

Topics in the November 2006 Exam Paper for CHEM1101

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- [Wave Theory of Electrons and Resulting Atomic Energy Levels](#)
- [Material Properties \(Polymers, Liquid Crystals, Metals, Ceramics\)](#)

2006-N-3:

- [Nuclear and Radiation Chemistry](#)

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- [Bonding - MO theory \(larger molecules\)](#)

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2006-N-12:

- [Bonding - MO theory \(H₂\)](#)
- [Electrochemistry](#)
- [Batteries and Corrosion](#)

- In the spaces provided, explain the meanings of the following terms. You may use an equation or diagram where appropriate.

Marks
5

(a) allotropes

Different structural forms of the same element. Examples include graphite and diamond for carbon and O₂ and O₃ for oxygen.

(b) ionisation energy

The energy required to remove one mole of electrons from a mole of gaseous atoms, molecules or ions. The energy required for the process:



(c) diamagnetic

Property of atoms or molecules with no unpaired electrons. Diamagnets are weakly repelled by magnetic fields.

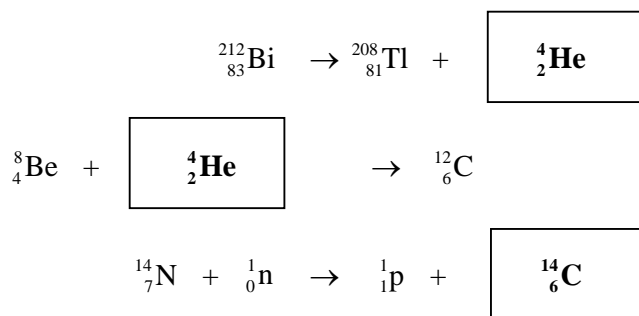
(d) intrinsic semiconductor

An intrinsic semiconductor has electrical conductivity in between that of a metal and that of an insulator. An undoped semiconductor has a small energy gap between the valence and conductance bands allowing some electrons to be thermally excited into the latter resulting in conductivity which increases with temperature.

(e) σ bond

A bond produced by the occupation of a σ -bonding molecular orbital. This orbital is made by overlap of atomic orbitals, such as end-on/end-on overlap of p-orbitals or of s-orbitals, to produce a molecular orbital with no nodes along the internuclear axis. The electron density is along the internuclear axis.

- Balance the following nuclear reactions by identifying the missing nuclear particle or nuclide.



What is a common source of the neutrons in the previous reaction?

Stars

- Explain why solid α emitters are generally considered as low risk radioisotopes while gaseous α emitters are high risk.

α -Radiation is highly ionising and causes severe tissue damage, but it is not very penetrating and easily stopped by our skin. Gaseous α -emitters are high risk as they can be breathed in and lodge in the lungs and then be transported round the body. Solid α -emitters are not dangerous unless ingested, which only happens in rare circumstances.

Marks

4

2

- Calculate the energy (in J) and the wavelength (in nm) of the photon of radiation absorbed when the electron in B^{4+} jumps from the $n = 3$ state to the $n = 4$ state.

Marks
3

As B^{4+} has one electron, the equation $E_n = \frac{-E_R Z^2}{n^2}$ where $E_R = 2.18 \times 10^{-18} \text{ J}$ can be used. Boron has $Z = 5$. The energies of the $n = 3$ and $n = 4$ levels are:

$$E_3 = \frac{-E_R (5)^2}{(3)^2} = -\frac{25}{9} E_R = -2.778 E_R \text{ and } E_4 = \frac{-E_R (5)^2}{(4)^2} = -\frac{25}{16} E_R = 1.5625 E_R$$

The separation is:

$$\Delta E = (2.7778 - 1.5625) E_R = 1.2153 E_R = 1.2153 \times (2.18 \times 10^{-18}) = 2.65 \times 10^{-18} \text{ J.}$$

$$\text{As } E = \frac{hc}{\lambda}, \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}) \times (2.998 \times 10^8)}{(2.65 \times 10^{-18})} = 7.50 \times 10^{-8} \text{ m} = 75.0 \text{ nm}$$

Energy: $2.65 \times 10^{-18} \text{ J}$

Wavelength: **75.0 nm**

- Explain why the atomic radius of elements are observed to decrease from left to right across a period.

