

## Solution problem 4: Heat Conductivity

4.1 The heat flows are:

$$P_W = 150 \text{ m}^2 \cdot (0.24 \text{ m})^{-1} \cdot 0.81 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \cdot (25^\circ\text{C}-10^\circ\text{C}) = 7.59 \text{ kW and}$$

$$P_W = 150 \text{ m}^2 \cdot (0.36 \text{ m})^{-1} \cdot 0.81 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \cdot (25^\circ\text{C}-10^\circ\text{C}) = 5.06 \text{ kW}$$

4.2  $P_W = 150 \text{ m}^2 \cdot (0.1 \text{ m})^{-1} \cdot 0.040 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \cdot (25^\circ\text{C}-10^\circ\text{C}) = 0.90 \text{ kW}$

Although the wall is much thinner, the energy loss is much lower due to the much lower heat conductivity.

4.3  $k = \lambda \cdot d^{-1} \rightarrow d = \lambda \cdot k^{-1} = 0.81 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \cdot (0.5 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1})^{-1} \quad d = 1.62 \text{ m}$

4.4  $\Lambda^{-1} = k^{-1} = (0.50 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1})^{-1} = d_1 \cdot (\lambda_1)^{-1} + d_2 \cdot (\lambda_2)^{-1} + d_3 \cdot (\lambda_3)^{-1} + d_4 \cdot (\lambda_4)^{-1} =$   
 $0.15 \text{ m} \cdot (0.81 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})^{-1} + 0.10 \text{ m} \cdot (1.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})^{-1} + d_3 \cdot (0.040 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})^{-1} + 0.05 \text{ m} \cdot$   
 $(0.35 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})^{-1}$

The thickness of the insulation foam layer is  $d_3 = 6.3 \text{ cm}$

The total thickness is:  $15 \text{ cm} + 10 \text{ cm} + 6.3 \text{ cm} + 5 \text{ cm} = 36.3 \text{ cm}$

4.5  $k = \Lambda_1 \cdot A_1 \cdot (A_{\text{tot}})^{-1} + \Lambda_2 \cdot A_2 \cdot (A_{\text{tot}})^{-1}$   
 $0.50 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1} = 0.70 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1} \cdot 4 \text{ m}^2 \cdot (15 \text{ m}^2)^{-1} + \Lambda_2 \cdot 11 \text{ m}^2 \cdot (15 \text{ m}^2)^{-1}$   
 $\Lambda_2 = 0.427 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ .

The calculation is similar to that of 4.4:

The thickness of the insulation foam layer is  $d_3 = 7.7 \text{ cm}$

The total thickness is:  $5 \text{ cm} + 10 \text{ cm} + 7.7 \text{ cm} + 5 \text{ cm} = 37.7 \text{ cm}$

due to the much higher heat conductivity of the window.

The thickness of the foam layer has to be increased by 22%.

## Solution problem 5: Supercritical CO<sub>2</sub>

5.1  $dW = -n \cdot R \cdot T \cdot dV \cdot V^{-1}$  or  $W = -n \cdot R \cdot T \cdot \ln(p_1/p_2)$

$$n = p \cdot V \cdot (R \cdot T)^{-1} = (50 \cdot 10^5 \text{ Pa} \cdot 50 \cdot 10^{-6} \text{ m}^3) \cdot (8.314 \text{ JK}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K})^{-1} = 0.10 \text{ mol}$$

$$W = -0.10 \text{ mol} \cdot 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \cdot 298 \text{ K} \cdot \ln(1/50) = 969 \text{ J}$$

5.2 The calculation can be most easily carried out with the molar volume  $V_m = M \cdot \rho^{-1}$ . The equation  $[p + a \cdot (n \cdot V^{-1})^2] \cdot (V - n \cdot b) = n \cdot R \cdot T$  can be simplified to

$$[p + a \cdot V_m^{-2}] \cdot (V_m - b) = R \cdot T$$

Example of the calculation (density  $\rho = 440 \text{ g dm}^{-3}$  or  $V_m = 0.10 \text{ dm}^3 \text{ mol}^{-1}$ ;  $T = 305 \text{ K}$ )

