

Chemistry for Students of Mechanical Engineering

Friday, 4th October 2013, 15:00-18:00

No unauthorised resources (e.g. lecture notes, textbooks etc.) may be used during the examination. Any attempt to use such unauthorised resources will be considered as cheating, and will lead to immediate exclusion from the examination and a mark of 5,0.

Foreign students may use a dictionary (mother tongue – English) but this may not contain any handwritten notes. The use of a calculator is not permitted.

Numerical answers that are given without showing any working or explanation will receive no marks.

In general, short answers with keywords will be sufficient; long essays are not necessary! To illustrate or explain a point, a clear sketch is often sufficient!

The maximum number of points for each question is given in parentheses.

0-49,5	50-54	55-59	60-64	65-70	71-75	76-80	81-85	86-90	91-95	96-100
5,0	4,0	3,7	3,3	3,0	2,7	2,3	2,0	1,7	1,3	1,0

Question 1:

- (a) What is understood by atomic number, and what are isotopes? (2P)

Atomic number = number of protons in the nucleus

Isotopes = Atoms with the same atomic number (i.e. same element) but with different numbers of neutrons in the nucleus (different atomic mass)

- (b) Give the numbers of protons, neutrons and electrons in nitrogen atoms with atomic weights 14 and 15, respectively. (2P)

Electrons = protons = 7

¹⁴N: 14 – 7 = 7 neutrons

¹⁵N: 15 – 7 = 8 neutrons

- (c) Name the four quantum numbers that describe the energy levels of electrons in an atom. Briefly describe the significance of each quantum number. (4P)

***n* – principal QN (size of the orbital)**

***l* – auxiliary QN (shape of the orbital)**

***m* – magnetic QN (orientation of the orbital)**

***s* – spin QN (orientation of the electron's spin)**

- (d) What do (i) the Pauli Principle and (ii) Hund's Rules tell us? (2P)

Pauli Principle: No two electrons in an atom can have all four quantum numbers identical. Or an orbital can be occupied by at most two electrons, which must then have antiparallel spin.

Hund's Rule: Orbitals will be filled with electrons in order of increasing energy; orbitals of the same energy will first each be filled singly, and only when each contains one electron will they begin to be doubly occupied.

- (e) Give the electronic configuration of the molybdenum (Mo) atom. (1P)

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^5$ or: $[\text{Kr}]5s^1 4d^5$ (but $[\text{Kr}]5s^2 4d^4$ also OK!)

(f) What method is used to determine the mass of an atom? What are the three main stages in this experimental method? (4P)

Mass Spectrometry

Sample injection; Ionisation and acceleration of the ions; deviation of the ions by a magnetic field

(g) Use the VSEPR model to determine the 3-D geometries of SF_6 , $[\text{Al}(\text{OH})_4]^-$, CO_2 and SbF_5 . (4P)

**SF_6 : octahedral $[\text{Al}(\text{OH})_4]^-$: tetrahedral CO_2 : linear
 SbF_5 : trigonal bipyramidal
(A clear sketch is also OK)**

(h) State the ideal gas equation. (1P)

$$PV = nRT$$

Question 2:

a) What is understood by (i) the standard enthalpy of formation of a compound, and (ii) enthalpy of reaction? (2P)

Standard enthalpy of formation: The change in enthalpy (heat energy) when a compound (in its standard state) is formed from its constituent elements (each in their standard states).

Enthalpy of reaction: The change in heat energy of the system when a chemical reaction is carried out (under constant temperature and pressure).

b) Give the Gibbs-Helmholtz equation. (1P)

$$\Delta G = \Delta H - T \cdot \Delta S$$

What is the criterion for a spontaneous chemical reaction?

A chemical reaction is spontaneous, when $\Delta G < 0$. (1P)

What conditions must be fulfilled if an endothermic process is to occur spontaneously?

$$\Delta S > 0 \text{ und } (T \cdot \Delta S) > \Delta H \quad (1P)$$

c) What are the characteristics of a chemical equilibrium?

The concentrations (or partial pressures for a gas-phase reaction) of all the substances involved (starting materials and products) reach constant values; the rates of the forward and reverse reactions are then equal.

This final equilibrium position depends only on the initial concentrations (or partial pressures) and the temperature. (1P)

Give the equation that relates the equilibrium constant K of a typical reaction to the concentrations of the products and starting materials, and also the equation that relates K to thermodynamic quantities.

$$\text{For a reaction } aA + bB \rightleftharpoons cC + dD: \quad K = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

$$\Delta G = -RT \ln K \quad \text{or} \quad K = \exp(-\Delta G/RT) \quad (2P)$$

What effect does an increase in temperature have on the equilibrium position of an endothermic reaction, and what is the effect of removing a product of the reaction?

