Aalto University

CHEM-E6100 Fundamentals of chemical thermodynamics

Week 5, Fall 2022

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- **Single component systems**
- **Phase transformations**
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Single component systems

- Stated earlier that the (practical) intensive variables of systems (often) are temperature (T), pressure (P) and chemical potentials of the components *i* (μ_i).
- At the same time, these properties are variables of the other potential functions of the system:
  - **temperature** of the system indicates its ability to release (extract) heat to (from) its surroundings
  - **pressure** of the system gives an indication of its capability to expand or contract, and then the pressure difference (gradient) reflects the tendencies of volumetric changes – the mechanical equilibrium assumes the absence of any pressure gradients!
  - a **difference in chemical potential** of a component between two phases or systems indicates need of material transport from one to another.

About phase transformations

- In single component systems only phase transformations, e.g. (s)→(l) and (l)→(g), are possible but no chemical reactions.
- Let's look water as an example.
- At temperature 273.15 K (0°C) under normal pressure 1 atm ice melts, when gets heat (or thermal energy), and a chemical reaction (i.e. phase transformation) occurs, turning solid water to liquid

$$H_2O(\text{solid}) \rightarrow H_2O(\text{liquid}).$$

Energetics of phase transformations (I)

- Based on previously presented correlations, for a phase transformation in equilibrium of two phases (at phase transformation temperature) the following condition is valid: $\Delta G = G_{H2O(l)} - G_{H2O(s)} = 0$.
- Thus the **equilibrium condition** between (solid) ice and (liquid) water is:

  $G_{H2O(l)} = G_{H2O(s)}$

  where $G_{H2O(s)}$ is Gibbs energy of solid water at the temperature and pressure and $G_{H2O(l)}$ is the corresponding value of liquid water.
- Total Gibbs energy of the system can be written as:

$$G' = n_{H2O(s)}G_{H2O(s)} + n_{H2O(l)}G_{H2O(l)} = (n_{H2O(s)} + n_{H2O(l)})\, G_{H2O(s)} = n_{tot}G_{H2O(l)}$$

meaning that in the phase transformation point total Gibbs energy is independent of the relative fractions of the (molten and solid) phases of the system.

Energetics of phase transformations (II)

When temperature is higher than the phase transformation point, melting of ice is spontaneous reaction and 'process' (s) → (l) proceeds from left to right.

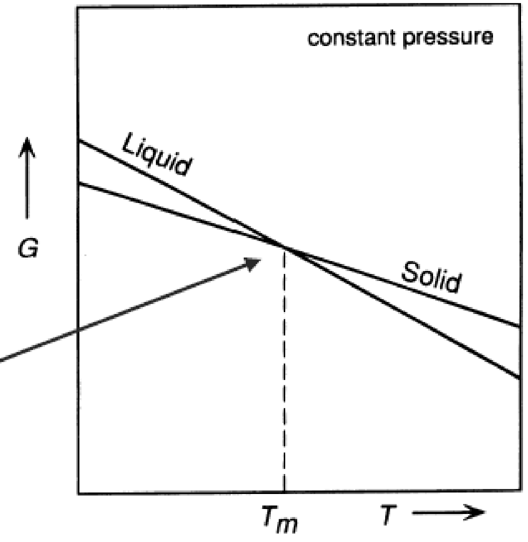
Then, according to the general equilibrium criterion, G function decreases and the following relation is valid:

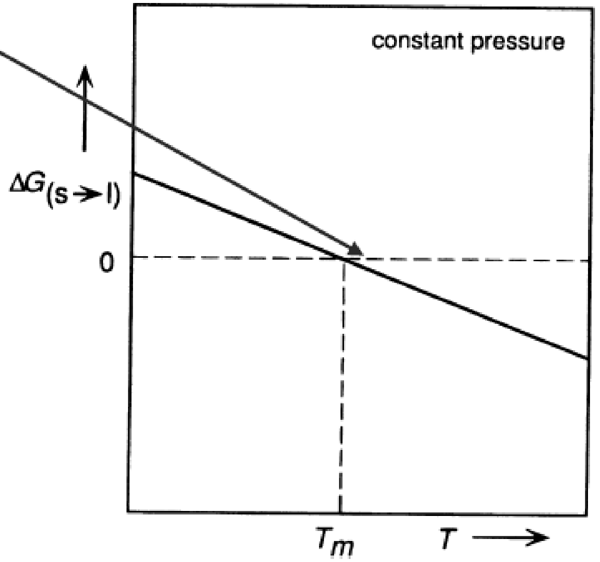
$$\Delta G = G_{H2O(l)} - G_{H2O(s)} < 0$$

$$\text{Or} \quad G_{H2O(l)} < G_{H2O(s)}$$

the same is valid with the inverse reaction at temperatures lower than the melting point.

- *In general:* G function of a stable phase is always more negative than those of the unstable phases.





Energetics of phase transformations (III)

- For isobaric conditions we have for any transformation

$$(\partial G/\partial T)_P = -S,$$

which gives us the slope of G function and its connection to the other thermodynamic properties of the system;

- further the curvature of G function or its 2nd derivative a

$$(\partial^2 G/\partial^2 T)_P = -(\partial S/\partial T)_P = -c_p/T$$

where we have obtained a solid connection to and a relation with the measurable properties of a system.