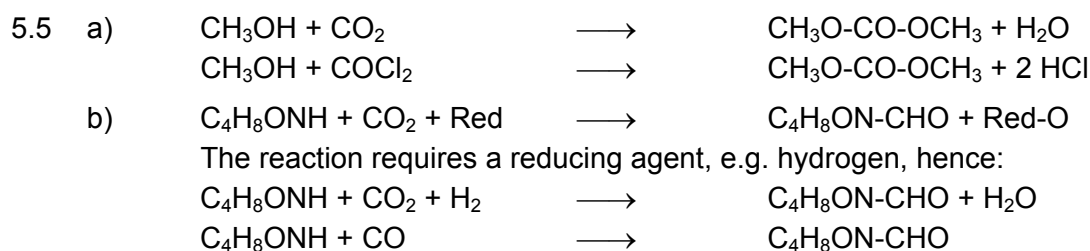
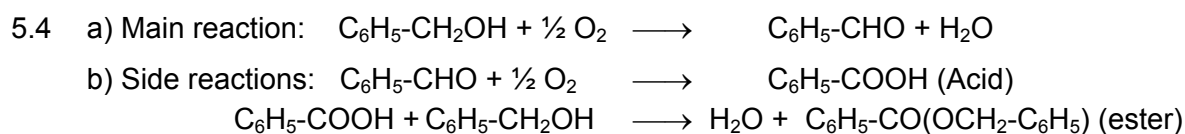
$$[p + (3.59 \cdot 10^5 \text{ Pa} \cdot 10^{-6} \text{ m}^6 \text{ mol}^{-2}) \cdot (0.1^2 \cdot 10^{-6} \text{ m}^6 \text{ mol}^{-2})^{-1}] \cdot$$

$$(0.1 \cdot 10^{-3} \text{ m}^3 \text{ mol}^{-1} - 0.0427 \cdot 10^{-3} \text{ m}^3 \text{ mol}^{-1}) = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \cdot 305 \text{ K}$$

$$p = 83.5 \cdot 10^5 \text{ Pa}$$

$\rho \cdot (\text{g}\cdot\text{dm}^{-3})^{-1}$	$V_m \cdot (\text{dm}^3\cdot\text{mol}^{-1})^{-1}$	$T \cdot \text{K}^{-1}$	$p \cdot \text{Pa}^{-1}$
220	0.200	305	$71.5 \cdot 10^5$
330	0.133	305	$77.9 \cdot 10^5$
440	0.100	305	$83.5 \cdot 10^5$
220	0.200	350	$95.2 \cdot 10^5$
330	0.133	350	$119.3 \cdot 10^5$
440	0.100	350	$148.8 \cdot 10^5$

5.3 The results in the table above show that a 10 bar change in pressure near the critical temperature results in nearly double the density. Far above the critical temperature, however, such a change requires higher pressures. Hence, it is useful to work near the critical temperature/pressure.

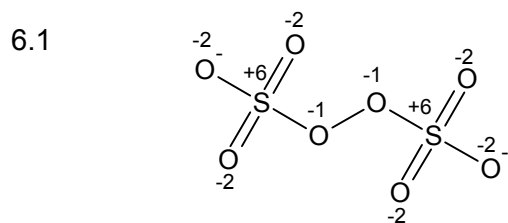


5.6 The advantage of using carbon dioxide is that it is not poisonous in contrast to carbon monoxide and phosgene.  $\text{CO}_2$  makes the process safer. Moreover, using  $\text{CO}_2$  both as reactant and as solvent is advantageous, since no additional solvent is necessary.

Another reason may be the reduction of the  $\text{CO}_2$ -emission, but this will not be significant.

One of the disadvantages is that  $\text{CO}_2$  is much less reactive than  $\text{CO}$  or  $\text{COCl}_2$  – therefore a search for suitable catalysts is inevitable (catalysts have been found only for a few reactions, such as the formylation of amines).

## Solution problem 6: Chemical Kinetics of the Peroxodisulfate Ion



6.2  $r = k \cdot c(\text{S}_2\text{O}_8^{2-}) \cdot c(\text{I}^-)$

6.3 reaction order: 2

partial reaction order of  $\text{S}_2\text{O}_8^{2-}$ : 1

partial reaction order of  $\text{I}^-$ : 1

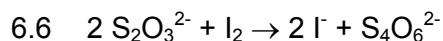
6.4  $k = \frac{r}{c(\text{S}_2\text{O}_8^{2-}) \cdot c(\text{I}^-)} = \frac{1.1 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}{0.1 \cdot 10^{-3} \cdot 1 \cdot 10^{-2} \text{ mol}^2 \cdot \text{L}^{-2}} = 0.011 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

6.5 Using the Arrhenius equation we may write

$$k_1 = A \cdot e^{-\frac{E_a}{R \cdot T_1}}, k_2 = A \cdot e^{-\frac{E_a}{R \cdot T_2}} \quad \Rightarrow \quad \frac{k_1}{k_2} = e^{\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$

because  $k_1/k_2 = 1/10$ , it follows that

$$\ln \frac{1}{10} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \Leftrightarrow \frac{1}{T_2} = \frac{R}{E_a} \cdot \ln \frac{1}{10} + \frac{1}{T_1} \quad \Rightarrow T_2 = 345 \text{ K} \approx 72^\circ\text{C}$$



6.7 It has to be noticed that the concentration of the iodide ions does not vary any longer, because iodine formed reacts quickly with thiosulfate ions (which are available in excess according to the precondition) forming iodide ions again.

