

Problem 1. Polar winter in Antarctic

$$\text{a) } \Delta_r G_{190}^\circ = \Delta_r H^\circ \cdot \left(1 - \frac{190 \text{ K}}{220 \text{ K}}\right) + \Delta_r G_{220}^\circ \cdot \frac{190 \text{ K}}{220 \text{ K}}$$

$$\Delta_r G_{190}^\circ (\text{HNO}_3 \cdot \text{H}_2\text{O}) = 127 \cdot \left(1 - \frac{190 \text{ K}}{220 \text{ K}}\right) \text{ kJ/mol} + 46.2 \text{ kJ/mol} \cdot \frac{190 \text{ K}}{220 \text{ K}} = 57.2 \text{ kJ/mol}$$

$$\Delta_r G_{190}^\circ (\text{HNO}_3 \cdot 2\text{H}_2\text{O}) = 188 \cdot \left(1 - \frac{190 \text{ K}}{220 \text{ K}}\right) \text{ kJ/mol} + 69.4 \text{ kJ/mol} \cdot \frac{190 \text{ K}}{220 \text{ K}} = 85.6 \text{ kJ/mol}$$

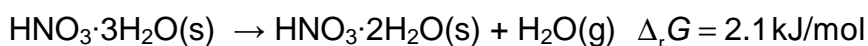
$$\Delta_r G_{190}^\circ (\text{HNO}_3 \cdot 3\text{H}_2\text{O}) = 237 \cdot \left(1 - \frac{190 \text{ K}}{220 \text{ K}}\right) \text{ kJ/mol} + 93.2 \text{ kJ/mol} \cdot \frac{190 \text{ K}}{220 \text{ K}} = 112.8 \text{ kJ/mol}$$

$$\text{b) } Q = p(\text{H}_2\text{O})^n \cdot p(\text{HNO}_3), \quad \Delta_r G = \Delta_r G^\circ + RT \ln Q$$

$$\Delta_r G(\text{HNO}_3 \cdot \text{H}_2\text{O}) = \left[57.2 + 1.58 \cdot \ln(1.3 \cdot 10^{-7} \cdot 4.1 \cdot 10^{-10}) \right] \text{ kJ/mol} = -2.0 \text{ kJ/mol}$$

$$\Delta_r G(\text{HNO}_3 \cdot 2\text{H}_2\text{O}) = \left[85.6 + 1.58 \cdot \ln\left(\left(1.3 \cdot 10^{-7}\right)^2 \cdot 4.1 \cdot 10^{-10}\right) \right] \text{ kJ/mol} = 1.3 \text{ kJ/mol}$$

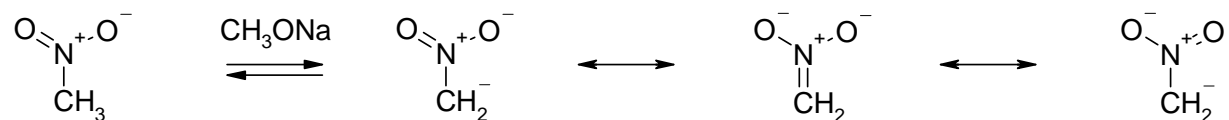
$$\Delta_r G(\text{HNO}_3 \cdot 3\text{H}_2\text{O}) = \left[112.8 + 1.58 \cdot \ln\left(\left(1.3 \cdot 10^{-7}\right)^3 \cdot 4.1 \cdot 10^{-10}\right) \right] \text{ kJ/mol} = 3.5 \text{ kJ/mol}$$



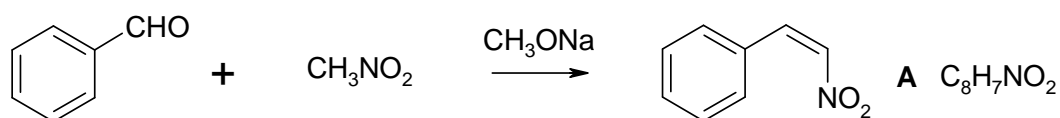
Under these conditions $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ does not sublime and is stable. $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ is metastable hydrate.