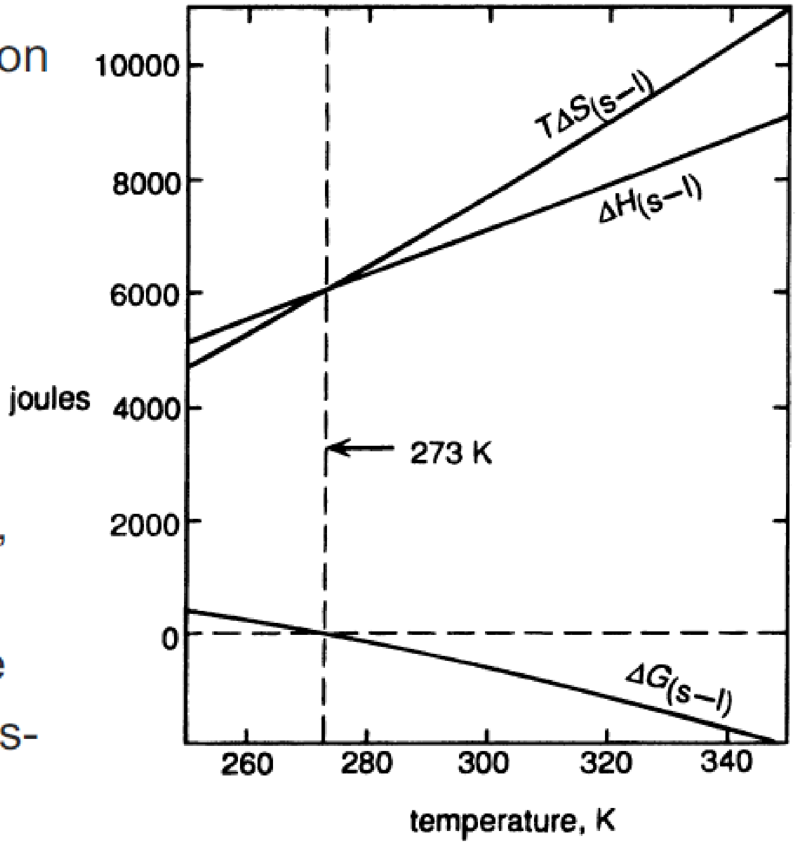
Energetics of phase transformations (IV)

- The previous treatment includes, in addition to the Gibbs energies, also its change or difference ΔG; it is by definition

$$\Delta G(s\rightarrow l) = \Delta H(s\rightarrow l) - T\cdot\Delta S(s\rightarrow l).$$

- Enthalpy and entropy terms, ΔH and $T\Delta S$, behave in respect with temperature in isobaric conditions as shown in the above graph; it is also evident that at phase transformation temperature T_{tr} :

$$\Delta H(s\rightarrow l, T_{tr}) = T\cdot\Delta S(s\rightarrow l, T_{tr}).$$

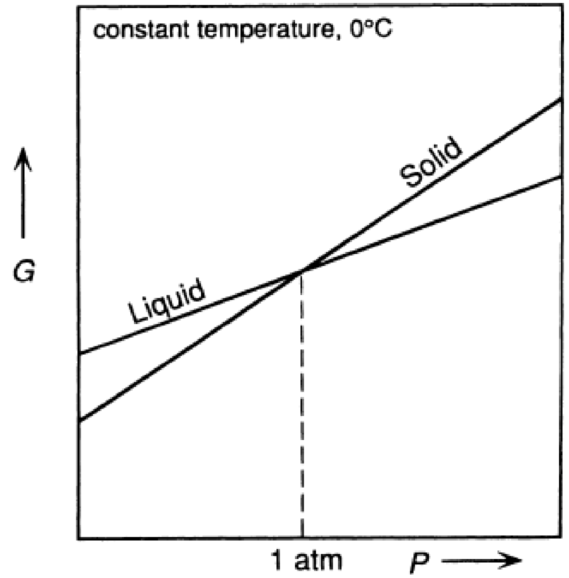


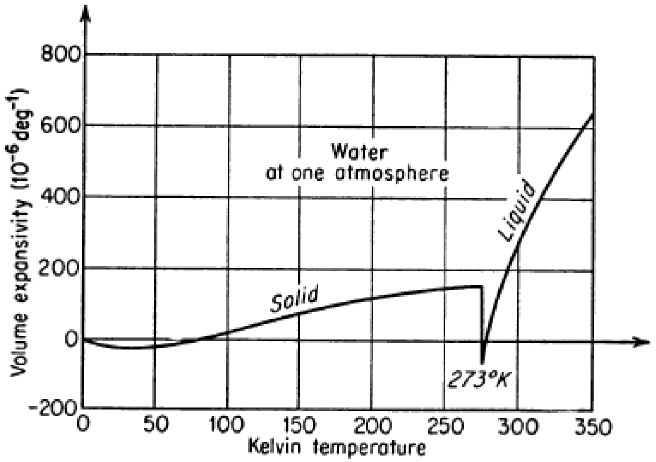
Energetics of phase transformations (V)