Therefore the reaction is of pseudo-1<sup>st</sup>-order and the rate equation is given by  $r = k' \cdot c(\text{S}_2\text{O}_8^{2-})$

(It is important to note that the rate constant  $k'$  is different from  $k$  of the parts 6.2 - 6.5 of this problem, because it includes the pseudo-constant concentration of the iodide ions).

## Solution problem 7: Catalytic Hydrogenation of Ethylene

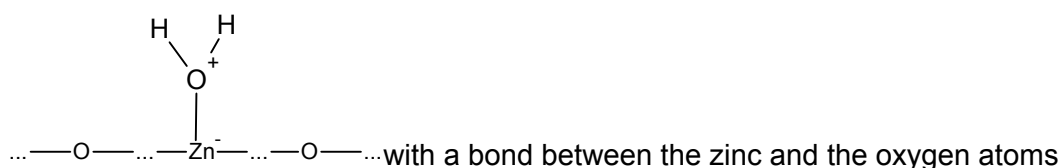
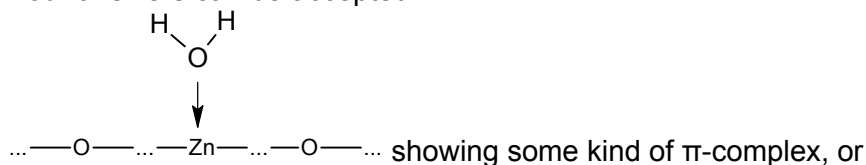
7.1

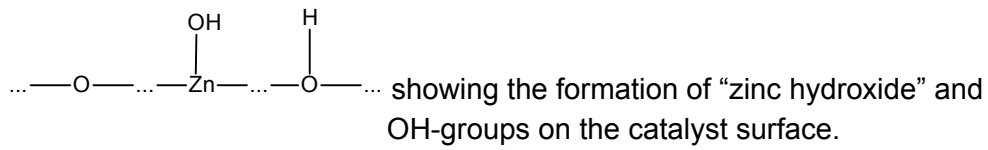
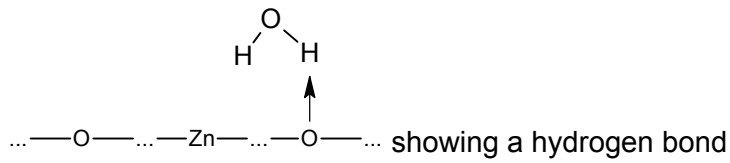
No.		No.	
1		5	
3		7	
4		2	
6			

7.2 The hydrogenation of the adsorbed intermediate is the slowest step of the reaction. This is the reason why the concentration, or in this case the fraction of surface sites that are occupied, has to be part of the rate equation.

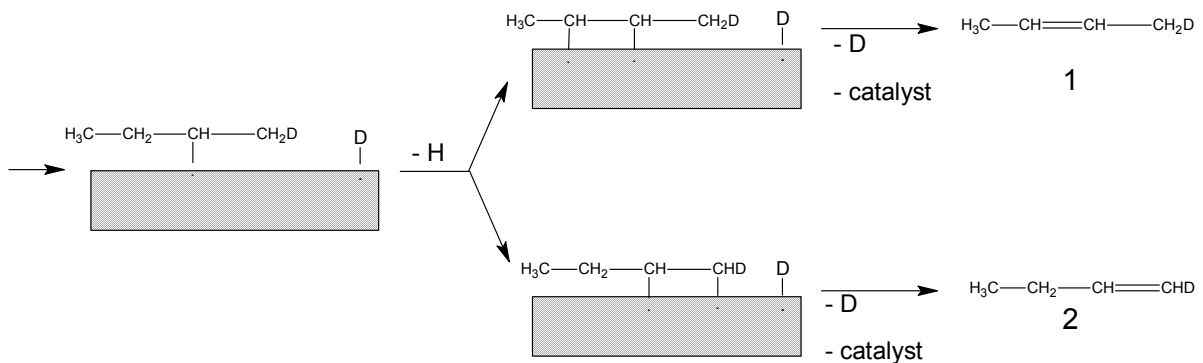
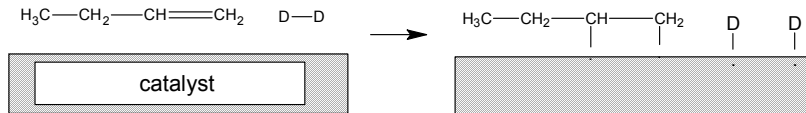
Answer (4) is correct.