Problem 2. Synthesis of bicyclic compound

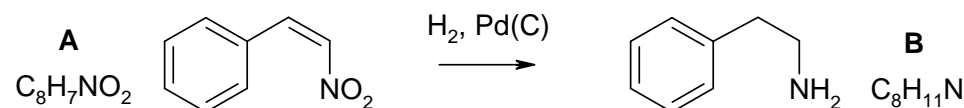
1. Increased acidity of nitromethane is due to formation of the resonance stabilized anion.



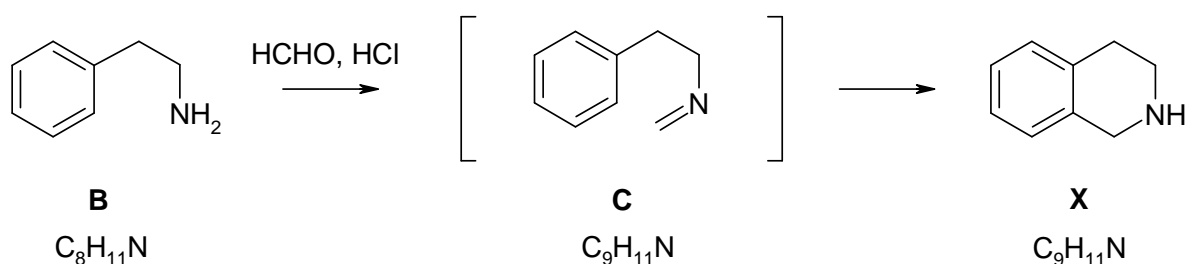
2. Each correct structure (A, B, C, X) is 2 pts.



3.



4.



Problem 3. Isoleucine dating

$$\text{a) } \ln\left(\frac{[\text{L-iLeu}] - [\text{L-iLeu}]_{\text{eq}}}{[\text{L-iLeu}]_0 - [\text{L-iLeu}]_{\text{eq}}}\right) = -k_{\text{sum}} t$$

$$[\text{L-iLeu}]_0 = [\text{L-iLeu}] + [\text{D-aLeu}] = [\text{L-iLeu}] \cdot (1 + 0,42)$$

$$[\text{L-iLeu}]_0 = [\text{L-iLeu}]_{\text{eq}} + [\text{D-aLeu}]_{\text{eq}} = [\text{L-iLeu}]_{\text{eq}} \cdot (1 + 1,38)$$

$$[\text{L-iLeu}]_{\text{eq}} = [\text{L-iLeu}]_0 / (1 + 1,38) = [\text{L-iLeu}] \cdot (1 + 0,42) / (1 + 1,38)$$

$$\frac{[\text{L-iLeu}] - [\text{L-iLeu}]_{\text{eq}}}{[\text{L-iLeu}]_0 - [\text{L-iLeu}]_{\text{eq}}} = \frac{1 - \frac{1,42}{2,38}}{1,42 - \frac{1,42}{2,38}} = 0,49$$

$$k_{\text{sum}} = -\ln(0,49) / (38600 \text{ y}) = 1,85 \cdot 10^{-5} \text{ y}^{-1}$$

$$\begin{cases} k_1 / k_{-1} = 1,38 \\ k_1 + k_{-1} = 1,85 \cdot 10^{-5} \text{ y}^{-1} \end{cases} \Rightarrow \begin{cases} k_1 = 1,07 \cdot 10^{-5} \text{ y}^{-1} \\ k_{-1} = 7,77 \cdot 10^{-6} \text{ y}^{-1} \end{cases}$$

$$\text{b) } \ln(k_{293}/k_T) = -16800 \cdot (0,003411 - 1/T), \quad k_{293} = \ln 2 / T_{1/2} = 5,55 \cdot 10^{-6} \text{ y}^{-1}$$

$$1/T = \ln(5,55/18,5) / 16800 + 0,003411 = 0,003339$$

$$T = 299,5 \text{ K} = 26,3^\circ\text{C} \quad (26\text{--}27^\circ\text{C})$$

Problem 4. Goblin's element

a) When a body is immersed in a liquid it experiences gravitation and Archimede's force. Assume the sample of metal X has the mass of m and the volume of V :