- The point of phase transformation is also **function of pressure.**
- The relation derived earlier between isothermal pressure dependence of G and (molar) volume is $(\partial G/\partial P)_T = V$.
- Thus in general in phase transformations:

$$(\partial \Delta G(s\rightarrow l)/\partial P)_T = \Delta V(s\rightarrow l).$$

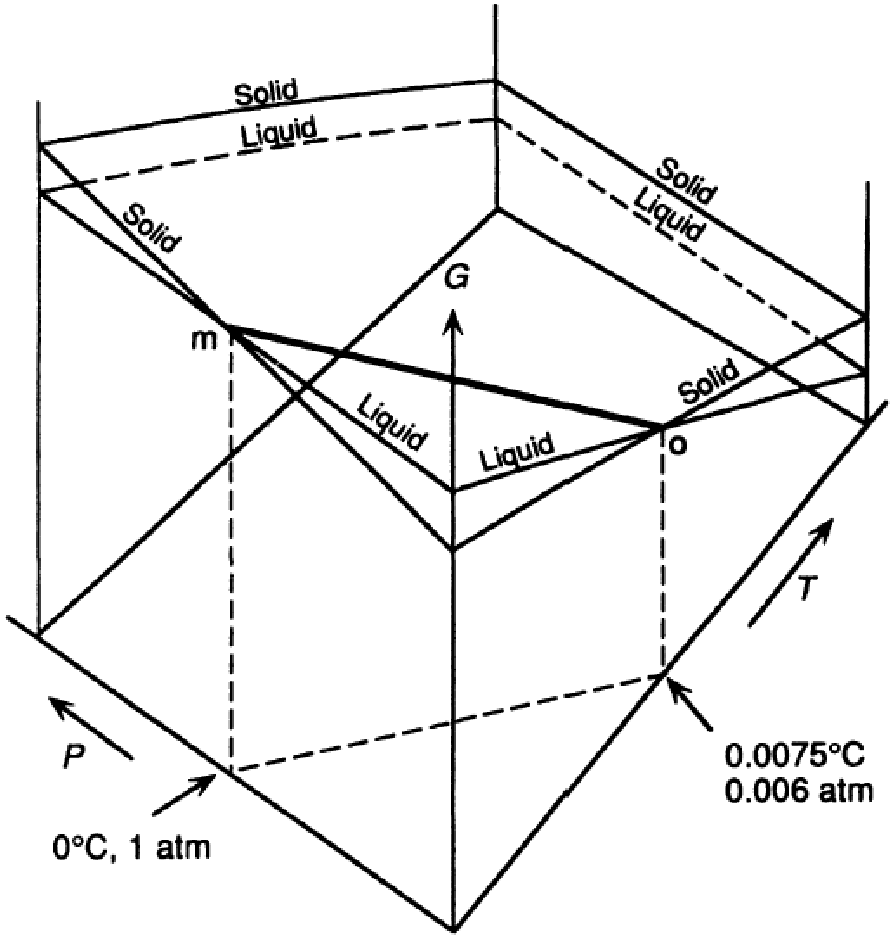
- In case of water, around its melting point, ΔV is negative; this means that ice melts under higher pressures than ambient (1 atm) at temperatures higher than 0°C!





Graphical description of the above: P-T-G coordinates

- An overall picture of the phase transformation of water as a function of pressure and temperature can be obtained from a 3D-plot of the above relations with P and T as variables.
- This graph shows (thick line *m-o*) the line of the melting point of water from 1 atm (total) pressure down to 0.006 atm.
- Its y-axis is G function and those for solid and liquid water are shown as surfaces.



Clapeyron equation

- In general phase transformations we have a relation, linking the phases (s and l) as G(l) = G(s).

  Thus in infinitesimal changes of the system, with respect of pressure and temperature, we get dG(l) = dG(s).

- This equation can be re-written with pressure and temperature as variables, using the entropy and volume contributions of the phases

$$dG(l) = \boxed{-S(l)dT + V(l)\,dP}$$

$$dG(s) = \boxed{-S(s)dT + V(s)dP.}$$

- In equilibrium, dG(l) = dG(s); this gives Clapeyron equation as

$$-S(l)\,dT+V(l)\,dP = -S(s)\,dT + V(s)\,dP$$

$$(S(s) - S(l))\,dT = (V(s) - V(l))\,dP$$

Or $(dP/dT)_{eq} = [S(s)-S(l)]/[V(s)-V(l)] = \Delta S(l\rightarrow s)/\Delta V(l\rightarrow s).$

Vapour pressure

- Let's study the equilibrium between a condensed (non-gaseous) phase and its vapour (gas).
- In such vaporisation process (or condensation) we denote $\underline{\Delta v}$ as the change of molar volume and ΔH is the corresponding change of enthalpy $V_{vapo} \gg V_{cond}$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$$

$$\Delta v = v_{vapour} - v_{condensed\ phase}$$

and here we can simplify with a good accuracy $\Delta v \sim v_{vapour}$.