7.3 Four answers can be accepted:





7.4



7.5 Knowing the derivation of the Langmuir isotherm from the law of mass action you can obtain:

$$\theta(i) = \frac{K_i \cdot p_i}{1 + \sum_j K_j \cdot p_j}$$

**Solution problem 8: Kinetics of an Enzymatic Reaction**

8.1  $x = 1, y = -1, z = 1$

8.2.  $\frac{dc(E)}{dt} = -k_1c(S)c(E) + k_{-1}c(ES) + k_2c(ES)$

8.3 The reciprocal rate is plotted as a function of the reciprocal substrate concentration:

$$\frac{1}{r} = \frac{K_M}{k_2c_T(E)} \cdot \frac{1}{c(S)} + \frac{1}{k_2c_T(E)}$$

Intercept at  $1/c(S) = 0$  yields  $\frac{1}{r} = \frac{1}{k_2 c_T(E)} = 0.02 \cdot 10^6 \text{ L min mol}^{-1}$

With  $c_T(E) = 10^{-9} \text{ mol L}^{-1}$  we obtain  $k_2 = 50000 \text{ min}^{-1}$

Intercept at  $1/r = 0$  yields  $\frac{1}{c(S)} = -\frac{1}{K_M} = -0.09 \cdot 10^6 \text{ L mol}^{-1}$

$K_M = 1.1 \cdot 10^{-5} \text{ mol L}^{-1}$ .

Alternatively, the slope is  $\frac{K_M}{k_2 c_T(E)} = 0.22 \text{ min}$

$K_M = 1.1 \cdot 10^{-5} \text{ mol L}^{-1}$

The rate of the enzymatic reaction is given as

$$\frac{dc(P)}{dt} = k_2 c(ES) = k_2 c_T(E) \frac{c(S)}{K_M + c(S)}$$

$$c(ES) = c_T(E) \frac{c(S)}{K_M + c(S)}$$

$$c(ES) = c_T(E) \frac{0.01 K_M}{K_M + 0.01 K_M}$$

$$c(ES) = 9.9 \cdot 10^{-3} c_T(E)$$

$$c(ES) = 9.9 \cdot 10^{-12} \text{ mol L}^{-1}$$

8.4  $K = \frac{c(I)c(E)}{c(EI)} = \frac{c(I) \cdot 0.5c_T(E)}{0.5c_T(E)} = c(I) = 9.5 \cdot 10^{-4} \text{ mol L}^{-1}$

The total inhibitor concentration is

$$c_T(I) = c(I) + c(EI) = K + 0.5 \cdot c_T(E) = 1.35 \cdot 10^{-3} \text{ mol L}^{-1}$$

- 8.5 true (the inhibitor reduces the free enzyme concentration and thus the rate of ES formation. A lower ES concentration results and leads to a smaller reaction rate)  
 false (the maximum rate is reached for  $c(S) = \infty$  where the inhibitor concentration can be ignored)  
 false (the inhibitor reduces the free enzyme concentration and thus promotes the dissociation of the complex ES into E and S (Le Chatelier's principle))  
 false (the activation energy depends on the rate constants that are independent of concentrations)

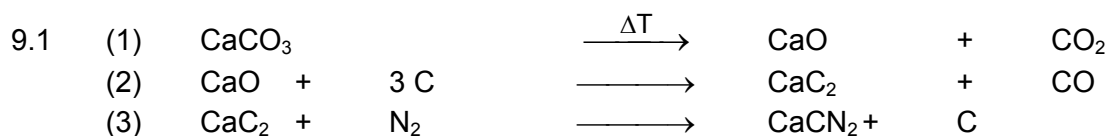
8.6 The enzyme is only a catalyst. The net reaction is  $S \rightleftharpoons P$

true (because  $K = c^{eq}(P) / c^{eq}(S)$ )

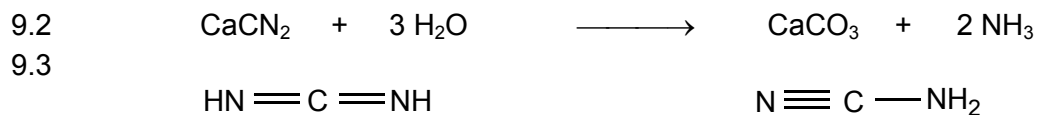
false (because K does not depend on the enzyme concentration)

true (because K is the ratio of the rate constants for the forward and the reverse reaction)

## Solution problem 9: $\text{CaCN}_2$ – An Old but still Important Fertilizer



This process that is technically important is called the Frank-Caro process.