$$\begin{cases} m_{\text{CCl}_4} g = mg - \rho_{\text{CCl}_4} Vg \\ m_{\text{H}_2\text{O}} g = mg - \rho_{\text{H}_2\text{O}} Vg \end{cases}, \quad \begin{cases} m_{\text{CCl}_4} = m - \rho_{\text{CCl}_4} V \\ m_{\text{H}_2\text{O}} = m - \rho_{\text{H}_2\text{O}} V \end{cases}, \quad \begin{cases} 12,046 = m - 1,5940V \\ 13,031 = m - 1,000V \end{cases}, \quad \begin{cases} m = 14,689 \\ V = 1,658 \end{cases}$$

$$\text{So } \rho = \frac{14,689 \text{ g}}{1,658 \text{ cm}^3} = 8,859 \text{ g/cm}^3.$$

b) Using de Bogies relation the wavelength of neutrons is

$$\lambda = \frac{6,626076 \cdot 10^{-34} \text{ J} \cdot \text{s}}{1,674929 \cdot 10^{-27} \text{ kg} \cdot 3115,0 \text{ m/s}} = 1,2700 \cdot 10^{-10} \text{ m} = 127,00 \text{ pm}.$$

According to Bragg's law the separation between (222) planes is

$$d_{222} = \frac{1,2700 \cdot 10^{-10} \text{ m}}{2 \sin 38,478^\circ} = 1,0205 \cdot 10^{-10} \text{ m} = 102,05 \text{ pm}.$$

With simple geometrical relations it can be proved that $a = d_{222} \sqrt{12}$. So $a = 353,51 \text{ pm}$

c) The FCC structure contains 4 atoms: $\rho = \frac{4 \frac{M}{N_A}}{a^3}$.

$$\text{So } M = \frac{\rho a^3 N_A}{4},$$

$$M = \frac{8859 \text{ kg/m}^3 (353,51 \cdot 10^{-12} \text{ m})^3 \cdot 6,022142 \cdot 10^{23} \text{ mol}^{-1}}{4} = 0,058922 \text{ kg/mol} \approx 58,9 \text{ g/mol}$$

So metal X is Co.

- d) The simplest chemical formula satisfying the chemical composition of compound A is Co_3O_4 .
- e) Co_3O_4 consists of Co atoms with different oxidation states: $\text{CoO} \cdot \text{Co}_2\text{O}_3$. It is expected the Co_3O_4 reaction with diluted HCl to give two salts as products, but there is compound B only. Moreover O_2 is released indicating an oxidation-reduction reaction.

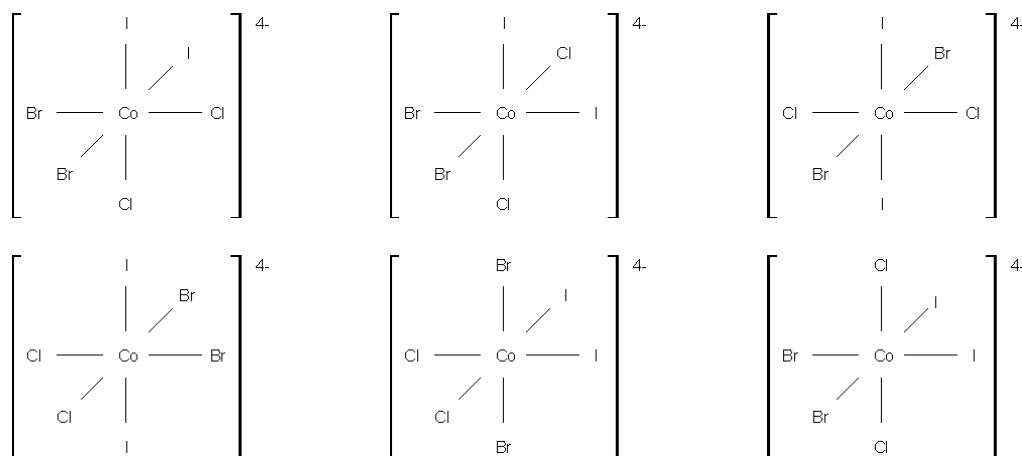
$$\text{There are: } n(\text{Co}_3\text{O}_4) = \frac{n(\text{Co})}{3} = \frac{m(\text{Co})}{3M(\text{Co})} = \frac{14.689\text{g}}{3 \cdot 58.9332\text{g/mol}} = 0.083083\text{mol}$$

$$\text{and } n(\text{O}_2) = \frac{pV}{RT} = \frac{0.1 \cdot 10^6 \text{ Pa} \cdot 0.0010298 \text{ m}^3}{8.314472 \text{ Jmol}^{-1} \text{ K}^{-1} \cdot 298.15 \text{ K}} = 0.041642\text{mol}$$