- This relation allows writing the Clapeyron equation as:

$$(dP/dT)_{eq} = \Delta H/(T \times \cancel{\Delta} v_{höyry}).$$

$$= \frac{\Delta H}{T \cdot \underline{V_{vap}}}$$

Vapour pressure

- Assuming the gas/vapour phase as 1 mol of ideal gas, by inserting the PV=RT $\rightarrow V = \frac{RT}{P}$

$$(dP/dT)_{eq} = P \cdot \Delta H/(R \cdot T^2)$$

and after organising its terms we have

$$dP/P = \underline{d(\ln P)} = \underline{\Delta H/(R \cdot T^2)dT}.$$

- If ΔH is independent of temperature (which is never the fact in real systems, due to c_p(vapour) $\neq$ c_p(condensed)), after integration:

$$\underline{\ln P = -\Delta H/(RT^{\cancel{2}}) + \text{constant}.}$$

Vapour pressure

- The above equation (and phyiscal model for vapour pressure) allows us to fit experimental vapour pressures of pure substances over limited temperature ranges.
- A next order of magnitude improvement in the equation of vapour pressures is obtained by taking into account Δc_p of the vapourisation as constant.
- Thus the previous equation gets the form of

$$\ln P = (298\Delta c_p - \Delta H_{298})/(RT) + \Delta c_p/R \ln T + \text{constant}$$

$$\text{Or } \ln P = A/T + B \ln T + C.$$

Saturated vapour pressure of water

- The specific heat of vapour and water (273-373 K) are

  $c_p(H_2O(g)) = 30+10.7\times10^{-3}T+0.33\times10^{5}T^{-2}$ J/(K·mol)

  $c_p(H_2O(l)) = 75.44$ J/(K·mol).

- Thus for the vaporisation $H_2O(l)\rightarrow H_2O(g)$ we get

  $\Delta c_p(H_2O) = -45.44 +10.7\cdot10^{-3}T+0.33\cdot10^{5}T^{-2}$ J/(K·mol).

- At 1 atm and boiling point $\Delta_{evap}H_{H2O} = 41.09$ kJ/$\cancel{K}$ mol and the general equation of enthalpy results in

  $\Delta_{evap}H(T)=D_{evap}H(373)+{}_{373}\int^{T} \Delta c_p(l\rightarrow g)\, dT =$

  $= 57383 - 45.44T +5.35\times10^{-3}T^{2}-0.33\times10^{5}/T$ J/mol.

Saturated vapour pressure of water

- Inserting the above values into relation derived above

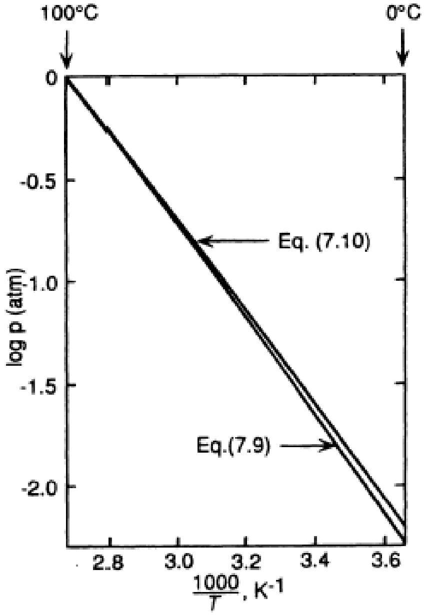
$$d \ln P = \Delta_{evap}H/(RT^2)\, dT$$

gives for R=8.3144 J/(K·mol) after simplifications

$$\log P = -2997/T - 5.465 \log T + 0.279\times10^{-3}T + 862/T^2 + 21.75.$$

- This is equation for saturated water vapour, i.e. water vapour in equilibrium with liquid water, in range 0-100°C.
- Fitted from the experimental observations