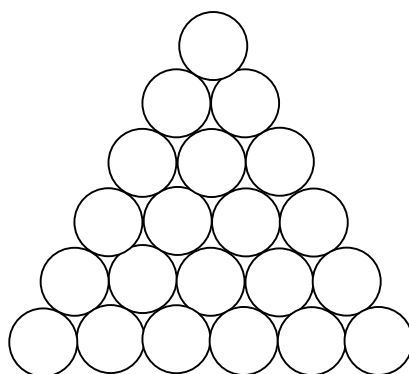


The first compound is the acid of the carbodiimide ion, the second is that of cyanamide. The equilibrium favours the more symmetric structure.

(Inorg.Chem. 2002, 41, 4259 - 4265)

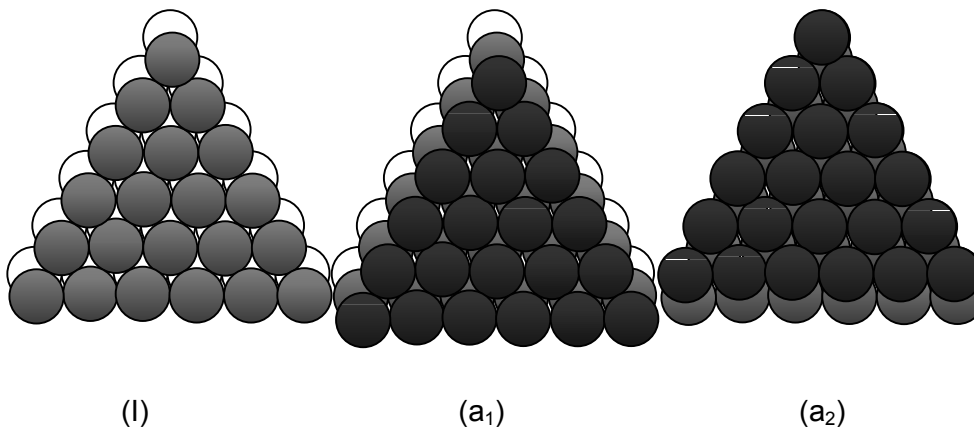
## Solution problem 10 : Closed-Packed Structures

10.1



In the two-dimensional model each indistinguishable atom is surrounded by six other atoms.

10.2

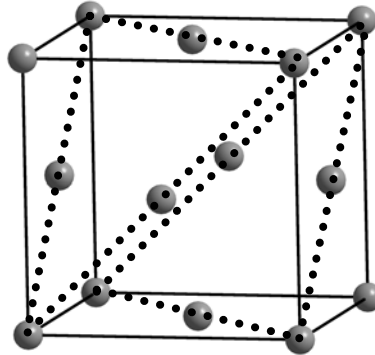


A transformation into a three-dimensional model can be achieved by stacking the 2D closed-packed layers (I). Each atom has six neighbours in the plane surrounding it, and three further atoms located in the holes above the atom and three atoms located in the holes below the atom.

- a) Looking at the second layer, there are two possibilities of putting a third layer on top. Either the atoms are put into the holes such that there is no atom directly beneath them in the first layer (a<sub>1</sub>), or into the same positions they occupy in the first layer (a<sub>2</sub>). These possibilities create the two different closed-packed structures, ABCABC (cubic closed-packed) and ABAB (hexagonal closed packed).

- b) In principle, an infinite number of stacking patterns can be generated by the combination of these two basic stacking possibilities.

