SYNTHESIS OF INORGANIC MATERIALS AND NANOMATERIALS

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Outline

II - SOLID-STATE REACTIONS

1) **Reactions between solid compounds**
   - a) **Ceramic method**
   - b) **Carbothermal reduction**
   - c) **Combustion synthesis**
   - d) **Sintering**

2) **Solid-gas reactions**

3) **Decomposition and dehydration reactions**

4) **Intercalation reactions**

3) Decomposition and dehydration reactions

Formation of gas + solid products

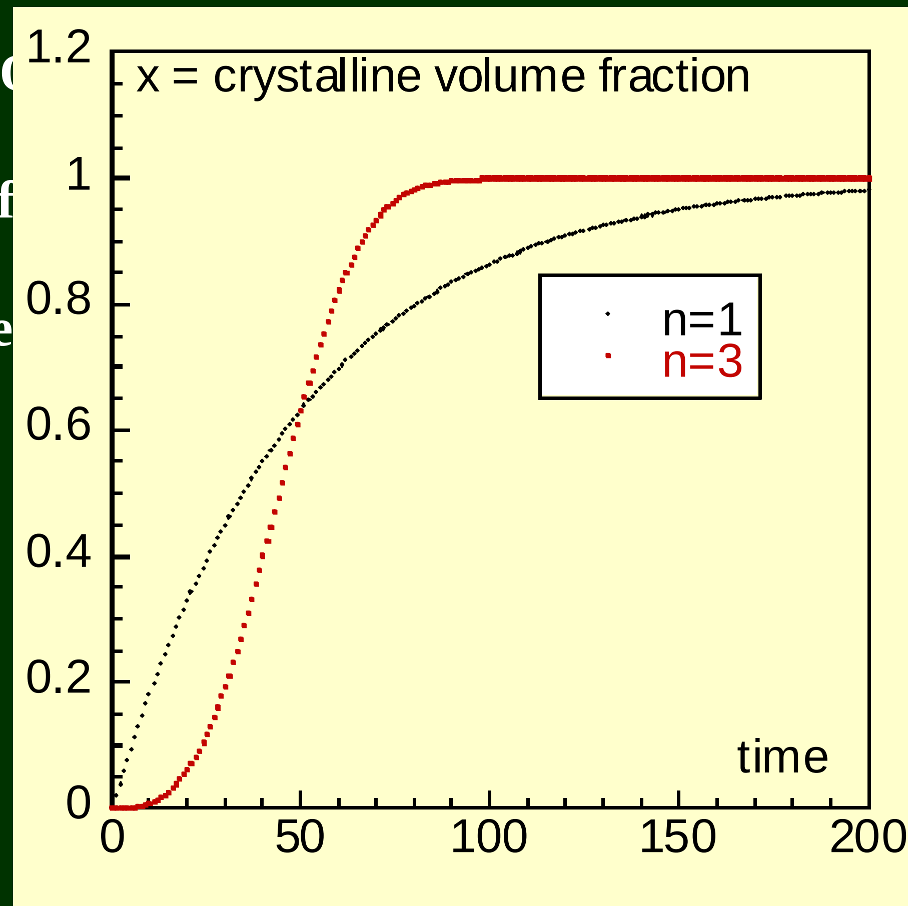
carbonate	➔	CO_2
oxalate	➔	$CO + CO_2$
nitrate	➔	$NO + NO_2 + O_2$
hydroxide	➔	$H_2O(g)$