2

The number of electrons and protons increase across a period. As all electrons are being added to the same shell, the nuclear charge increases with minimal increase in shielding and the attraction between the nucleus and the electron cloud increases. This results in smaller atoms as we move from left to right across a period.

- Explain why samples must be atomised for atomic absorption spectrometry, but not for X-ray spectrometry.

2

X-ray spectrometry investigates high energy transitions involving core electrons. These electrons are not involved in bonding and hence insensitive to whether atom is bonded or not. The X-ray spectrum of an element is approximately the same whatever compound the element is in.

Atomic absorption spectrometry measures transitions involving the valence electrons. These change depending upon the bonding of the atom, so samples must be atomised. The atomic absorption spectrum of an element depends crucially on the compound the element is in.

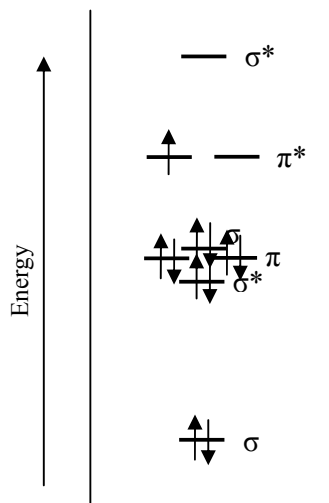
- The NO molecule plays an important signalling role in the human body.

Marks
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How many valence electrons are in the molecule NO?

11 (5 from N, 6 from O)

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the NO molecule. Indicate on this diagram the ground state electronic configuration of NO using the arrow notation for electron spins.



Calculate the bond order of NO.

Bond order = $\frac{1}{2} (8 - 3) = 2.5$

Is the NO molecule diamagnetic or paramagnetic? Explain your answer.

NO contains an unpaired electron so it is paramagnetic.

Would removing an electron from NO to form NO⁺ strengthen or weaken the bond between the two atoms? Explain your answer.

The highest energy electron in NO is in the π^* (antibonding) level. Removal of this electron to form NO⁺ increases the bond order to:

bond order = $\frac{1}{2} (8 - 2) = 3$

The higher bond order signifies a stronger bond.

- Complete the table below showing the number of valence electrons, the Lewis structure and the predicted shape of each of the following species.

Marks
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Formula	Total number of valence electrons	Lewis structure	Geometry of species
e.g. NH_3	8	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\ \\ \text{H} \end{array}$	trigonal pyramidal
NO_3^-	24	$\left[\begin{array}{c} \ddot{\text{O}}: \\ \\ :\ddot{\text{O}}-\text{N}-\ddot{\text{O}}: \\ \quad \\ :\ddot{\text{O}}: \quad :\ddot{\text{O}}: \end{array} \right]^\ominus$	trigonal planar
HCN	10	$\text{H}-\text{C}\equiv\text{N}:$	linear

Which of NH_3 , NO_3^- and HCN have a non-zero dipole moment?

NH_3 and HCN both have dipole moments. Although the N-O bonds in NO_3^- are polar, the trigonal planar shape means that these cancel and there is no overall dipole moment.

- List the following five solids in order of increasing melting points.

NaCl, H₂, CH₄, H₂O, SiO₂

Marks**4**

H₂ < CH₄ < H₂O < NaCl < SiO₂

Briefly explain your ordering based on the types of forces that are involved.

The interactions between the molecules of H₂ and between the molecules of CH₄ are dispersion forces, involving induced dipole-induced dipole interactions. CH₄ is a larger molecule with more electrons so has a larger polarizability than H₂ and, as a result, has stronger dispersion forces and a higher melting point.

