Topics in the June 2008 Exam Paper for CHEM1901

Click on the links for resources on each topic.

2008-J-2:

- Nuclear and Radiation Chemistry
- Atomic Electronic Spectroscopy
- Bonding in H_2 - MO theory
- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O
- Band Theory - MO in Solids
- Types of Intermolecular Forces

2008-J-3:

- Nuclear and Radiation Chemistry

2008-J-4:

- Bonding in O_2, N_2, C_2H_2, C_2H_4 and CH_2O
- Shape of Atomic Orbitals and Quantum Numbers
- Filling Energy Levels in Atoms Larger than Hydrogen

2008-J-5:

- Lewis Structures
- VSEPR

2008-J-6:

- Wave Theory of Electrons and Resulting Atomic Energy Levels

2008-J-7:

- Polar Bonds
- Types of Intermolecular Forces
- Wave Theory of Electrons and Resulting Atomic Energy Levels

2008-J-8:

- Thermochemistry
- First and Second Law of Thermodynamics

2008-J-9:

- Nitrogen in the Atmosphere

2008-J-10:

- Thermochemistry
- First and Second Law of Thermodynamics

2008-J-11:

- Thermochemistry
- First and Second Law of Thermodynamics

2008-J-13:

- Electrochemistry

2008-J-14:

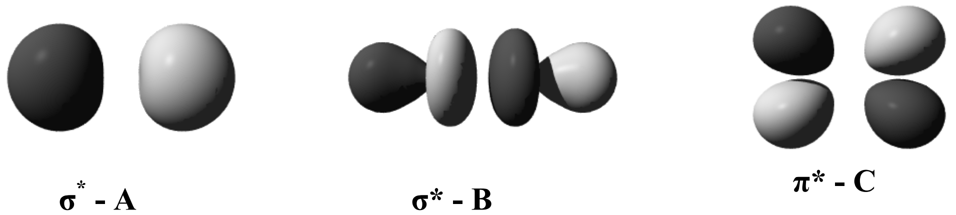
- Electrochemistry
- First and Second Law of Thermodynamics

Marks 6

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

(a) antibonding molecular orbital

An orbital with a nodal plane perpendicular to the bond. Occupation of an antibonding orbital lowers the bond order and weakens a bond. The diagram below show the antibonding orbitals produced from overlap of s-orbitals (σ^* - A) and p-orbitals (σ^* - B and π^* - C):



(b) emission spectroscopy

The study of radiation emitted as an atom or molecule relaxes from an initial excited state. Because of the quantized nature of energy levels, emission occurs at particular wavelengths which are characteristic of the atom or molecule.

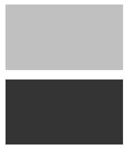
(c) half-life

The time required for a material to decay to half its initial amount. Half-life is commonly used as a measure of radioactivity but is also used in studying the decrease in concentration of other materials during chemical or biochemical reactions.

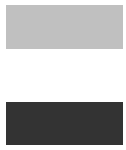
(d) band gap

The energy gap between the valence and conductance bands in a solid. The diagram below shows this schematically.

When this gap is large (as opposite), the solid is an insulator as there is insufficient energy to excite an electron from the filled valence band to the empty conductance band.



When this gap is small (as opposite), the solid is a semi-conductor as, except at very low temperatures, there is thermal excitation into the conductance band.



(e) dispersion interaction

The attraction arising between fluctuating dipoles. At any given instant, the electron distribution around an atom or molecule will not be symmetrical. This will give the particle an instantaneous dipole moment and this will induce a dipole in neighbours. The interaction increases with the size of the electron cloud and with the number of electrons, and hence increases with atomic number and molecular size.

ANSWER CONTINUES ON THE NEXT PAGE

(f) a triple bond

A "bond" between two atoms involving the sharing of three electron pairs. It usually consists of 1 σ-bond and 2 π-bonds. The most common molecules containing triple bonds are N_2 and CO. Triple bonds are represented by drawing three lines between the atoms. For example, N≡N and C≡O.

Marks

- Explain why a sustained fission chain reaction can only occur when a critical mass is prepared. **2**

Below the critical mass, so many neutrons are lost from the material that a chain reaction cannot be sustained.