10.3



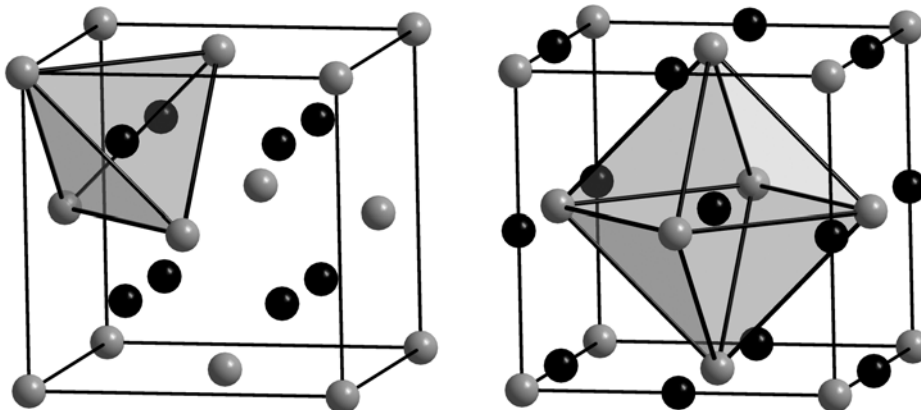
- 10.4 In this illustration, the atoms touch on the face diagonals. The length of the edges of the cube is  $2r \cdot \sqrt{2}$ . There are 4 complete atoms in the cube (8 corners with one eighth of an atom in each and 6 sides with one half of an atom in the middle of each). So the packing efficiency is:

$$\frac{4 \cdot \frac{4}{3} \pi r^3}{(2r\sqrt{2})^3} = \frac{16}{3} \frac{\pi r^3}{16r^3\sqrt{2}} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

A cubic primitive packing has a packing efficiency of:

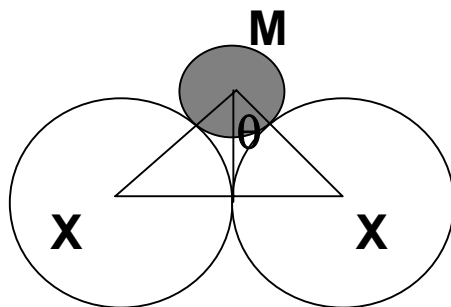
$$\frac{1 \cdot \frac{4}{3} \pi r^3}{(2r)^3} = \frac{4}{8} \pi = 0.52 \text{ or } 52\%$$

10.5



The elemental cube of a face centered cubic structure contains 4 packing atoms (one at the corner and three on the faces of the cube), eight tetrahedral holes (one in each octant of the cube) and 4 octahedral holes (one in the centre of the cube, 12 additional holes in the middle of the edges of the cube, each shared of 4 cubes).

10.6



A line perpendicular to the edge divides the tetrahedral angle into two halves. The length of the edge is  $2 r_X$ . The distance from a tetrahedral vertex to the center is  $r_M + r_X$ . The angle is  $109,5^\circ/2$ .

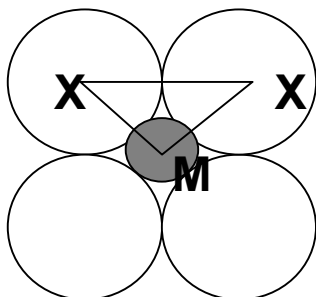
$$\sin \theta = r_X / (r_M + r_X)$$

$$0.816 r_M = 0.184 r_X$$

$$\sin (109,5^\circ/2) \cdot (r_M + r_X) = r_X$$

$$r_M/r_X = 0.225$$

10.7



$$(2r_X)^2 = (r_M + r_X)^2 + (r_M + r_X)^2$$

$$4r_X^2 = 2 (r_M + r_X)^2$$

$$\sqrt{2} r_X = r_M + r_X$$

$$r_M/r_X = (\sqrt{2} - 1) = 0.414$$

$$r_M/r_X = 0.414$$

## Solution problem 11: Titanium Carbide – A High-Tech Solid

11.1  $r(\text{Ti}^{4+}) / r(\text{C}^{4-}) = 0.527 \rightarrow \text{NaCl-type}$



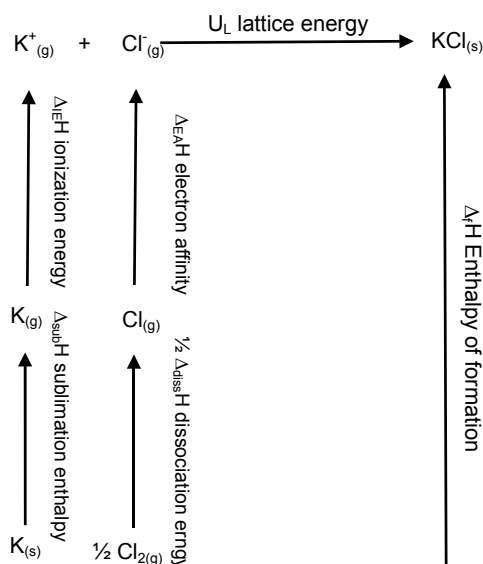
(a) + 3·(b) :