$$\log P(\text{atm}) = -2900/T - 4.65 \log T + 19.732.$$



Vapour pressure of metals

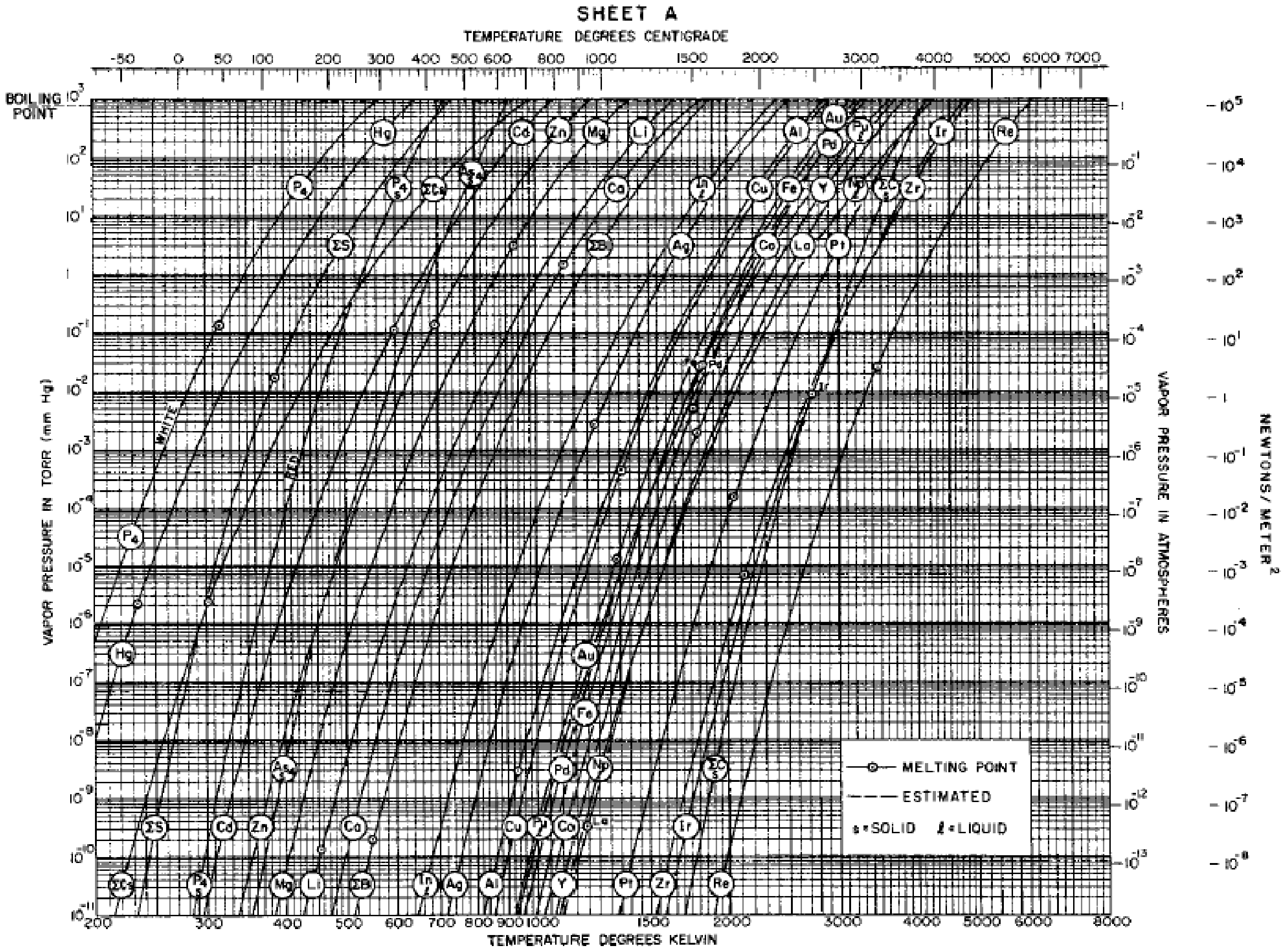


Fig. 1A. Vapor pressure data for the solid and liquid elements.

