ENTRANCE EXAMINATION AT THE UNIVERSITIES OF TECHNOLOGY IN FINLAND (HELSINKI, TAMPERE, LAPPEENRANTA, OULU, ÅBO, TURKU, VAASA)
Chemistry Exam 31 May 2006

1. The production of uranium metal from purified uranium dioxide ore consists of the following reaction steps:

   (1) $UO_2\,(s) + 4\,HF\,(g) \rightarrow UF_4\,(s) + 2\,H_2O\,(l)$

   (2) $UF_4\,(s) + 2\,Mg\,(s) \xrightarrow{heat} U\,(s) + 2\,MgF_2\,(s)$

   a) What is the oxidation number of uranium in UO_2, UF_4 and U?
   b) Identify the reducing agent in reaction (2). Justify your answer.
   c) How many liters of HF gas are required to produce 0.500 g uranium metal, U? Temperature is 300 ^oC and pressure is 101.325 kPa.
   d) Uranium metal can be produced also by electrolysis of molten UF_4 according to following total reaction: $UF_4\,(l) \rightarrow U(l) + 2\,F_2\,(g)$. What quantity of electric charge is required to produce 0.500 g uranium metal, U?

2. In the burning of sulfur-containing fuels like oil and coal sulfur dioxide is released into the atmosphere. Sulfur dioxide oxidizes in the air to sulfur trioxide, which further reacts with water to form sulfuric acid. Sulfuric acid falls down with rain. As a result of sulfuric acid accumulated into the lake during years the pH of one lake had fallen to 5.00. Calcium hydroxide, $Ca(OH)_2$, can be used to neutralize the water of the lake.

   a) Write the reaction equation for neutralization reaction.
   b) How many kilograms of calcium hydroxide are needed to neutralize the water of the lake with a surface area of 1.5 km^2 and an average depth of 6.0 m? Temperature is 25 ^oC.

3. When H_2 and I_2 gases were led into a closed 1.00-liter container and temperature was raised to 229 ^oC, the hydrogen and iodine gases reacted to hydrogen iodide gas according to the following reaction equation:

   $H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$

   When equilibrium was established, the following concentrations were present in the container: $[HI] = 0.490$ mol/dm^3, $[H_2] = 0.080$ mol/dm^3 and $[I_2] = 0.060$ mol/dm^3

   a) Calculate the value for the equilibrium constant, K_c, at 229 ^oC.
   b) In which direction will the position of the equilibrium be shifted if HI gas is added to the container? Temperature is 229 ^oC. Justify your answer.
   c) An additional 0.300 mol of HI gas is added to the equilibrium mixture. Calculate the gas concentrations present in the container when the new equilibrium is established? Temperature is 229 ^oC.

4. a) Calculate the solubility (mg) of calcium carbonate, $CaCO_3$, in 1 dm^3 of pure water (25 ^oC)? The solubility product of calcium carbonate, $K_s(CaCO_3)$, is $5.0 \cdot 10^{-9}$ mol^2/dm^6 at 25 ^oC.

   b) Hard water contains Ca^{2+}-ions, which can be precipitated as slightly soluble calcium carbonate ($CaCO_3$), if CO_3^{2-} ions are added to the water. Will a $CaCO_3$ precipitate form if 10 mg of solid sodium carbonate (Na_2CO_3) is added to 250 cm^3 of hard water where $[Ca^{2+}]$ is $8.0 \cdot 10^{-4}$ mol/dm^3. (Volume of the solution can be assumed to be constant).

5. a) Draw structural formulas for the following compounds:

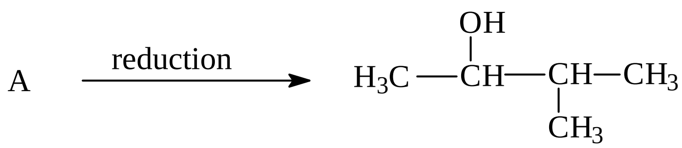
1) diethyl ether
2) tertiary alcohol with four carbon atoms
3) 3-buten-1-ol
4) butanal

b) Which of the compounds in part a) are structural isomers of 2-butanone? Justify your answer.

6. a) Write reaction equations using structural formulas, when 2-methyl-2-penten with molecular formula C_6H_{12} reacts with following compounds:

1) H_2, catalyst
2) H_2O, catalyst
3) HCl

b) Write the structural formula for starting material A and name A in the following reaction:



c) Write the reaction equation using structural formulas for hydrolysis reaction of ethyl benzoate (also known as ethyl ester of benzoic acid).