The equilibrium position of an endothermic reaction shifts to the right if the temperature increases (the system attempts to reduce the increase in T). Removal of a product shifts the equilibrium position to the right. (1P)

What is the effect of an increase in pressure on the equilibrium position of a reaction in which the number of gas-phase molecules decreases?

The equilibrium is shifted to the right (fewer gas molecules = lowering of P) (1P)

Which general Principle determines the effect of external influences (changes in temperature or pressure, removal of a reaction component etc) on a system such as an equilibrium?

Le Chatelier's Principle (1P)

Ethene can be obtained by the elimination of hydrogen from ethane. Write down the reaction equation.



Calculate the Standard Enthalpy of Reaction (ΔH°), the Standard Entropy of Reaction (ΔS°) and the Gibbs free Energy of Reaction (ΔG°) using the following values:

$$\begin{aligned} \Delta H_f^\circ(\text{C}_2\text{H}_6) &= -84.7 \text{ kJ mol}^{-1}, \Delta H_f^\circ(\text{C}_2\text{H}_4) = 52.4 \text{ kJ mol}^{-1} \\ S^\circ(\text{C}_2\text{H}_6) &= 229.6 \text{ J mol}^{-1} \text{ K}^{-1}, S^\circ(\text{C}_2\text{H}_4) = 219.3 \text{ J mol}^{-1} \text{ K}^{-1}, \\ S^\circ(\text{H}_2) &= 130.7 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$\Delta H = 52.4 \text{ kJ mol}^{-1} + 0 - (-84.7 \text{ kJ mol}^{-1}) - 0 = +137.1 \text{ kJ mol}^{-1}$$

$$\Delta S = 219.3 \text{ J mol}^{-1} \text{ K}^{-1} + 130.7 \text{ J mol}^{-1} \text{ K}^{-1} - 229.6 \text{ J mol}^{-1} \text{ K}^{-1} = 120.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G = 137100 - (298 \times 120.4) \text{ J mol}^{-1} = +101221 \text{ J mol}^{-1} = +101.2 \text{ kJ mol}^{-1} \quad (3\text{P})$$

- d) The formation of sulphur trioxide (SO_3) from sulphur dioxide (SO_2) and oxygen is an equilibrium reaction. Give the reaction equation, and decide if entropy increases or decreases as the reaction proceeds.



The entropy decreases, since the number of gas molecules (and so the disorder of the system) decreases. (1/2P)

In which direction is the equilibrium position displaced, if

- the temperature is increased
- an excess of oxygen is added to the initial gas mixture?

Explain your answers, given that the reaction is exothermic ($\Delta H = -99 \text{ kJ mol}^{-1}$)

• **Higher T: towards the left-hand side (starting materials) (1/2P)**

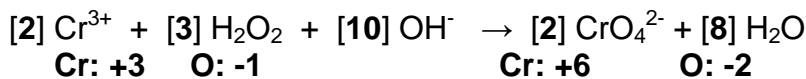
• **Excess of O_2 : towards the right-hand side (SO_3) (1/2P)**

According to Le Chatelier's Principle:

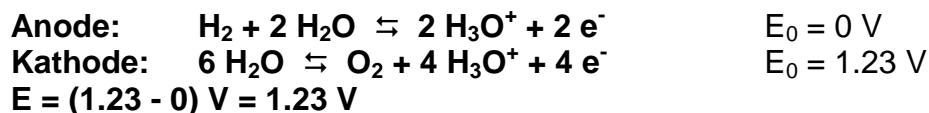
If T is increased, the equilibrium will shift in the endothermic direction, to counteract this change. (1/2P)

If an excess of a starting material is added, the equilibrium will shift towards the side of the products, to consume some of this excess. (1/2P)

- e) Determine the stoichiometric coefficients for the following redox reactions, and give the oxidation states for the species taking part: (4P)



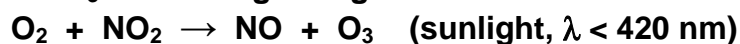
- f) In each of the half-cells of a Galvanic cell, a sheet of platinised platinum is dipped in a 1 M H₂SO₄ solution at 25 °C, and the respective gas is passed over the platinum at a pressure of 1.013 bar. What voltage will be measured when H₂ is passed through one half-cell, and O₂ through the other? What are the two half-reactions? (3P)



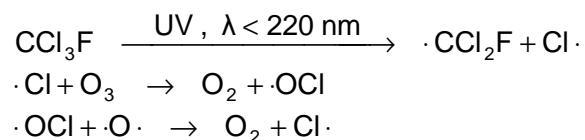
Question 3:

- a) What is understood by "Los Angeles Smog" (also known as "Summer Smog")? Give the equation for the chemical reaction that results in "Los Angeles Smog". (2P)

An O₃-containing Smog



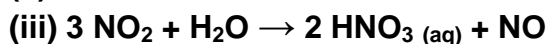
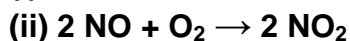
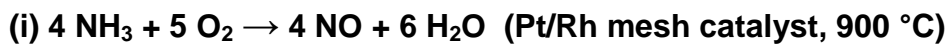
- b) Give the equations for the stratospheric reactions involving CFCs (chlorofluorocarbons, such as CCl₃F) that are responsible for the formation of the Ozone Hole. (2P)



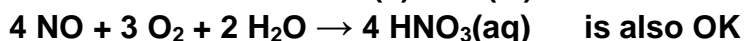
- c) What is the oxidation state of sulphur in the following compounds: H₂S, S₈, Na₂SO₃ and SO₃? (2P)



- d) How is ammonium nitrate made from ammonia? Give the equations for the four reactions. (4P)



The overall reaction for (ii) and (iii)

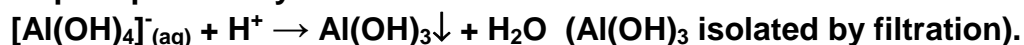


- e) Bauxite, a mixture of Al₂O₃ and Fe₂O₃, is an important raw material in the production of aluminium. What are the three main steps in the production of aluminium from bauxite? Give chemical equations for the reaction(s) taking place in each step.

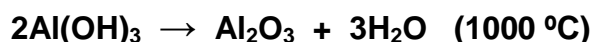
(i) Reaction with aqueous NaOH at 200 °C:



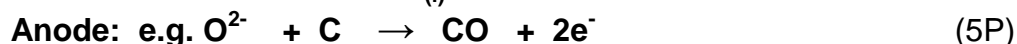
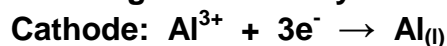
(ii) Re-precipitation by acidification:



(iii) Calcination:



(iv) Smelting flux electrolysis in molten cryolite at 900 °C:



Calculate the electric current that must be passed through the electrolysis cell, if aluminium is to be produced at a rate of 54 kg/h.

Assume the Faraday constant $F = 96500 \text{ C/mol}$, and round the atomic mass of Al to 27 g mol^{-1} .

$$54 \text{ kg(Al)/h} = 2000 \text{ mol(Al)/h} = 2000/3600 \text{ mol(Al)/s} = (2000 \times 3)/3600 \text{ mol(e}^-)/\text{s} \\ = (2000 \times 3 \times 96500)/3600 \text{ C/s} = (1000 \times 96500)/600 \text{ C/s} = 160633 \text{ A} \quad (1\text{P})$$

e) Name two raw materials from which iron can be obtained.

Two from Magnetite (Fe_3O_4), Haematite (Fe_2O_3), Limonite ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ or " $\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$ "), Siderite (FeCO_3), Pyrites (FeS_2) (1P)

Which industrial process is used to obtain iron? What substance is the reducing agent of the iron ore?

Blast Furnace. Reducing agent = CO (1P)

Why is lime (CaCO_3) used in iron production? Give equations for the reactions in which the lime (or a substance derived from it) is involved?

Removal of P or Si as slag



During the chemical reactions involved in the formation of iron, finely-divided carbon is formed via the Boudouard reaction, and this carbon dissolves in the liquid iron. Give the equation for the chemical equilibrium involved in the Boudouard reaction.



What negative effect does this dissolved carbon have on the properties of the raw iron?

It becomes brittle (½P)

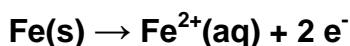
Name a process used during steel production, to reduce the carbon content of the steel!

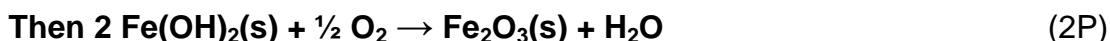
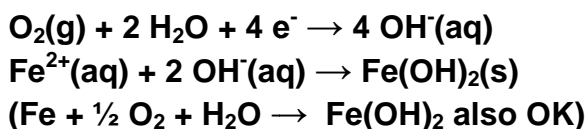
Air-refining (½P)

f) What is understood by corrosion? (1P)

The destruction of a material by redox reactions with its environment

g) Give equations for the chemical reactions that take place when iron rusts in moist air.





What are two important methods that can be used to prevent such rusting?