Left axis on the graph has units of [p]=torr, the right atm

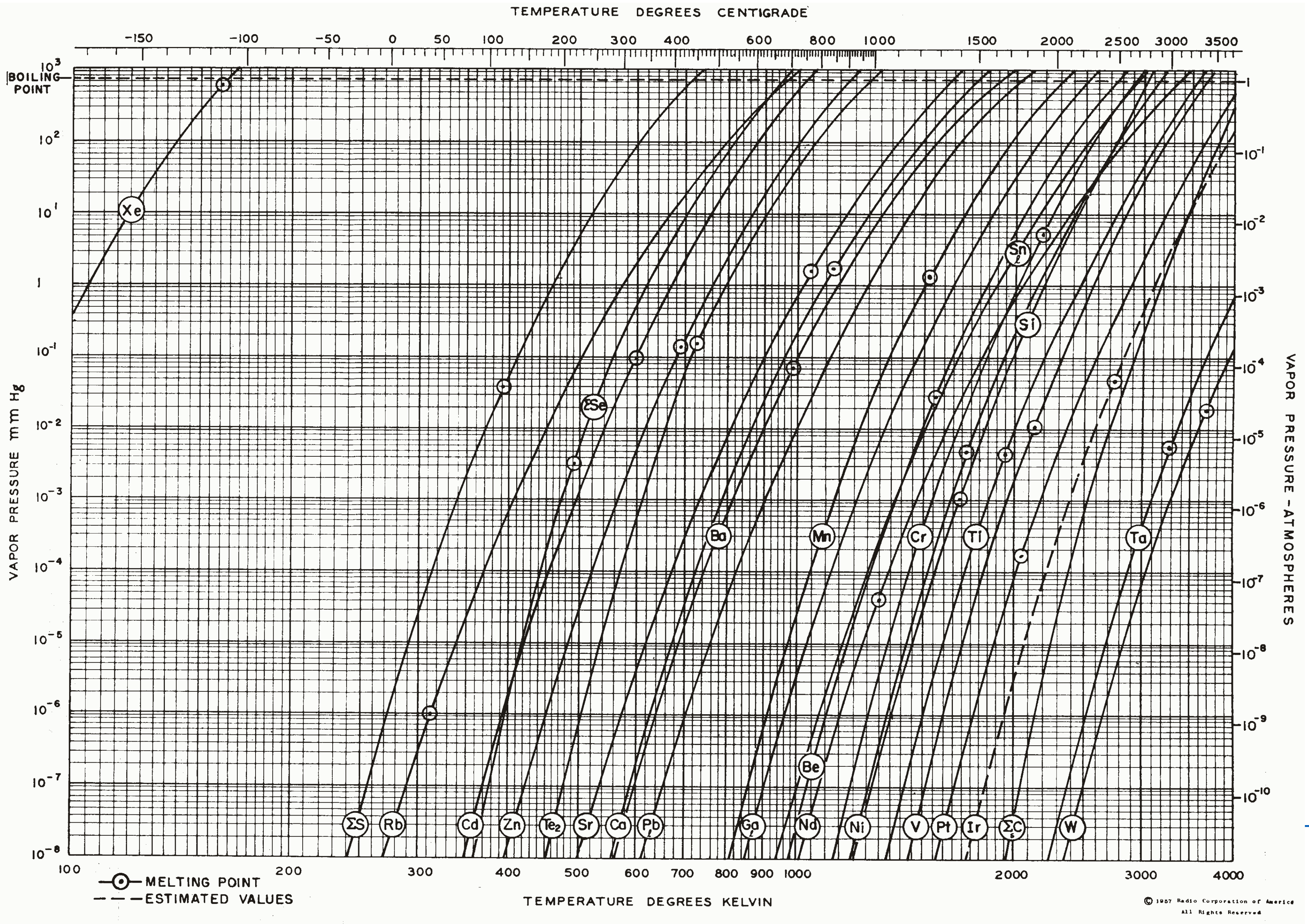


Figure A1(b). Vapor pressure curves for the more common elements (cont.). After Honig (Ref. 5:14). (Courtesy RCA Laboratories.)

Complex gases

- The previous treatment did not assume anything about the structure of gas, or reactions in the vaporisation process.
- Many metals and non-metals, without speaking about compounds and solutions with ‘reactive’ vaporisation, form polymers in the gas phase as

$$Me(g) \rightarrow {}^{1}/_{n}Me_{n}(g), \qquad \text{where } n = 2\dots N.$$

- The easiest and very straightforward way of estimating vapour pressures is to calculate equilibrium of the process as a chemical reaction instead of phase transformation (c)→(g).

Gas phase of elemental sulphur

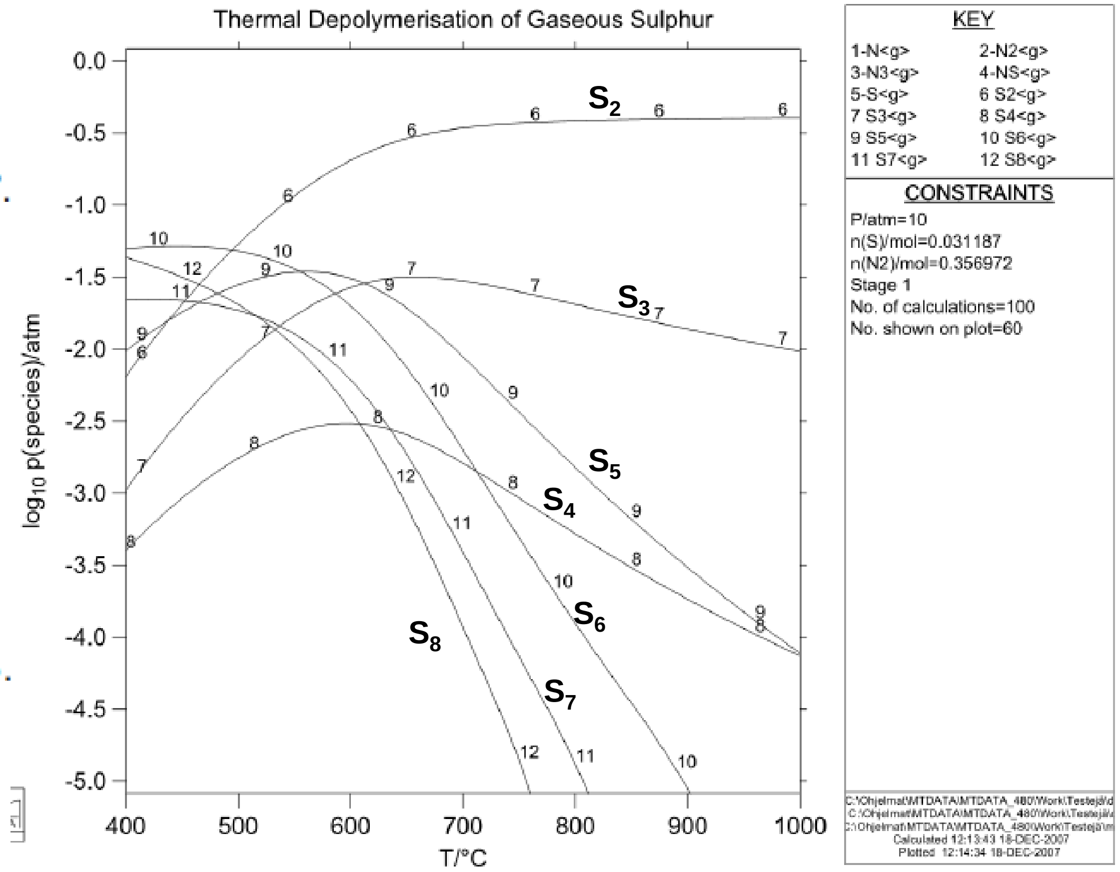
- As an example, the next case deals with the composition of vapour above pure liquid sulphur [S(l)] calculated from the thermodynamic data as a function of temperature.

