{bas}}{a_{acid} \cdot a_{H_2O}}$$

Very limited ionization, very low conc. of the ions. therefor $a_{H_2O} = 1$

$$K_a = \frac{a_{H_3O^+} \cdot a_{base}}{a_{HA}}$$

Acidic dissociation constant

$$pK_a = -\lg K_a$$

The standard Gibbs free energy of the protondonation:

$$\Delta G^{\varnothing} = -RT \ln K_a$$

K_a values of selected acids/bases, 298 K

HI	10^{11}
HCl	10^{7}
H_2SO_4 (1)	10^{2}
H_2SO_4 (2)	$1{,}2\times10^{-2}$
$CH_3CH(OH)COOH$ (Lactic acid)	$8{,}4\times10^{-4}$
CH_3COOH (acetic acid)	$1{,}8\times10^{-5}$
H_2CO_3 (1)	$4{,}3\times10^{-7}$
phenol	$1{,}3\times10^{-10}$
H_2CO_3 (2)	$4{,}8\times10^{-11}$
NH_4^+	$5{,}6\times10^{-10}$
ethylamine	$1{,}5\times10^{-11}$

$$pK_a = -\lg K_a$$

Water

Dual behaviour acid + water ⇆ As a base

base + water ⇆ As an acid

Ampholitic

autoprotolysis

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

$$K_w = a_{H_3O^+} \cdot a_{OH^-} \qquad pK_w = -\log K_w$$

In pure water $a_{H3O+} = a_{OH-}$

$$K_w = a^2_{H_3O^+} \rightarrow a_{H_3O^+} = \sqrt{K_w}$$

$$-\lg a_{H_3O^+} = pH \approx -\lg c_{H^+}$$ pH scale

$$pK_w = pH + pOH = f(T)$$

Temperature dependence of K_w and pH

Temperature, °C	K_w	pH
0	0.13×10^{-14}	7.45
10	0.36×10^{-14}	7.07
20	0.86×10^{-14}	7.04
22	1.00×10^{-14}	7.00
25	1.27×10^{-14}	6.95
30	1.89×10^{-14}	6.87
40	3.80×10^{-14}	6.71

Relationship between a base and its conjugated acid

$$\mathrm{B(aq)+H_2O(l)} \rightleftarrows \mathrm{BH^+(aq)} + \mathrm{OH^-(aq)}$$

Conjugated acid

$$K_b = \frac{a_{\mathrm{BH^+}} \cdot a_{\mathrm{OH^-}}}{a_{\mathrm{B}}}$$

$$\mathrm{BH^+(aq)+H_2O(l)} \rightleftarrows \mathrm{H_3O^+(aq)} + \mathrm{B(aq)}$$

$$K_a = \frac{a_{\mathrm{H_3O^+}} \cdot a_{\mathrm{B}}}{a_{\mathrm{BH^+}}}$$

$$K_a K_b = a_{\mathrm{H_3O^+}} \cdot a_{\mathrm{OH^-}} = K_w$$

$$pK_a + pK_b = pK_w$$

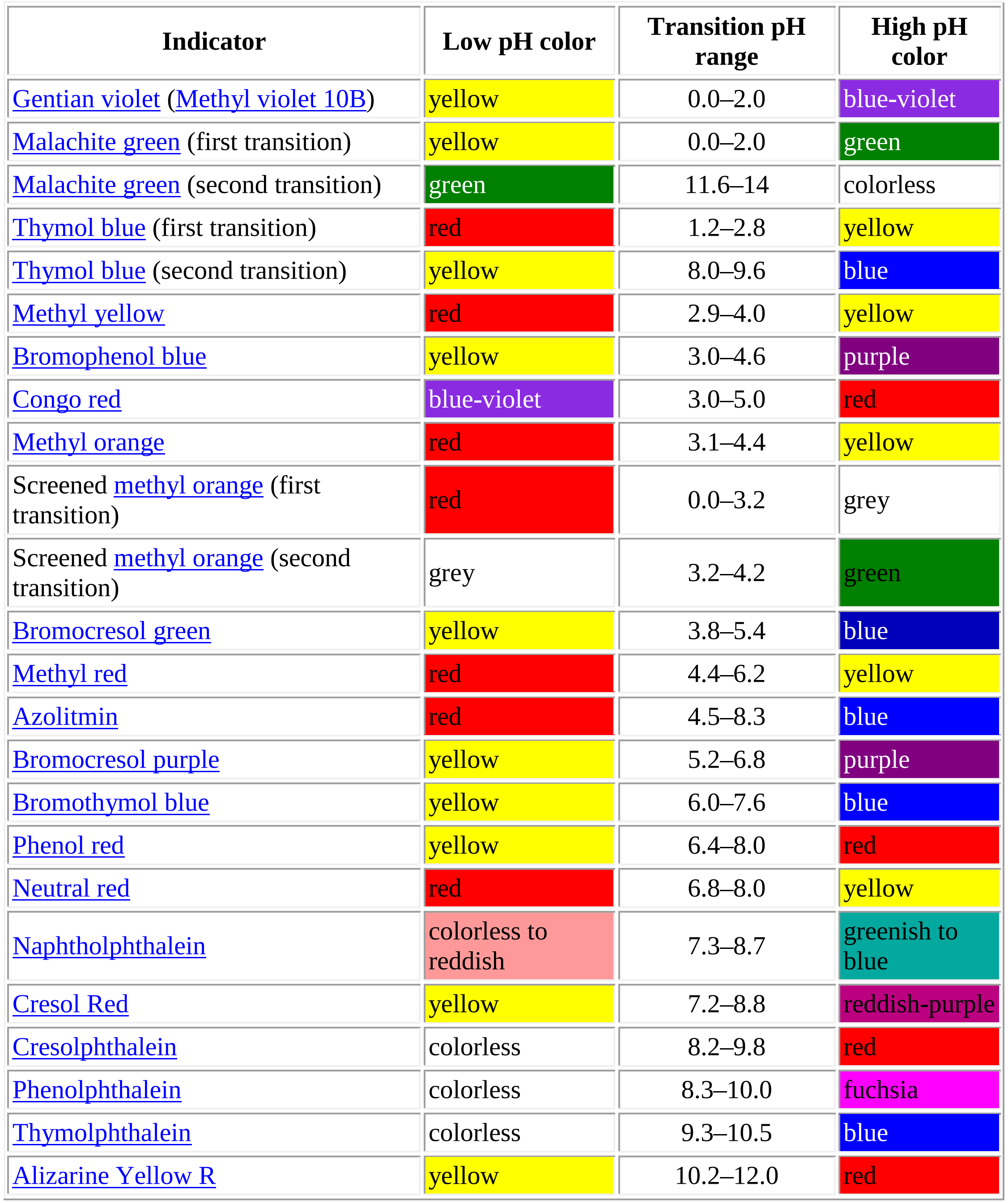
Weak acids/bases: only partial dissociation $K_a < 1$