Ex.: γ-AlO(OH) (boehmite) ➔ γ_Al_2O_3 + H_2

Gas formation ➔formation of structural def

Reaction rate: sigmoidal plot (Avrami-Erofe

Possibility to obtain metastable products



3) Decomposition and dehydration reactions

➔ **See figures**

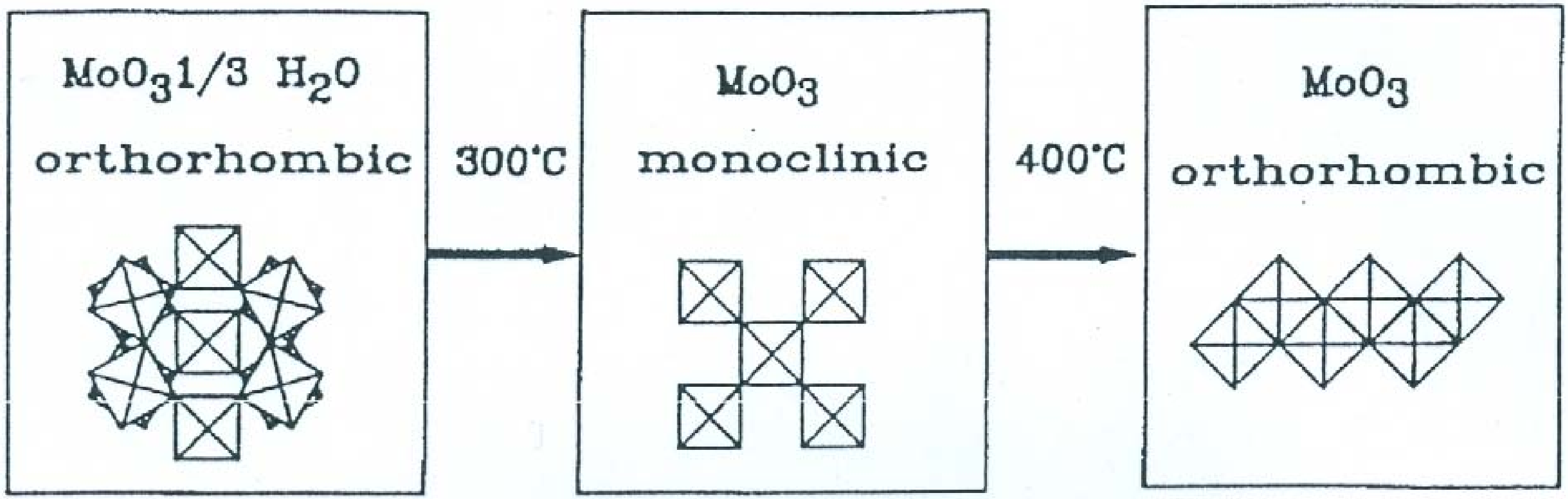
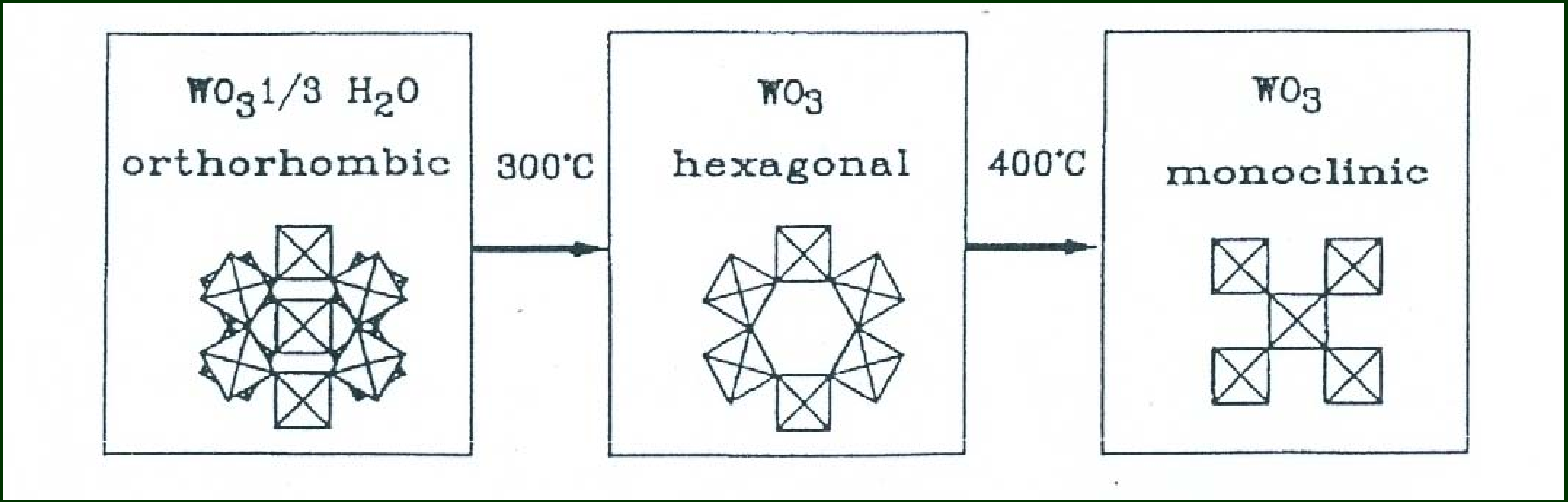


Figure 2-19. Structural relations in the dehydration of $MoO_3 \cdot {}^1/_3\ H_2O$ and $WO_3 \cdot {}^1/_3\ H_2O$ and in the phase transformations of MoO_3 and WO_3. Each crossed square represents an octahedron viewed from above.