H₂O has highly polar O-H bonds and lone pairs on the oxygen atom and hence quite strong H-bonds exist in the solid state. Hence, H₂O has a higher melting point than CH₄.

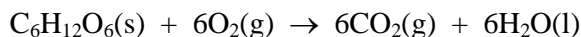
NaCl is an ionic compound with a close-packed arrangement of cations and anions which interact via strong coulombic interactions to give a solid with a high melting point.

SiO₂(s) is a covalent network with very strong Si-O bonds that need to be broken to melt the solid. Hence, SiO₂ has the highest melting point of these materials.

List those that are electrical conductors when molten. Briefly explain your answers.

Only NaCl conducts when molten as melting releases the Na⁺ and Cl⁻ ions from the lattice and these can carry electrical charge.

- Glucose is a common food source. The net reaction for its metabolism in humans is:



Calculate ΔH° for this reaction given the following heats of formation.

$$\Delta H^\circ_{\text{f}}(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) = -1274 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{CO}_2(\text{g})) = -393 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{f}}(\text{H}_2\text{O}(\text{l})) = -285 \text{ kJ mol}^{-1}$$

Marks**3**

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_{\text{f}}H^\circ(\text{products}) - \sum n\Delta_{\text{f}}H^\circ(\text{reactants})$ and recalling that the enthalpy of formation of an element in its standard state is zero, the reaction enthalpy is:

$$\begin{aligned}\Delta_{\text{rxn}}H^\circ &= [(6 \times \Delta_{\text{f}}H^\circ(\text{CO}_2(\text{g})) + (6 \times \Delta_{\text{f}}H^\circ(\text{H}_2\text{O}(\text{g}))) - [\Delta_{\text{f}}H^\circ(\text{C}_6\text{H}_{12}\text{O}_6(\text{s}))]] \\ &= [(6 \times -393) + (6 \times -285)] - [-1274] = -2794 \text{ kJ mol}^{-1}\end{aligned}$$

Answer: **-2794 kJ mol⁻¹**

If the combustion of glucose is carried out in air, water is produced as a vapour. Calculate ΔH° for the combustion of glucose in air given that



As energy is required to convert the liquid water into vapour, the combustion enthalpy will be lower:

$$\Delta_{\text{rxn}}H^\circ = (-2794 + 6 \times 44) \text{ kJ mol}^{-1} = -2540 \text{ kJ mol}^{-1}$$

Answer: **-2540 kJ mol⁻¹**

Will ΔS be different for the two oxidation reactions? If so, how will it differ and why?

Marks
4

The reaction in the body gives rise to an increase in entropy as a solid and 6 moles of gas react to give 6 moles of liquid and 6 moles of gas, which have higher entropy.

In air, the reaction gives rise to 12 moles of gas so will give rise to an even higher entropy increase.

Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of glucose.

The molar mass of glucose is:

$$(6 \times 12.01 \text{ (C)}) + (12 \times 1.008 \text{ (H)}) + (6 \times 16.00 \text{ (O)}) = 180.156$$

$$1.0 \text{ g of glucose corresponds to } \frac{\text{mass}}{\text{molar mass}} = \frac{1.00}{180.156} = 0.00555 \text{ mol}$$

From the chemical equation, oxidation of 1 mol of glucose leads 6 mol of CO_2 . Hence the number of moles of CO_2 produced is $6 \times 0.00555 = 0.0333 \text{ mol}$.

$$\text{The molar mass of } \text{CO}_2 \text{ is } (12.01 \text{ (C)}) + (2 \times 16.00 \text{ (O)}) = 44.01$$

Therefore, the number of mass of CO_2 produced is:

$$\text{mass} = \text{number of moles} \times \text{molar mass} = 0.0333 \times 44.01 = 1.47$$

Answer: **1.47 g**

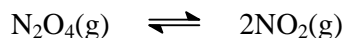
Calculate the volume of this mass of carbon dioxide at 0.50 atm pressure and 37 °C.