- The half life of ^{3}H is 12 years. Calculate how long it takes (rounded to the nearest year) for the activity of a sample of tritium to have dropped to 0.1% of its original value. **2**

From $t_{1/2} = \frac{\ln 2}{\lambda}$, the activity coefficient $\lambda = \frac{\ln 2}{t_{1/2}} = . \frac{\ln 2}{12\text{ years}} = 0.058\text{ years}^{-1}$

As the activity is directly proportional to the number of radioactive nuclei, the activity, A_t, at time t is related to the initial activity, A_0, by $\ln\left(\frac{A_0}{A_t}\right) = \lambda t$

With $A_t = 0.001 \times A_0$, the ratio $\frac{A_0}{A_t} = 1000$. Hence,

$\ln(1000) = (0.058)t$ or $t = 120$ years $= 1.2 \times 10^2$ years

Answer: **1.2×10^2 years**

- Consider the following list of unstable isotopes and their decay mechanisms. **3**

$^{33}_{17}Cl \rightarrow {}^{0}_{+1}e + {}^{33}_{16}S$ half-life = 2.5 s

$^{32}_{15}P \rightarrow {}^{0}_{-1}e + {}^{32}_{16}S$ half-life = 14.3 days

$^{199}_{82}Pb \rightarrow {}^{0}_{+1}e + {}^{199}_{81}Tl$ half-life = 90 minutes

$^{13}_{7}N \rightarrow {}^{0}_{+1}e + {}^{13}_{6}C$ half-life = 10 minutes

From this list, select the isotope that best satisfies the following requirements. Provide a reason for your choice in each case.

Requirement	Isotope	Reason for choice
Isotope used in medical imaging	$^{13}_{7}N$	**Positron emitter, non-toxic and has sufficiently long half life to be chemically incorporated.**
Decay represents the transformation of a neutron into a proton	$^{32}_{15}P$	**This nuclide is a β-emitter. The nuclear charge increases from 15 to 16 and the mass is unaffected. The charge is conserved by the emission of an electron.**
The isotope with the highest molar activity	$^{35}_{17}Cl$	**It has the shortest half-life and, as $\lambda = \frac{\ln 2}{t_{1/2}}$. it therefore has the highest activity.**

Marks

- The electronic energies of the molecular orbitals of homonuclear diatomics from the period starting with Li can be ordered as follows (with energy increasing from left to right): **3**

  $\sigma\ \sigma^*\ \sigma\ \sigma^*\ \pi\ \sigma\ \pi^*\ \sigma^*$

  Using this ordering by energy of the molecular orbitals, how many unpaired spins do you expect in the ground state configurations of each of B_2, C_2, N_2, O_2 and F_2?

B_2	C_2	N_2	O_2	F_2
2	**0**	**0**	**2**	**0**

Consider the 15 species X_2^-, X_2 and X_2^+ where X is B, C, N, O or F. What is the maximum bond order found among these 15 species and which molecules or ions exhibit this bond order?

Maximum bond order = 3. This is exhibited by N_2

What is the minimum bond order found among these 15 species and which molecules or ions exhibit this bond order?

Minimum bond order = ½. This is exhibited by B_2^+ and F_2^-.

- Imagine a Universe X in which electrons had *three* possible spin states (*i.e.* with electron spin quantum numbers –1, 0 and +1) instead of the two they have in our universe. Assume that all other properties of electrons and nuclei in Universe X are identical to those in our universe. **4**

What are the atomic numbers of the first two noble gases in Universe X?	**Z = 3; $1s^3$** **Z =15: $1s^3\ 2s^3\ 2p^9$**
Write down the ground state electron configuration of the atom with atomic number 14 in Universe X.	**$1s^3\ 2s^3\ 2p^8$**

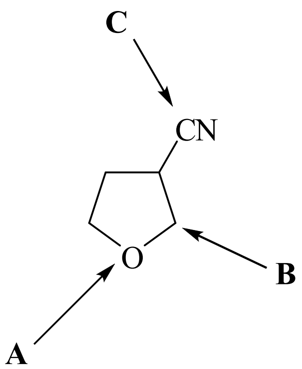
How would the energy difference between the 2*s* and 2*p* orbitals in multi-electron atoms compare between our universe and Universe X? Give a brief explanation of your answer.

The difference in energy between 2*s* and 2*p* is caused by the unequal shielding of electron in these orbitals by the 1*s* electrons. When there are no 1*s* electrons, there is no energy difference between 2*s* and 2*p*.