Molar masses of the elements:

Element:	H	C	O	Na	Ca	U
M / (g mol^{-1})	1.01	12.01	16.00	22.99	40.08	238.03

Constants: $R = 8.315\ J\ mol^{-1}\ K^{-1}$, $F = 96500\ A\ s\ mol^{-1}$

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Model Solutions (Chemistry Exam 31 May 2006)

1. a) oxidation states of uranium UO_2: +IV, UF_4: +IV and U: 0

   b) the reducing agent of reaction (2) is **Mg**, because it oxidizes 0 ⇒ +II

   c) m(U) = 0.500 g
   M(U) = 238.03 g/mol ➔ n(U) = $2.10 \cdot 10^{-3}$ mol

   (2) : $n(UF_4) = n(U)$
   (1): $n(UF_4) = \frac{1}{4} n(HF)$
   ➔ $n(HF) = 4\, n(U) = 8.40 \cdot 10^{-3}$ mol

   pV = nRT

   ➔ $V(HF) = \frac{nRT}{p} = \frac{8.40 \cdot 10^{-3} \text{mol} \cdot 8.315 \text{J/Kmol} \cdot 573.15 \text{K}}{101325 \text{Pa}} = 3.95 \cdot 10^{-4} \text{ m}^3 =$ **0.395 dm^3**

   d) $UF_4 (l) \rightarrow U (l) + 2 F_2 (g)$

   m(U) = 0.500 g
   M(U) = 238.03 g/mol ➔ n(U) = $2.10 \cdot 10^{-3}$ mol

   $Q = It = znF = 4 \cdot 2.10 \cdot 10^{-3} \text{ mol} \cdot 96500 \text{ A s mol}^{-1} =$ **811 A s**

2. Neutralization reaction: $H_2SO_4 (aq) + Ca(OH)_2 (s) \rightarrow CaSO_4 (aq) + 2 H_2O (l)$

   The pH of the lake water is 5.00 ➔ $[H_3O^+] = 10^{-5}$ mol/dm^3

   The volume of the lake is 1500000m^2 · 6.0 m = 9000000 m^3

   ➔ $n(H_3O^+) = cV = 10^{-5} \text{ mol/dm}^3 \cdot 9000000000 \text{ dm}^3 = 90000$ mol

   $H_2SO_4 + 2 H_2O \rightarrow 2 H_3O^+ + SO_4^{2-}$ ➔ $n(H_2SO_4) = \frac{1}{2} n(H_3O^+) = 45000 \text{ mol} = n(Ca(OH)_2)$

   $M(Ca(OH)_2) = 74.10$ g/mol

   ➔ $m(Ca(OH)_2) = n \cdot M = 45000 \text{ mol} \cdot 74.10 \text{ g/mol} = 3334500$ g = **3300 kg**

3\. a) $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.490\,mol/dm^3)^2}{0.080\,mol/dm^3 \cdot 0.060\,mol/dm^3} = \underline{\mathbf{50}}$$

b) According to Le Chatelier´s principle a reaction tends to reduce the external change, that is tends to consume the added HI gas in which case the equilibrium will shift in the direction of the reactants, that is in the left.

c)

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
equilibrium (mol/dm^3)	0.080	0.060	0.490
addition (mol/dm^3)	0	0	+0.300
new initial concentrations (mol/dm^3)	0.080	0.060	0.790
change (mol/dm^3)	+x	+x	-2x
new equilibrium (mol/dm^3)	0.080 + x	0.060 + x	0.790 – 2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.790 - 2x)^2}{(0.080 + x)\cdot(0.060 + x)} = 50$$

➔ $0.624 - 3.16x + 4x^2 = 50x^2 + 7.0x + 0.24$

➔ $46x^2 + 10.16x - 0.384 = 0$

➔ $x = 0.033\ mol/dm^3$ ($x_2 < 0$)

➔ $[H_2] = (0.080 + 0.033)\ mol/dm^3 = \underline{\mathbf{0.113\ mol/dm^3}}$

$[I_2] = (0.060 + 0.033)\ mol/dm^3 = \underline{\mathbf{0.093\ mol/dm^3}}$

$[HI] = (0.790 - 2 \cdot 0.033)\ mol/dm^3 = \underline{\mathbf{0.724\ mol/dm^3}}$

4\. a)

	$CaCO_3\,(s)$ $\rightleftharpoons$	$Ca^{2+}\,(aq)$ +	$CO_3^{2-}\,(aq)$
at the beginning (mol/dm^3)	a	0	0
at equilibrium (mol/dm^3)	a-x	x	x