3) Decomposition and dehydration reactions

➔ **See figures**



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II - SOLID-STATE REACTIONS

1) Reactions between solid compounds
2) Solid-gas reactions
3) Decomposition and dehydration reactions
4) Intercalation reactions
   - ➡ a) General aspects
   - b) Preparative methods
   - c) Pillaring of layered compounds

3) Intercalation reactions a) General aspects

Topochemical reactions

→ insertion of guest species in host lattices → guest-host reactions

- 3D lattice with parallel or interconnected channels

→ zeolites Ex.: mordenite (see figure)

- 2D lattice → layers

- 1D lattice → chains, nanotubes, nanofibers

Ex.: intercalation compounds of graphite (see figure)

compound	interlayer distance /Å	
graphite	3.35	
graphite + Li	3.71	
graphite + K	5.35	C_8K
graphite + AsF_5	8.15	
graphtie + KHg	10.22	

3) Intercalation reactions a) General aspects

Charge of the layer:

- neutral: graphite, FeOCl, CdS_2, TiS_2 (layered compounds)

Ex.: TiS_2 (see figure)

- negatively charged: clays, phosphate layers → mobile cations
- positively charged: layered double hydroxides $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}$
  → mobile anions

Electrical properties:

- insulator host lattice: zeolites, aluminosilicates
  → adsorbants, catalysts, catalyst supports, ion exchangers
- conducting or semiconducting host lattice: graphite, metallic sulfides
  → oxidation and reduction reactions
  → electrode materials for cell, battery

$Li_{1-x}CoO_2 + x\ Li^+ + x\ e^-$ = $LiCoO_2$ cathode

What are the oxidation numbers?

$Li_{1-x}Co^{III}_{1-x}Co^{IV}_{x}O_2 + x\ Li^+ + x\ e^-$ = $LiCo^{III}O_2$ cathode

C_6Li_x = $6\ C(graphite) + x\ Li^+ + x\ e^-$ anode

$Li_{1-x}CoO_2 + C_6Li_x$ = $LiCoO_2 + 6\ C(graphite)$

charged discharged

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Direct reaction

Ex.: $8C(s) + K(g) \rightarrow C_8K(s)$ reduction

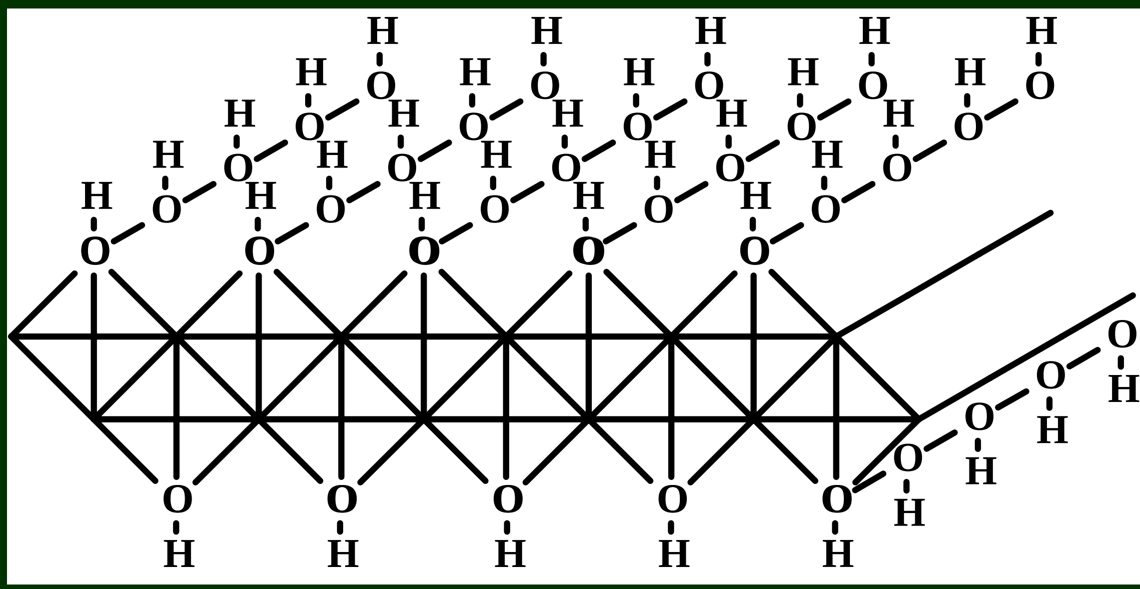
$16\ C(s) + Br_2(g) \rightarrow 2\ C_8Br(s)$ oxidation