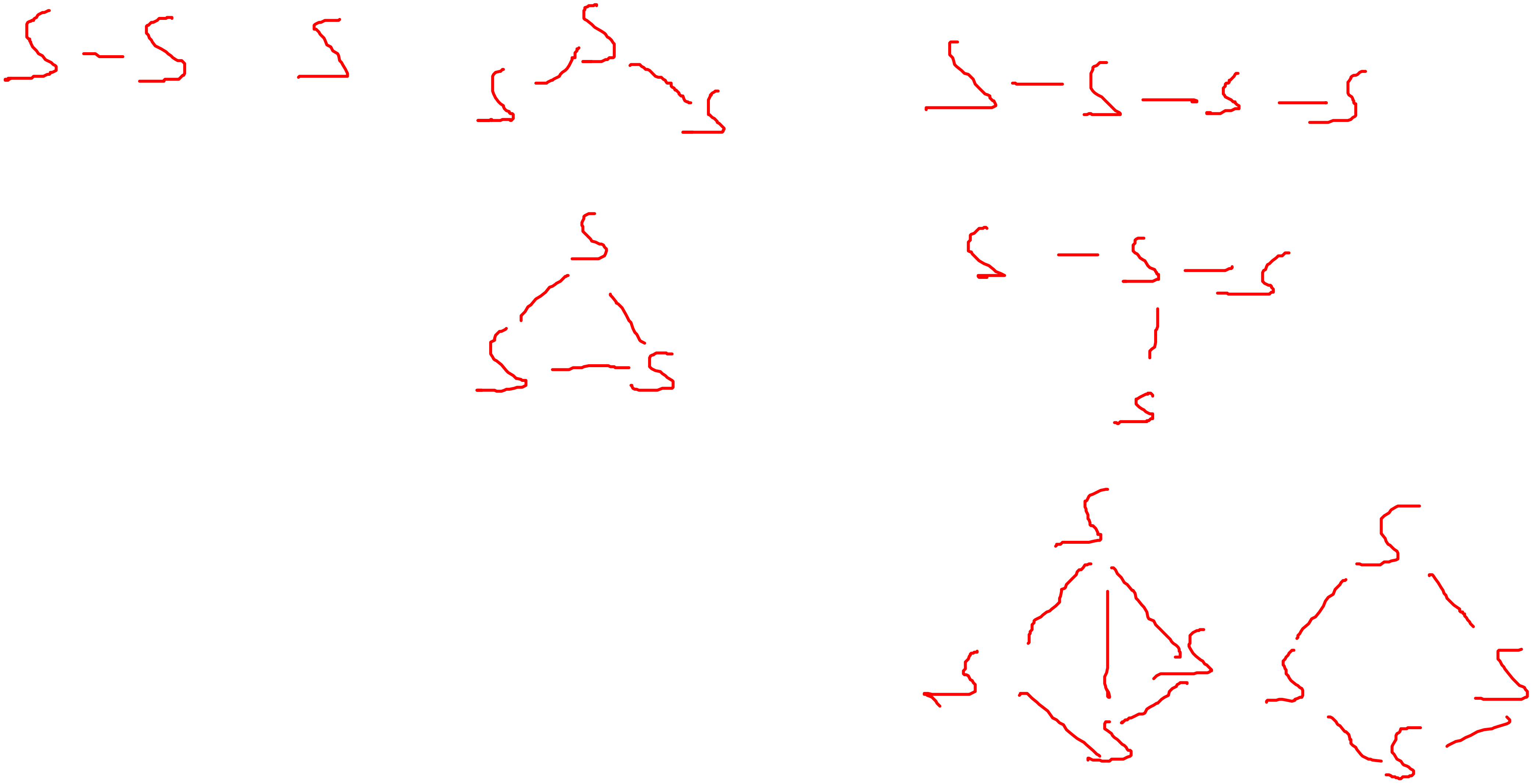
- Sulphur forms clusters in gas

  $S(l) \rightarrow {}^{1}/_{n}S_{n}(g)$ where n = *1-8.*

- The above process can be treated as chemical reaction.
- Total pressure of S in gas phase is (in ideal gas) sum of its species' partial pressures as:

  $P_{Stot(g)} = \Sigma\, p_{Sn(g)}$,   when n = 1…8.





Additional material:

COMMENTS ABOUT WS3

Equilibrium considerations

Stoichiometric reactions:

- Equilibrium condition can be written:

  $$G = \min \text{ or } d\,G = 0.$$

- Any chemical reaction can be written:

  $$\nu_A A + \nu_B B + \ldots = \nu_S S + \nu_T T + \ldots$$

  or generally as:

  $$\Sigma\, \nu_i B_i = 0.$$

- For constant T and p, i.e. **dT=0 and dp=0,** and no other work terms:

  $$d\,G = \Sigma\, \mu_i\, dn_i$$

Equilibrium of a single reaction

- For a stoichiometric reaction the **changes dn_i are given by the stoichiometric coefficients ν_i and the change in extend of reaction $d\xi$.**