$K_s = [Ca^{2+}]\,[CO_3^{2-}] = 5.0 \cdot 10^{-9}\ mol^2/dm^6$

➔ $x^2 = 5.0 \cdot 10^{-9}\ mol^2/dm^6$

➔ $x = 7.07 \cdot 10^{-5}\ mol/dm^3$

$M(CaCO_3) = 100.09\ g/mol$

➔ $m(CaCO_3) = c\cdot V \cdot M = 7.07 \cdot 10^{-5}\ mol/dm^3 \cdot 1\ dm^3 \cdot 100.09\ g/mol = 7.08 \cdot 10^{-3}\ g = \underline{\mathbf{7.1\ mg}}$

b) $m(Na_2CO_3) = 10$ mg, $M(Na_2CO_3) = 105.99$ g/mol ➔ $n(Na_2CO_3) = \frac{m}{M} =$

$$\frac{10\,mg}{105.99\,mg/mmol} = 0.0943 \text{ mmol}$$

$V = 250\ cm^3$ ➔ $c(Na_2CO_3) = \frac{n}{V} = \frac{0.0943\,mmol}{250\,cm^3} = 3.77 \cdot 10^{-4}\ mol/dm^3$

$c(CO_3^{2-}) = c(Na_2CO_3) = 3.77 \cdot 10^{-4}\ mol/dm^3$ ($Na_2CO_3 \rightarrow 2\ Na^+ + CO_3^{2-}$)

$c(Ca^{2+}) = 8.0 \cdot 10^{-4}\ mol/dm^3$

Ion product = $[Ca^{2+}]\,[CO_3^{2-}] = 8.0 \cdot 10^{-4}\ mol/dm^3 \cdot 3.77 \cdot 10^{-4}\ mol/dm^3 =$

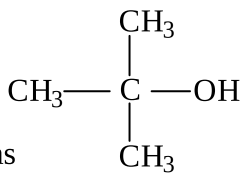
$\underline{3.0 \cdot 10^{-7}\ mol^2/dm^6} > 5.0 \cdot 10^{-9}\ mol^2/dm^9$ (=$K_s(CaCO_3)$)

➔ **precipitation occurs**

5.

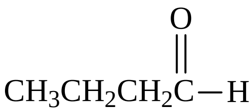
a) 1) diethyl ether $CH_3CH_2—O—CH_2CH_3$

2) tertiary alcohol with four carbon atoms

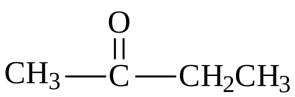


3) 3-buten-1-ol $H_2C{=}CHCH_2CH_2OH$

4) butanal



b) 2-butanone:



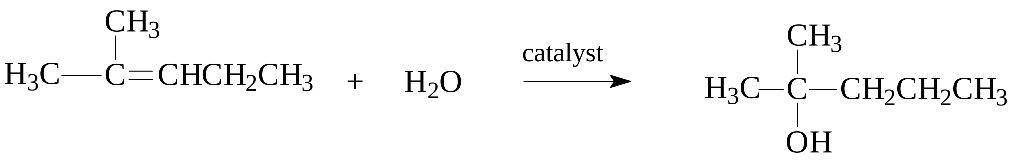
= C_4H_8O

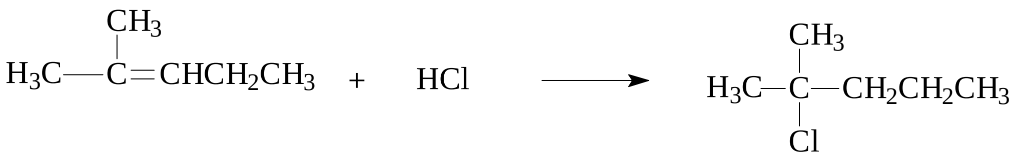
3-buten-1-ol and butanal are structural isomers of 2-butanone, since their have the same molecular formula (C_4H_8O) as 2-butanone

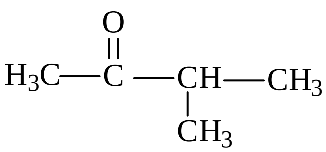
6.

a)

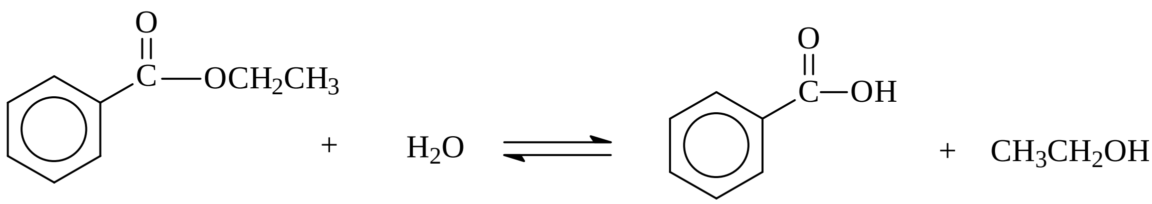
1) 

2) 

3) 

b) 

3-methyl-2-butanone

c) 

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