$TiS_2(s) + x\ Li(g) \rightarrow Li_xTiS_2(s)$

$MX_n(s) + x\ LiC_4H_9(\text{solvated}) \rightarrow Li_xMX_n + x/2\ C_8H_{18}$

Structure and coordination number of layered compounds

FeOCl (iron oxychloride)	AlO(OH) (boehmite)	AlO(OH) (diaspore)
6 4 2	6 4 2	6 3 3 (non layered)



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Structure of silicates and aluminosilicates

- Si coordination number 4 ➔ tetrahedral geometry
- O coordination number 1 (terminal) or 2 (bridge)
- For bridging O the angle varies between 120 to 180 °
- Al coordination number 6 (octehedra) or 4 (tetrahedra, replacing Si)

3D structure: silica, quartz, feldspath, zeolites (see figure)

➔ SiO_2, $[Al_xSi_{1-x}O_2]^{x-}$

2D structure: layers, clays (see figure)

➔ $[Si_2O_5]^{2-}$

➔ $[Al_xSi_{2-x}O_5]^{(2+x)-}$

➔ kaolinite $[Al_2(OH)_4]^{2+}[Si_2O_5]^{2-}$ (see figure)

➔ possibility to intercalate neutral species

➔ formation of colloidal suspension

1D structure: chains or cycles (see figure)

- single chains: $[SiO_3]^{2-}$
- double chains: $[Si_4O_{11}]^{6-}$ asbestos
- cycles: $[Si_3O_9]^{6-}$ $[Si_6O_{18}]^{12-}$

3) Intercalation reactions c) Pillaring of layered compounds

Ex.: Muscovite $K^+[Al_2(OH)_2]^{4+}[AlSi_3O_{10}]^{5-}$ (See structure)

Replacement of K^+ by larger cations

➔ Possibility to introduce pillars to increase and control interlayer distance

➔ catalyst with shape selectivity

➔ ion exchangers

Ex.: $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{n+}$ diameter 0.86 nm (see figure) ➔value of n?

Answer: $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$

➔ thermal treatment 500 °C ➔ Al_2O_3 particles 0.7 – 0.8 nm (S_{BET} ~ 300 m^2 g^{-1})

Positive layers with hydroxides $[Mg^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$ (M = Al^{3+}, Fe^{3+})

➔ anion exchangers

➔ pillars

Ex.: polyvanadates $[V^V_{10}O_{28}]^{6-}$

Ex.: heteropoly anions $[P^VW^{VI}_{12}O_{40}]^{n-}$ (Keggin structure) ➔ value of n?

Answer: $[P^VW^{VI}_{12}O_{40}]^{3-}$

3) Intercalation reactions c) Pillaring of layered compounds

Ex.: model of pillared clays (restaurant in Dan Dong City)

Outline

III - FORMATION OF SOLIDS FROM THE GAS PHASE

1) Chemical vapor transport
   - ➡ a) General aspects of chemical transport
   - b) Halogen lamp
   - c) Transport reactions