The ideal gas law gives $PV = nRT$, hence:

$$V = \frac{nRT}{P} = \frac{(0.0333) \times (0.08206) \times (273+37)}{(0.50)} = 1.7 \text{ L}$$

Answer: **1.7 L**

- Consider the following reaction.



An experiment was conducted in which 0.1000 mol of $\text{N}_2\text{O}_4(\text{g})$ was introduced into a 1.00 L flask. After equilibrium had been established at 100 °C, the concentration of $\text{N}_2\text{O}_4(\text{g})$ was found to be 0.0491 M. Calculate the equilibrium constant, K_c , for the reaction as written at 100 °C.

Marks
5

The initial concentration of $\text{N}_2\text{O}_4(\text{g})$ is:

$$[\text{N}_2\text{O}_4(\text{g})]_0 = \frac{\text{number of moles}}{\text{volume}} = \frac{0.1000}{1.00} = 0.100 \text{ M}$$

At equilibrium, $[\text{N}_2\text{O}_4(\text{g})] = 0.0491 \text{ M}$.

The change in the concentration is $(0.100 - 0.0491) = 0.051 \text{ M}$. From the chemical equation, each mole of N_2O_4 that reacts leads to two moles of NO_2 . Hence, $[\text{NO}_2(\text{g})] = 2 \times 0.051 = 0.10 \text{ M}$.

The equilibrium constant in terms of concentrations, K_c , is therefore:

$$K_p = \frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]} = \frac{(0.10)^2}{(0.0491)} = 0.21$$

$$K_c = 0.21$$

Use your calculated value for K_c to calculate whether a mixture of $\text{N}_2\text{O}_4(\text{g})$ (0.120 M) and $\text{NO}_2(\text{g})$ (0.550 M) is at equilibrium at 100 °C? If not, in which direction will it move?

Using these concentrations, the reaction quotient Q is:

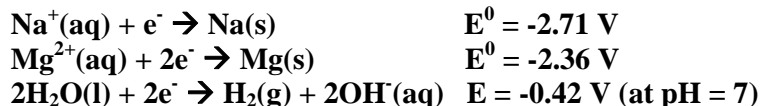
$$Q = \frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]} = \frac{(0.550)^2}{(0.120)} = 2.52$$

As $Q > K_p$, the reaction will proceed to reduce Q by increasing the amount of reactant ($\text{N}_2\text{O}_4(\text{g})$) and decreasing the amount of product ($\text{NO}_2(\text{g})$). It will proceed towards the left.

- A chemical engineer dissolves a mixture of NaBr and MgCl₂ in water and decomposes it in an electrolytic cell. Predict the substance formed at each electrode and write balanced half reactions and the overall cell reaction.

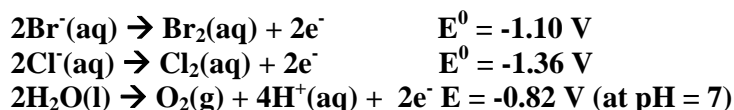
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The possible reduction reactions at the cathode are:



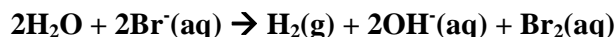
The reduction potential for water is the least negative. The overpotential for water is around 0.6 V so the potential needed to reduce water is ~ -1 V. This is still smaller than for reduction of the cations. H₂(g) is produced at the cathode.

The possible oxidation reactions at the anode are:



The oxidation potential for water is the least negative. The overpotential for water is around 0.6 V so the potential actually needed to oxidise water is ~-1.4 V. Because of this overpotential, Br₂(aq) is actually produced at the anode.

The overall reaction is therefore:



- What mass of PbSO₄ is reduced at the cathode when a lead-acid storage battery is charged for 1.5 hours with a constant current of 10.0 A?