$\Delta_r H = (870.7 + 3 \cdot (-110.5)) \text{ kJmol}^{-1}$

$\Delta_r H = 539.2 \text{ kJmol}^{-1}$

11.3.



$$-U_L = \Delta_{\text{sub}}H + \Delta_{\text{IE}}H + 0.5 \cdot \Delta_{\text{diss}}H + \Delta_{\text{EA}}H - \Delta_fH$$

$$U_L = -(89 + 425 + 122 - 355 + 438 \text{ kJ mol}^{-1})$$

$$U_L = -719 \text{ kJ mol}^{-1}$$

(If the lattice energy is defined in the opposite way the result will be + 719 kJmol<sup>-1</sup>)

## Solution problem 12: Metal Nanoclusters

12.1 The potential of a half-cell is described by the Nernst equation:

$$E = E^0 + \frac{RT}{nF} \cdot \ln \frac{c(\text{ox})}{c(\text{red})}$$

The total voltage is:  $U = E(\text{cathode}) - E(\text{anode})$

$$E = E^0 + RTF^{-1} \ln(c(\text{Ag}^+) \text{ mol}^{-1}\text{L})$$

$$U_1 = E_2 - E_1 \text{ and } U_1 = \frac{RT}{F} \cdot \ln \frac{c_2(\text{Ag}^+)}{c_1(\text{Ag}^+)}$$

and with  $U_1 = 0.170 \text{ V}$   $c_2(\text{Ag}^+) = 0.01 \text{ mol L}^{-1}$   $c_1(\text{Ag}^+) = x \text{ mol L}^{-1}$

$$0.170 \text{ V} = \frac{8.314 \cdot 298.15}{96485} \text{ V} \cdot \ln \frac{c_2(\text{Ag}^+)}{c_1(\text{Ag}^+)}$$

$$c_1(\text{Ag}^+) = 1.337 \cdot 10^{-5} \text{ mol L}^{-1}$$

In the saturated solution  $c(\text{Ag}^+) = c(\text{Cl}^-) = 1.337 \cdot 10^{-5} \text{ mol L}^{-1}$  and thus

$$K_{\text{sp}} = (1.337 \cdot 10^{-5} \text{ mol L}^{-1})^2 \quad K_{\text{sp}} = 1.788 \cdot 10^{-10} \text{ mol}^2\text{L}^{-2}$$

12.2 For the right cell of (II):  $E(\text{AgCl}) = 0.8 \text{ V} + RTF^{-1} \ln(1.337 \cdot 10^{-5})$

$$E(\text{AgCl}) = 0.512 \text{ V}$$

thus  $U = E(\text{AgCl}) - E(\text{Ag}_n, \text{Ag}^+)$

and  $E(\text{Ag}_n/\text{Ag}^+) = E^0(\text{Ag}_n/\text{Ag}^+) + RTF^{-1} \ln(0.01)$

$\text{Ag}_{10}$ :  $E(\text{Ag}_{10}/\text{Ag}^+) = 0.512 \text{ V} - 0.430 \text{ V} = 0.082 \text{ V}$

$$E^0(\text{Ag}_{10}/\text{Ag}^+) = 0.082 \text{ V} - RTF^{-1} \ln(0.01) \quad E^0(\text{Ag}_{10}/\text{Ag}^+) = 0.200 \text{ V}$$

$\text{Ag}_5$ :  $E(\text{Ag}_5/\text{Ag}^+) = 0.512 \text{ V} - 1.030 \text{ V} = -0.518 \text{ V}$

$$E^0(\text{Ag}_5/\text{Ag}^+) = -0.518 \text{ V} - RTF^{-1} \ln(0.01) \quad E^0(\text{Ag}_5/\text{Ag}^+) = -0.400 \text{ V}$$

12.3 The standard potential increases with increasing particle size until it reaches the bulk value at a certain particle size.

The potential is lower for smaller particles, because they have a larger surface and the process of crystallization is energetically less favourable for the surface atoms. Thus, the free energy of formation of metallic silver is larger (less negative) for smaller particles, i.e. the standard potential is lower. The effect decreases with increasing particle size due to the decreasing relative amount of surface atoms.

Additional remark: However, the potential does not continuously increase with increasing size. The electrochemical potentials of some small clusters of a certain size are much higher. This is due to complete shells of these clusters (clusters consist of a "magic number" of atoms) which make them more stable.

(Instead of the crystallization energy you can also argue with the sublimation energies of silver atoms.)