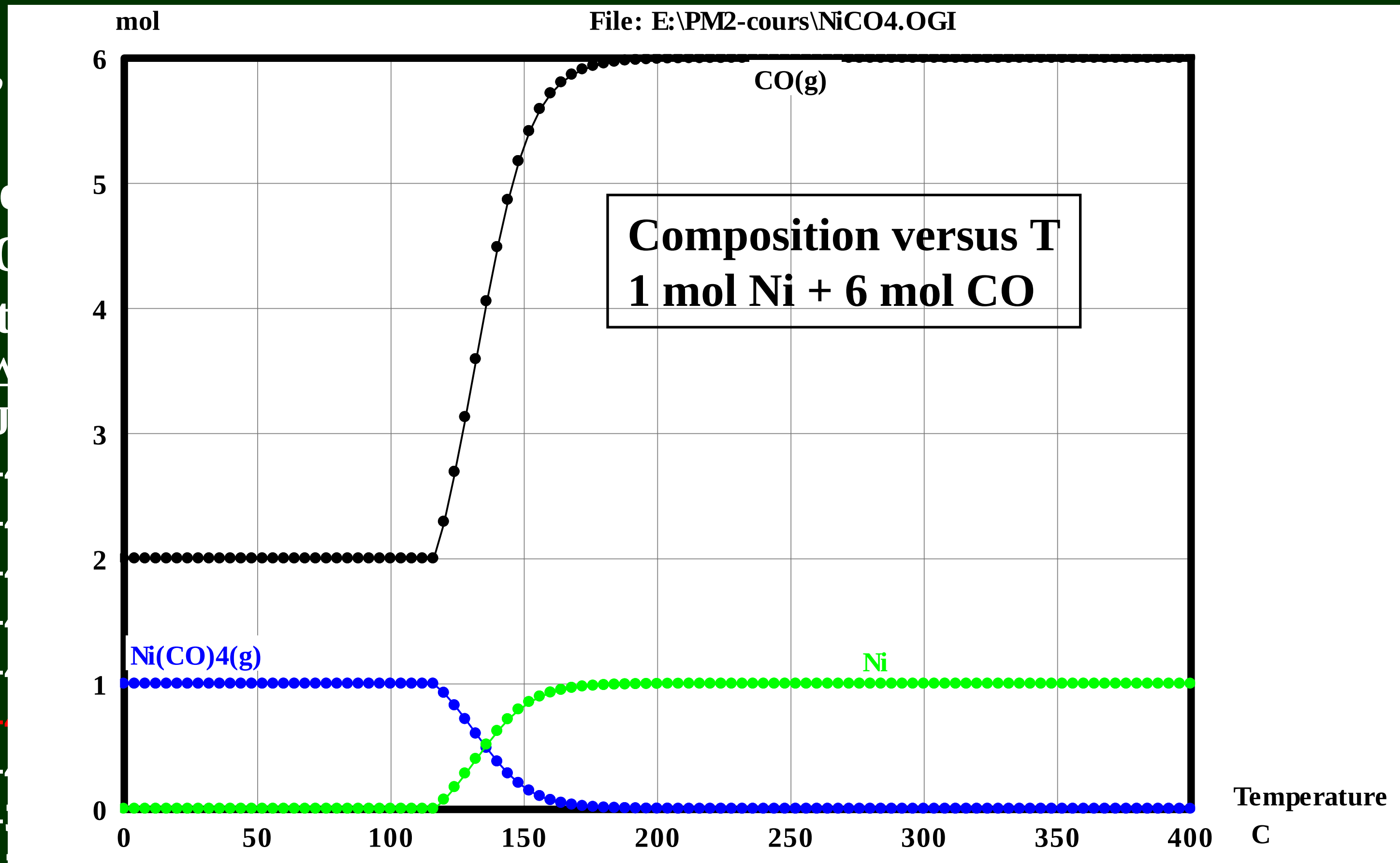
2) Chemical vapor deposition (CVD)

3) Aerosol processes

$$A(s) + B(g) = AB(g)$$

Closed system

Parameters: pressure,



Ex. 1: Mond proc

$Ni(s) + 4\ C$

Results from HSC soft

T	$\Delta_r H°$	Δ	
°C	kJ mol^{-1}	J	
0.000	-159.538		
25.000	-159.435		
50.000	-159.231		
75.000	-158.967		
100.000	-158.657		
125.000	-158.309		
150.000	-157.932		
175.000	-157.532		
200.000	-157.122	-399.008	31.669
225.000	-156.706	-398.153	41.634