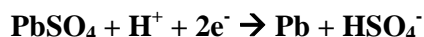
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The total charge delivered is:

$$Q = It = (10.0) \times (1.5 \times 60 \times 60) = 54000 \text{ A}$$

This is equivalent to $\frac{Q}{F} = \frac{54000}{96485} = 0.56$ moles of electrons.

The reduction reaction during recharging is a 2e⁻ process:



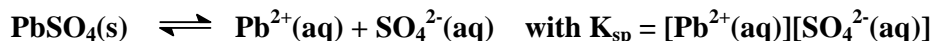
Hence, $\frac{0.56}{2} = 0.28$ moles of PbSO₄ are reduced. The molar mass of PbSO₄ is (207.2 (Pb)) + (32.07 (S)) + (4 × 16.00 (O)) = 303.27. Hence, the mass reduced is given by:

$$\text{mass of PbSO}_4 \text{ reduced} = 0.28 \times 303.27 = 85 \text{ g}$$

- Lead sulfate is used as a white pigment and also in car batteries. Its solubility in water at 25 °C is 4.25×10^{-3} g per 100 mL of solution. Write an equation for the dissolution of lead sulfate in water and determine K_{sp} at 25 °C.

Marks
3

The dissolution equilibrium is:



The molar mass of PbSO₄ is (207.2 (Pb)) + (32.07 (S)) + (4 × 16.00 (O)) = 303.27 so 4.25×10^{-3} g corresponds to:

$$\text{moles of PbSO}_4 = \frac{4.25 \times 10^{-3}}{303.27} = 1.40 \times 10^{-5} \text{ moles}$$

As this amount dissolves in 100 mL, 1.40×10^{-4} moles will dissolve in a litre. From the dissolution equilibrium, 1 mole of PbSO₄ gives rise to 1 mole of Pb²⁺(aq) and 1 mole of SO₄²⁻(aq) so K_{sp} is given by:

$$K_{sp} = [\text{Pb}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})] = (1.40 \times 10^{-4}) \times (1.40 \times 10^{-4}) = 1.96 \times 10^{-8}$$

$$K_{sp} = 1.96 \times 10^{-8}$$

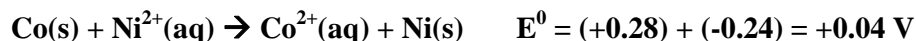
- A voltaic cell consists of Ni/Ni²⁺ and Co/Co²⁺ half cells with initial concentrations of [Ni²⁺] = 0.80 M and [Co²⁺] = 0.20 M. What is the initial E_{cell} at 298 K?

5

The standard reduction potentials and half cells are:



The least positive (Co/Co²⁺) cell is reversed giving the overall cell reaction as:



This is the cell potential with all reactants and products in their standard (1M) concentrations. At other concentrations, the Nernst equation gives the potential as:

$$E_{\text{cell}} = E^0 - \frac{2.303RT}{nF} \log(Q)$$

The overall reaction is a 2e⁻ process (n = 2) with $Q = \frac{[\text{Co}^{2+}(\text{aq})]}{[\text{Ni}^{2+}(\text{aq})]}$, hence,

$$E_{\text{cell}} = E^0 - \frac{2.303RT}{2F} \log\left(\frac{[\text{Co}^{2+}(\text{aq})]}{[\text{Ni}^{2+}(\text{aq})]}\right) = (+0.04) - \frac{(2.303) \times (8.314) \times (298)}{2 \times 96485} \log\left(\frac{0.20}{0.80}\right) = +0.06 \text{ V}$$

$$E_{\text{cell}} = +0.06 \text{ V}$$

What is the value of the equilibrium constant, K , for this cell?

The equilibrium constant is related to E^0 by:

$$E^0 = \frac{2.303RT}{nF} \log(K) \quad \text{so } \log(K) = \frac{E^0 \times nF}{2.303RT} = \frac{(+0.04) \times (2) \times (96485)}{(2.303) \times (8.314) \times (298)} = 1.35$$

Hence:

$$K = 10^{1.35} = 23$$

$$K = 23$$