12.4 a) For a solution with a pH of 13:

$$E(\text{H}_2/2\text{H}^+) = \text{RTF}^{-1} \ln(10^{-7}) \quad E(\text{H}_2/2\text{H}^+) = -0.769 \text{ V}$$

As an estimate, this potential can be compared with the standard potentials of the silver clusters calculated in 12.2. Both are higher than the standard potential of hydrogen. Thus, the silver clusters behave as noble metals and are not oxidized in this solution. No reaction takes place.

Quantitatively, a small amount of silver is oxidized into  $\text{Ag}^+$  ions until equilibrium is reached and  $E(\text{Ag}_n/\text{Ag}^+) = E(\text{H}_2/2\text{H}^+)$ .

$$E^0(\text{Ag}_n/\text{Ag}^+) + \text{RTF}^{-1} \ln(c(\text{Ag}^+) \text{ mol}^{-1} \text{L}) = -0.769 \text{ V}$$

$$\text{for Ag}_{10}: c(\text{Ag}^+) = 4.17 \cdot 10^{-17} \text{ mol L}^{-1} \quad \text{and for Ag}_5: c(\text{Ag}^+) = 5.78 \cdot 10^{-7} \text{ mol L}^{-1}$$

b) For a solution with a pH of 5:

$$E(\text{H}_2/2\text{H}^+) = \text{RTF}^{-1} \ln(10^{-2}) \quad E(\text{H}_2/2\text{H}^+) = -0.269 \text{ V}$$

As an estimate, the standard potential of the  $\text{Ag}_{10}$  clusters is higher than the standard potential of the hydrogen. No reaction takes place. The standard potential of the  $\text{Ag}_5$  clusters is lower than the standard potential of hydrogen. Thus, hydronium ions will be reduced to hydrogen while  $\text{Ag}_5$  clusters (metallic silver) are oxidized into silver ions: The Ag-clusters dissolve.

Quantitatively, equilibrium is reached for  $\text{Ag}_{10}$  at:  $c(\text{Ag}^+) = 4.16 \cdot 10^{-9} \text{ mol L}^{-1}$

and for  $\text{Ag}_5$  at:  $c(\text{Ag}^+) = 57.29 \text{ mol L}^{-1}$  (which will probably not be reached in a diluted solution and all nanoclusters dissolve)

(After some time, silver ions that are present in the solution can also be reduced to metallic bulk silver. Under this condition, this reduction will preferably take place, because the electrochemical potential is even higher than that of the hydronium-ion reduction.)

c) Potentials of all possible reactions are considered:

1.	$E(\text{Cu}/\text{Cu}^{2+})$	$= 0.345 \text{ V} + 0.5 \cdot \text{RTF}^{-1} \ln(0.001)$	$= 0.256 \text{ V}$
2.	$E(\text{Ag}/\text{Ag}^+)$	$= 0.800 \text{ V} + \text{RTF}^{-1} \ln(10^{-10})$	$= 0.208 \text{ V}$
3.	$E(\text{Ag}_{10}/\text{Ag}^+)$	$= 0.200 \text{ V} + \text{RTF}^{-1} \ln(10^{-10})$	$= -0.392 \text{ V}$
4.	$E(\text{Ag}_5/\text{Ag}^+)$	$= -0.400 \text{ V} + \text{RTF}^{-1} \ln(10^{-10})$	$= -0.992 \text{ V}$
5.	$E(\text{H}_2/2\text{H}^+)$	$= \text{RTF}^{-1} \ln(10^{-7})$	$= -0.414 \text{ V}$

The reduction with the highest potential and the oxidation with the lowest potential will preferably take place: Copper(II) ions will be reduced into metallic copper while  $\text{Ag}_5$  clusters dissolve and form silver(I) ions.

After some time, the silver concentration of the solution increases,  $\text{Ag}_5$  clusters are used up and the concentration of copper ions decreases. Since the latter is comparably high, it is expected to have minor influence. The next possible steps of the reaction are the following:

- (i) After the  $\text{Ag}_5$  clusters are used up,  $\text{Ag}_{10}$  clusters will start to be oxidized. (Note that if a hydrogen electrode was present,  $\text{H}_2$  would be oxidized. In this system, however, there are protons instead of  $\text{H}_2$ ).
- (ii) After the increase of the silver ion concentration, the potential of the silver ion reduction (into metallic bulk silver) increases, so that it might exceed the potential of the copper reduction. Afterwards, the silver ions will be reduced to metallic silver (after further dissolution of silver nanoclusters).