$$Ni(s) + 4\ CO(g) \rightarrow Ni(CO)_4(g) \quad 80\ °C$$

$$Ni(s) + 4\ CO(g) \leftarrow Ni(CO)_4(g) \quad 230\ °C$$

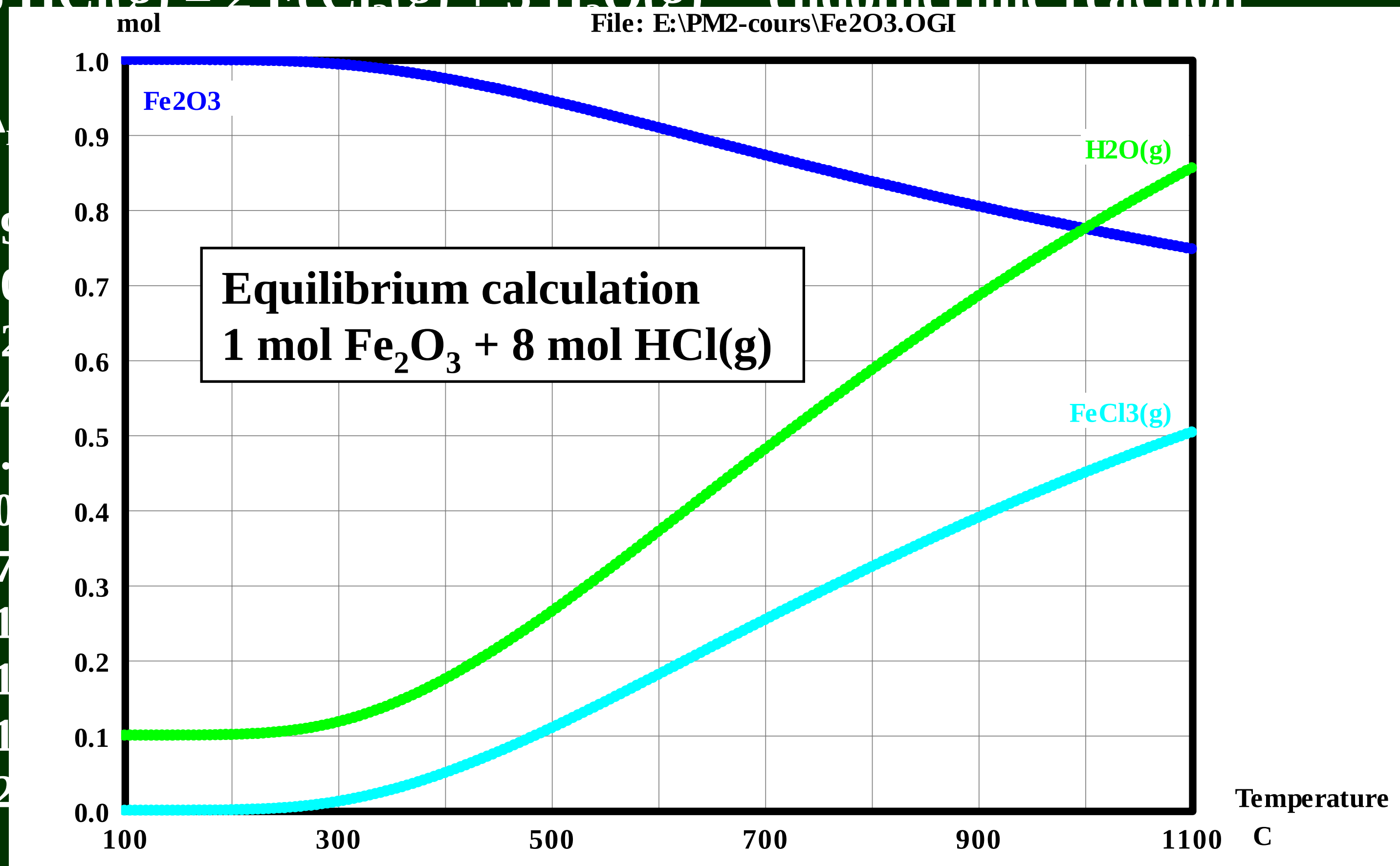
$$A(s) + B(g) = AB(g)$$

Closed system

Parameters: pressure, temperature (see figure)

Ex. 2: $Fe_2O_3(s) + 6\,HCl(g) = 2\,FeCl_3(g) + 3\,H_2O(g)$ endothermic reaction

T	$\Delta_r H°$	Δ_r
°C	kJ mol^{-1}	J
100.000	142.845	39
200.000	139.123	30
300.000	134.923	22
400.000	130.231	14
500.000	124.933	7.
600.000	118.751	-0
700.000	111.486	-7
800.000	106.949	-1
900.000	102.855	-1
1000.000	98.814	-1
1100.000	94.788	-2



➔ **Geological interest for transportation of Fe_2O_3 in volcanos**

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1) Chemical vapor transport b) Halogen lamp

1879: first incandescent lamp;

carbon filament replaced by tungsten filament

- low vapor pressure
- high melting point (3400 °C)
- inert gas filling (Ar + N_2)
- but condensation at the colder region of the lamp bulb
- wire becomes thinner ➔ wire rupture

➔ introduction of traces of I_2 (0.1 mg per cm^3)

$$W(s) + I_2(g) = WI_2(g)$$

== self-healing process