$$K_a = \frac{\alpha^2 c_0}{1-\alpha}$$

α : degree of dissociation

acid/base (pH-) indicators

$$HInd + H_2O \rightleftharpoons H_3O^+ + Ind^-$$



Indicator	Low pH color	Transition pH range	High pH color
Gentian violet (Methyl violet 10B)	yellow	0.0–2.0	blue-violet
Malachite green (first transition)	yellow	0.0–2.0	green
Malachite green (second transition)	green	11.6–14	colorless
Thymol blue (first transition)	red	1.2–2.8	yellow
Thymol blue (second transition)	yellow	8.0–9.6	blue
Methyl yellow	red	2.9–4.0	yellow
Bromophenol blue	yellow	3.0–4.6	purple
Congo red	blue-violet	3.0–5.0	red
Methyl orange	red	3.1–4.4	yellow
Screened methyl orange (first transition)	red	0.0–3.2	grey
Screened methyl orange (second transition)	grey	3.2–4.2	green
Bromocresol green	yellow	3.8–5.4	blue
Methyl red	red	4.4–6.2	yellow
Azolitmin	red	4.5–8.3	blue
Bromocresol purple	yellow	5.2–6.8	purple
Bromothymol blue	yellow	6.0–7.6	blue
Phenol red	yellow	6.4–8.0	red
Neutral red	red	6.8–8.0	yellow
Naphtholphthalein	colorless to reddish	7.3–8.7	greenish to blue
Cresol Red	yellow	7.2–8.8	reddish-purple
Cresolphthalein	colorless	8.2–9.8	red
Phenolphthalein	colorless	8.3–10.0	fuchsia
Thymolphthalein	colorless	9.3–10.5	blue
Alizarine Yellow R	yellow	10.2–12.0	red

BUFFERS

A buffer is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid (blood, natural waters, gastric juice, etc.).

HX / MX

$$\mathrm{HX(aq)+H_2O(l)} \rightleftarrows \mathrm{H_3O^+(aq)+X^-(aq)}$$

$$K_a \approx \frac{c_{\mathrm{H_3O^+}} \cdot c_{\mathrm{X^-}}}{c_{\mathrm{HX}}}$$

$$c_{\mathrm{H_3O^+}} = K_a \cdot \frac{c_{\mathrm{HX}}}{c_{\mathrm{X^-}}}$$

$$\mathrm{pH} = \mathrm{p}K_a - \lg \frac{c_{\text{acid}}}{c_{\text{conj. base}}}$$

$$\mathrm{pOH} = \mathrm{p}K_b - \log_{10} \frac{a_{\text{base}}}{a_{\text{conj. acid}}}$$

Henderson-Hasselbalch equation

SOLUBILITY

Salts with limited solubility

$AgCl\ (s) \leftrightarrows Ag^{+}\ (aq) + Cl^{-}\ (aq)$

$$K = \frac{a_{Ag^{+}(aq)} \cdot a_{Cl^{-}(aq)}}{a_{AgCl(s)}} = \frac{c_{Ag^{+}(aq)} \cdot c_{Cl^{-}(aq)}}{c_{AgCl(s)}}$$

Solubility product

$$L = c_{Ag^{+}(aq)} \cdot c_{Cl^{-}(aq)} \qquad 1,77 \times 10^{-10} = L_{\mathrm{AgCl}}$$

$Ag_2S\ (s) \leftrightarrows 2Ag^{+}\ (aq) + S^{2-}\ (aq)$

$$L = c^{2}_{Ag^{+}(aq)} \cdot c_{S^{2-}(aq)}$$

PROBLEM SOLVING

1. Show the equation of the deprotonation process of lactic acid, CH_3-CH(OH)-COOH in an aqueous solution. Calculate its degree of dissociation, pH and pOH in its 46 mg/L aqueous solution at 22 °C.

2. Propionic acid (E280) is one of the carboxylic acid occurring in nature Its formula is CH_3CH_2COOH and its pK_a value at 22 °C is 4.88.
Show its dissociation equation in aq. medium. Calculate its degree of Dissociation, pH and pOH in its 2 mmol/L solution at this temperature.

3. Ammonia (NH3) is produced in the catalytic reaction of N_2 and H_2. Write the equation of the equilibrium reaction and its equilibrium constant.

a) How can you force a better yield by adjusting pressure?

b) Advise alternative solutions to anhance the yield.