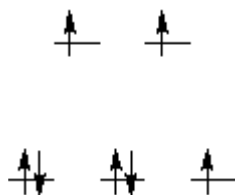
$$\text{so } n(\text{Co}_3\text{O}_4) : n(\text{O}_2) \approx 2 : 1$$

Taking into account the conservation law of matter and charge the balanced chemical equation of the reaction is: $2\text{Co}_3\text{O}_4 + 12\text{HCl} \longrightarrow 6\text{CoCl}_2 + \text{O}_2 + 6\text{H}_2\text{O}$

- f) The isomers of ion C

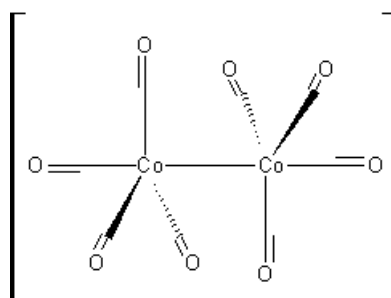


- g) The electronic configuration of Co^{2+} is $[\text{Ar}]3d^7$ and halogenides make a weak octahedral field. So



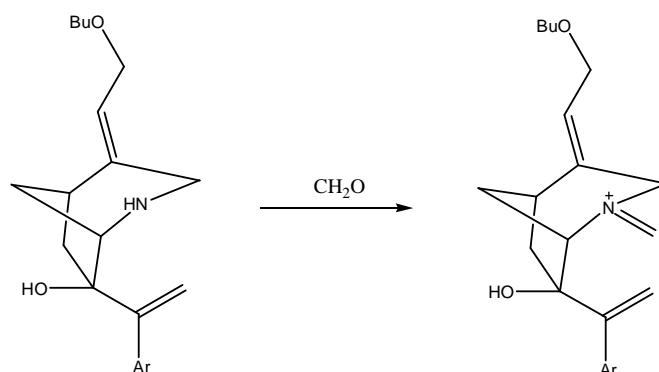
Therefore there are 3 unpaired electrons.