$$\mathbf{dn_i = \nu_i \, d\xi_i}$$

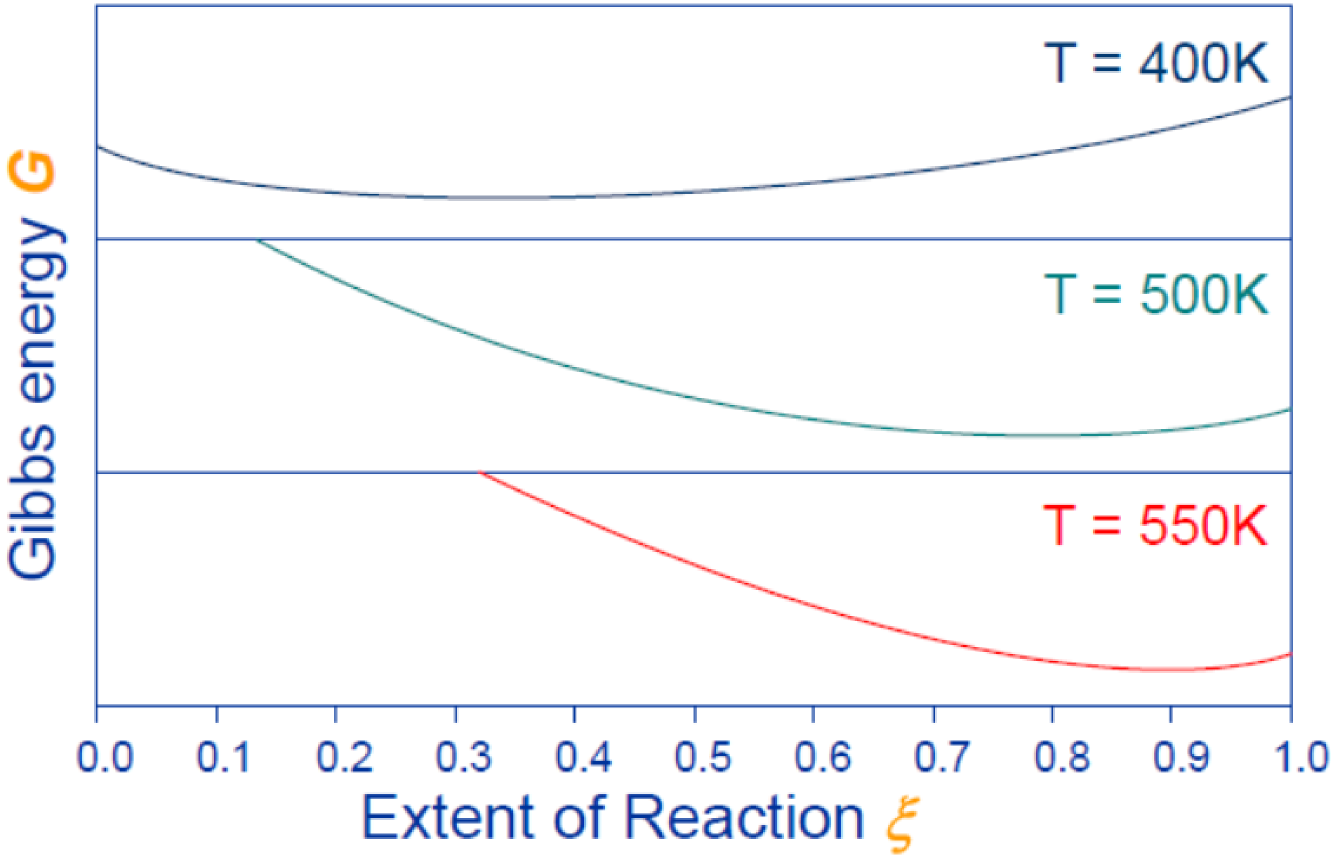
- Thus the problem becomes ***one-dimensional if there is only one single reaction in the system.***
- One obtains from $d\,G = \Sigma\, \mu_i\, dn_i$:

$$\mathbf{dG = \Sigma\, \mu_i\, \nu_i\, d\xi_i}$$

which in equilibrium gets $d\,G = 0$

The WP3 example
– as a reverse reaction

- Gibbs energy as a function of extent of the reaction $2NH_3 = N_2 + 3H_2$ for various temperatures; it is assumed, that the changes of enthalpy and entropy are constant.



Equilibrium of a single reaction

- Separation of variables results in:

$$dG/d\xi = \Sigma\ \nu_i\ \mu_i = 0$$

- Thus **the equilibrium condition** for a stoichiometric reaction is:

$$\Delta\ G = \Sigma\ \nu_i\ \mu_i = 0$$

- Introduction of standard potentials $\mu_i°$ and activities a_i yields:

$$\mu_i = {}^{\circ}\mu_i + RT\ \ln(\ a_i\ )$$

where a_i is activity of *i*

- One obtains:

$$\Sigma\ \nu_i{}^{\circ}\mu_i + RT\ \Sigma\ \ln(\ a_i\ )^{\nu i} = 0.$$

Equilibrium of a single reaction

- The expression further results in the definition of K:

$$\Delta G = \Delta G^\circ + RT \ln(K) = 0 \text{ where } K = \Pi\, a_i.$$

or

$$RT \ln(K) = -\Delta G^\circ$$

- This is called **the law of mass action** where the product of activities is commonly denoted as

$$K = \Pi\, a_i.$$

- K is called the equilibrium constant of reaction and it can be used for calculating *equilibrium states of single reactions*.