Coatings (paint, plastic, enamel)

Sacrificial electrodes (Mg or Zn)

Passivation (either natural: Zn, Al, or through addition of e.g. Cr)

Electroplating or galvanisation (2P)

h) Name three of the elements that belong to the Platinum Group of metals.

Three from ruthenium, rhodium, palladium, osmium, iridium und platinum (1½P)

What is the main industrial significance of these metals?

As catalysts (½P)

Question 4:

a) There are five organic compounds with the sum formula C_4H_6 . Choose any two of these, and draw their Lewis formulae, give their correct names, and state which class of organic compound each of them belongs to. (3P)

Alkene	Alkene (or allene)
Buta-1,3-diene	Buta-1,2-diene
Alkyne	Alkyne
1-Butyne	2-Butyne
Cycloalkene	
Cyclobutene	

½P each for Lewis formula, class and correct name

- b) What hybridisation do carbon atoms have that are involved in single, double or triple bonds? What is the spatial arrangement of the bonds around the carbon atom in each case? (3P)

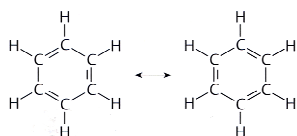
Single bonds: sp^3 hybridisation, tetrahedral geometry with bond angles ca. 109°

Double bond: sp^2 hybridisation, trigonal planar geometry with bond angles ca. 120°

Triple bonds: sp hybridisation, linear geometry with bond angle ca. 180°

- c) Give four characteristic structural features of the benzene molecule, and draw the two mesomeric structures for the molecule. (2P)

3 from: planar hexagon of C atoms, all C-C bonds equal length, bond angles 120° , 6 delocalised π -molecular orbitals, sp^2 hybridisation.

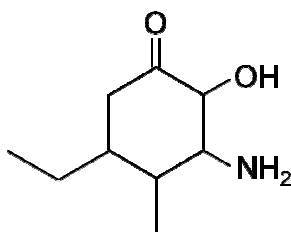


(1P)

- d) Draw the Lewis formulae for the characteristic functional groups of carboxylic acids, esters, ketones and alkenes. (4P)

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \backslash \\ \text{OH} \end{array}$	Carboxylic acids
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \backslash \\ \text{OR}' \end{array}$	Esters
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \backslash \\ \text{R}' \end{array}$	Ketones
$\begin{array}{c} \text{R}_1 \qquad \text{R}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R}_2 \qquad \text{R}_4 \end{array}$	Alkenes

- e) Draw the Lewis formula for the compound 2-hydroxy-3-amino-4-methyl-5-ethyl-cyclohexanone (4P)



- f) What is understood by the terms macromolecule and polymerisation? (1P)

Macromolecule: A molecule of very high molecular weight, built up from either identical or related repeating units.

Polymerisation: The chemical linkage of small molecules (monomers) into a macromolecule (polymer), either through radical reactions of double bonds or through condensation reactions

- g) Give the Lewis formulae for the repeating units in polyethene, polypropene, polyvinylchloride, polystyrene and polyacrylonitrile. From which monomers are these polymers produced? (5P)

Polyethene formed from ethene:	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$	Polypropene formed from propene:	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{CH}_3 \end{array} \right]_n$	Polyvinylchloride formed from chloroethene (vinyl chloride):	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{Cl} \end{array} \right]_n$
Polystyrene formed from styrene:	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{C}_6\text{H}_5 \end{array} \right]_n$	Polyacrylonitrile formed from acrylonitrile:	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{CN} \end{array} \right]_n$		

- h) How much CO₂ (in g/km) is emitted by a petrol motor with a fuel consumption of 5.7 litre/100km? Assume that the fuel is 100 % isooctane, with a density of $\rho = 0.7 \text{ g/cm}^3$

5.7 litre/100km = 57 ml isooctane / km:

$$m(\text{C}_8\text{H}_{18}) = V \times \rho = (57 \times 0.7) \text{ g/km}$$

$$n(\text{C}_8\text{H}_{18}) = m(\text{C}_8\text{H}_{18}) / MW(\text{C}_8\text{H}_{18}) = (57 \times 0.7) / 114 \text{ mol/km}$$

$$\text{C}_8\text{H}_{18} + 12\frac{1}{2}\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}: \quad n(\text{CO}_2) = (57 \times 0.7 \times 8) / 114 \text{ mol/km}$$

$$= (0.7 \times 8) / 2 \text{ mol/km} = 2.8 \text{ mol/km}$$

$$m(\text{CO}_2) = 2.8 \times 44 = 123.2 \text{ g/km} \quad (6\text{P})$$