- h) Compound D

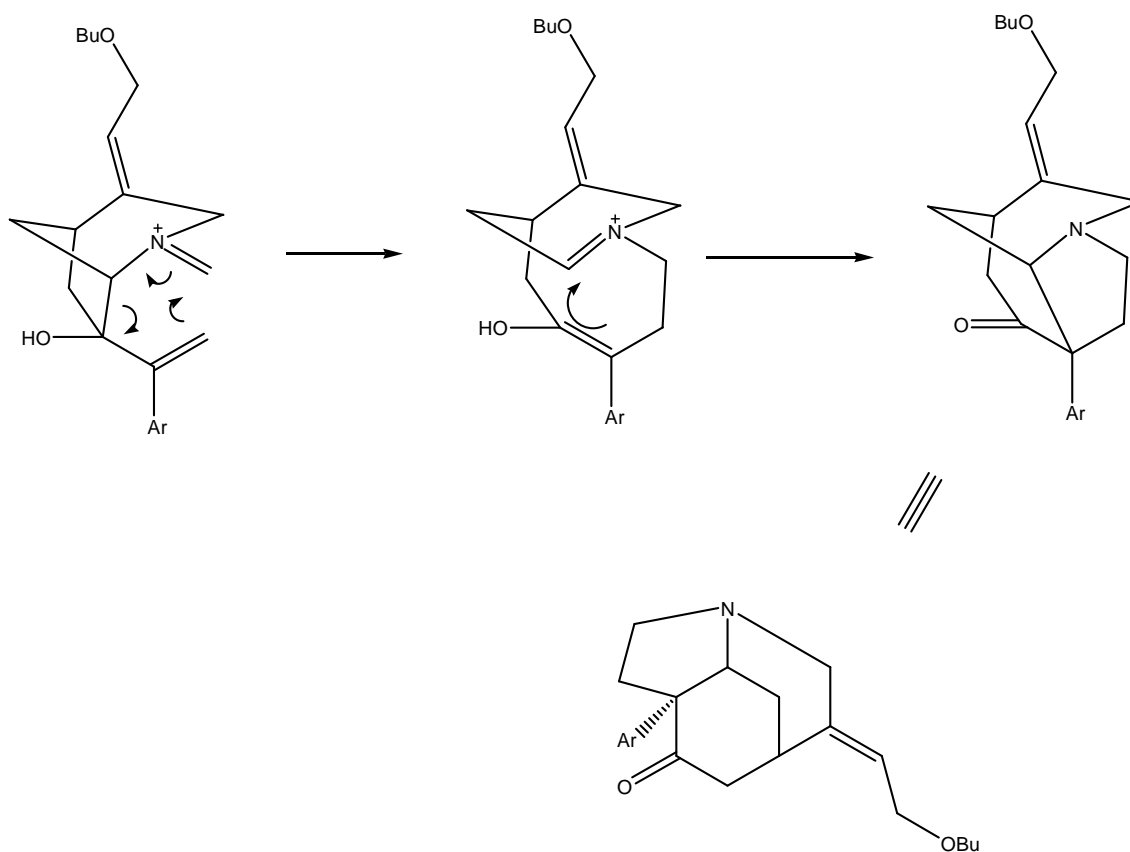


Problem 5. Sigmatropic rearrangement

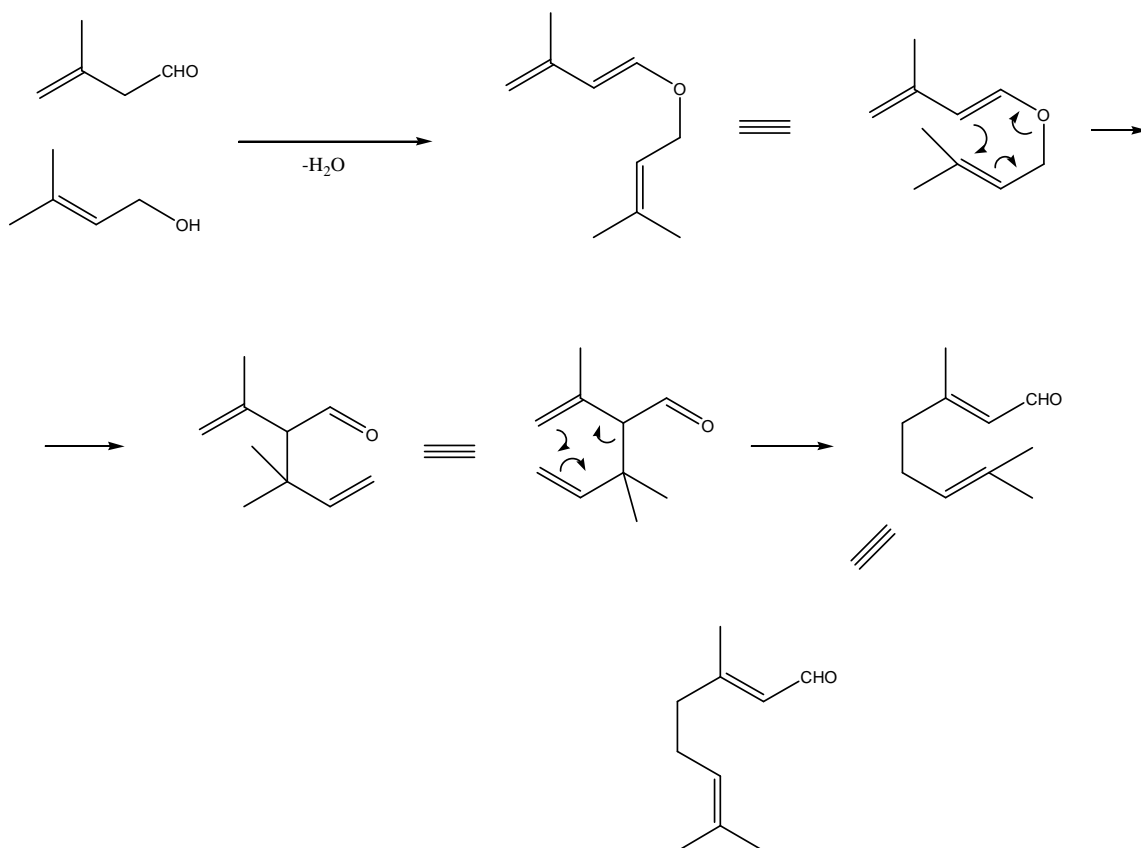
Example 1. First, the iminium ion is formed by condensation of the secondary amine and the aldehyde:



[3,3]-sigmatropic rearrangement gives an intermediate enol, shown below, which cyclizes onto the new iminium ion to give the ketone product:



Example 2. From the **HINT** it is clear that the reaction between alcohols and aldehydes under dehydration conditions affords enol ethers. The enol ether formed undergoes two subsequent [3,3]-sigmatropic rearrangements- first Claisen and then Cope ones:

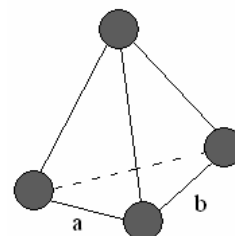


Problem 6. Dolomite

a) It is known that dolomite contains two metallic elements calcium and magnesium. For determination, which metal is which useful are metallic radii calculated from crystallographic data. Metal with smallest atomic radii will be magnesium, but metal with largest radii will be calcium.

In hexagonal close packed structure (ABAB type structure) smallest distance between atoms is on edge of tetrahedron, where three apices are in one layer, but fourth is in second layer.s

Length of tetrahedron edge is equal to sum of to metal atomic radii and also is equal to shortest edge length of unit cell.



$$r(A) = \frac{a}{2} = \frac{3,2094}{2} = 1,6047 \text{ \AA}$$

The second metal has cubic close packed structure. It refers to cubic face centred unit cell. The smallest distance between atoms is on face diagonal, it contains four atomic radii. .

$$4 \cdot r(B) = \sqrt{2a^2} = \sqrt{62,46} = 7,903 \text{ \AA}$$

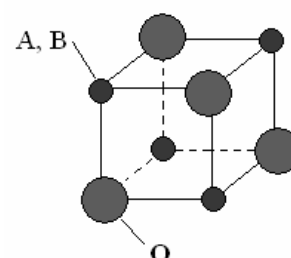
$$r(B) = 1,9758 \text{ \AA} > r(A)$$

So **A – magnesium and B – calciums.**

b) NaCl type crystalline lattice is shown in figure on right. (1/8 part of unit cell).

$$r(A \text{ vai } B) + r(O) = \frac{1}{2} \cdot a$$

a – cell paremeter



MgO

$$a = 4,213 \text{ \AA}$$

$$r(\text{A}^{2+}) = 2,1065 - 1,28 = 0,83 \text{ \AA} \quad \dots \text{ radii of Mg}^{2+}$$

decrease 48 %

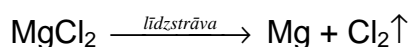
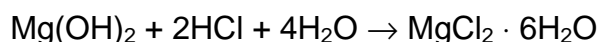
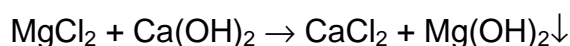
CaO

$$a = 4,811 \text{ \AA}$$

$$r(\text{B}^{2+}) = 2,4055 - 1,28 = 1,13 \text{ \AA} \quad \dots \text{ radii of Ca}^{2+}$$

decrease 42,8 %

c) Reaction equations:

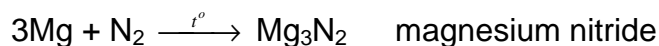


Mass of compound obtained in electrolysis can calculate from:

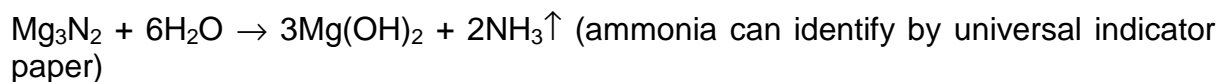
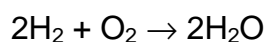
$$m = \frac{I \cdot t \cdot M}{z \cdot F}$$

$$1000000 = \frac{5 \cdot t \cdot 24,3}{2 \cdot 96485}$$

$$t = \frac{2 \cdot 96485 \cdot 10^6}{9,0 \cdot 10^3 \cdot 24,3} = 8,82 \cdot 10^5 \text{ s} = 245 \text{ h} = 10,2 \text{ days} \approx 10 \text{ days}$$

d) $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ 

Formation of magnesium nitride can prove:

e) $\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \uparrow$ 

$$\Delta H_{\text{reakc.}(1.)} = \Delta H_{\text{f},298}(\text{Mg(OH)}_2) - 2 \cdot \Delta H_{\text{f},298}(\text{H}_2\text{O},\text{l}) = -924,66 - 2 \cdot (-285,83) = -353 \text{ kJ}$$

$$\Delta H_{\text{reakc.}(2.)} = 2 \cdot \Delta H_{\text{f},298}(\text{H}_2\text{O},\text{l}) = 2 \cdot (-285,83) = -571,66 \text{ kJ}$$

from 24,3 grams (1 mol) magnesium forms $Q = -\Delta H_{\text{reakc.}(1.)} + \frac{1}{2} \cdot (-\Delta H_{\text{reakc.}(2.)}) = -638,83 \text{ kJ}$

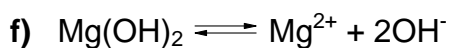
To heat 1 liter ($1000 / 18 = 55,56 \text{ mol}$) of water for $100^\circ - 20^\circ = 80^\circ\text{C}$ is necessary: $Q = C \cdot n \cdot \Delta t^\circ = 0,07530 \cdot 55,56 \cdot 80 = 334,67 \text{ kJ}$ of heat

Now write proportion:

... from 24 g magnesium forms 638,83 kJ of heat

from x g 334,67 kJ

$$x = \frac{334,67 \cdot 24,3}{638,83} = 12,73 \text{ g} = \underline{\underline{13 \text{ g}}} \quad (\text{two significant figures})$$



$$K_s = [\text{Mg}^{2+}][\text{OH}^-]^2 = 10^{-11,25} \text{ M}^3$$

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ M}^2$$

$$\text{Solubility is } S = [\text{Mg}^{2+}]$$

$$2 \cdot [\text{Mg}^{2+}] + [\text{H}^+] = [\text{OH}^-]$$

$$2 \cdot S + [\text{H}^+] = [\text{OH}^-]$$

$$S = \frac{K_s}{[\text{OH}^-]^2}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$$

$$2 \cdot \frac{K_s}{[\text{OH}^-]^2} + \frac{K_w}{[\text{OH}^-]} = [\text{OH}^-] \quad | \cdot [\text{OH}^-]^2$$

$$2 \cdot K_s + K_w \cdot [\text{OH}^-] = [\text{OH}^-]^3$$

Assume, that $K_w \cdot [\text{OH}^-] \ll 2 \cdot K_s$

$$2 \cdot K_s = [\text{OH}^-]^3$$

$$[\text{OH}^-] = \sqrt[3]{2 \cdot K_s} = \sqrt[3]{2 \cdot 5,62 \cdot 10^{-12}} = 2,24 \cdot 10^{-4} \text{ M}$$

$$S = \frac{K_s}{[\text{OH}^-]^2} = \frac{5,62 \cdot 10^{-12}}{(2,24 \cdot 10^{-4})^2} = 1,12 \cdot 10^{-4} \text{ M}$$

Verify correctness of assumption:

$$K_w \cdot [\text{OH}^-] = 10^{-14} \cdot 2,24 \cdot 10^{-4} = 10^{-17,6}$$

$$2 \cdot K_s = 10^{-10,9}$$

Difference more than 1000 times, so assumption is correct

Solubility (mg/L) = $S \cdot M = 1,12 \cdot 10^{-4} \cdot 58,3 = 6,530 \cdot 10^{-3} = \underline{\underline{6,530 \text{ mg}}}$ (four significant figures)