In our universe, there are a maximum of two electrons in 1*s*. In Universe X, there are a maximum of three electrons in 1*s*. As there are more electrons in the 1*s* orbital, there is a larger effect and hence a large energy difference in Universe X.

Marks 3

- Consider the molecule whose structure is shown below. Complete the table concerning the atoms **A**, **B** and **C** indicated by the arrows.



Selected atom	Number of lone pairs about the selected atom	Number of σ-bonds associated with the selected atom	Geometry of σ-bonds about the selected atom
A	**2**	**2**	**bent (~ 109°)**
B	**0**	**4**	**tetrahedral**
C	**0**	**2**	**linear**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

- Moseley discovered experimentally in 1913 that the atomic number, Z, of an element is inversely proportional to the square root of the wavelength, λ, of fluorescent X-rays emitted when an electron drops from the $n = 2$ to the $n = 1$ shell.

$$i.e. \quad \frac{1}{\sqrt{\lambda}} = kZ$$

Derive an expression for the constant of proportionality, k, for a hydrogen-like atom which would allow the value of k to be theoretically calculated.

Squaring Moseley's relationship gives $\frac{1}{\lambda} = (kZ)^2$ **(1)**

The energy of an X-ray with wavelength λ is given by $E = \frac{hc}{\lambda}$. Substituting in Moseley's value for $\frac{1}{\lambda}$ from (1) gives:

$$E = hc(kZ)^2 \qquad \textbf{(2)}$$

For a hydrogen like atom, an electron in an orbital with quantum number n has energy $E = -Z^2E_R\left(\frac{1}{n^2}\right)$ where E_R is the Rydberg constant.

The energy *emitted* when an electron moves from an orbital with quantum number $n = 2$ to an orbital with quantum number $n = 1$ is:

$$E = [-Z^2E_R\left(\frac{1}{2^2}\right)] - [-Z^2E_R\left(\frac{1}{1^2}\right)] = Z^2E_R\left(\frac{3}{4}\right) \qquad \textbf{(3)}$$

Equating equations (2) and (3) gives:

$$hc(kZ)^2 = Z^2E_R\left(\frac{3}{4}\right)$$

Rearranging for k gives:

$$k = \sqrt{\frac{3E_R}{4hc}}$$

Marks

- Describe two physical properties of liquid or solid N_2 that distinguish it from liquid or solid H_2O. **2**

Solid N_2 is denser than liquid N_2. Solid water is less dense than liquid water.

Liquid N_2 has a much lower melting and boiling point than than liquid water. The molecules in solid or liquid N_2 are held together only by weak dispersion forces. The molecules in solid and liquid water are held together by strong hydrogen bonds and by weak dispersion forces.

- One problem with the Rutherford model of the atom was that there was nothing to stop the electrons from spiralling into the nucleus. Briefly explain how the quantum theory of the electrons resolved this problem. **2**

Classical theory held that a negatively charged particle orbiting a positive one would lose energy continuously.

In quantum theory, the energy of the electrons is quantised and only certain values are allowed. The lowest allowed energy level has *n* = 1 and has zero probability of finding the electron at the nucleus.

- From the list of molecules below, select all the polar molecules and list them from left to right in order of increasing molecular dipole moment. **2**

BF_3, CH_3Cl, CH_3F, CO_2, CF_4, NF_3

The polar molecules are CH_3Cl, CH_3F and NF_3. Although the bonds in the other molecules are polar, the overall molecules are non-polar due to their symmetrical shape.

The molecular dipole moments increase in the order:

$$NF_3 < CH_3Cl < CH_3F$$

This increase is consistent with the difference in the electronegativity of the atoms: C < N < Cl < F.

- Write a balanced equation for (i) the explosive decomposition, and (ii) the combustion in air, of TNT, $C_7H_5N_3O_6$(s).

(i) $2C_7H_5N_3O_6(s) \rightarrow 12CO(g) + 3N_2(g) + 5H_2(g) + 2C(s)$

(ii) $2C_7H_5N_3O_6(s) + {}^{21}/_2O_2(g) \rightarrow 14CO_2(g) + 5H_2O(g) + 3N_2(g)$

What is the essential difference between these two processes?

In the combustion reaction, the oxidant comes from an external source (air). In the explosion, the oxidant is contained in the explosive material.

What is the increase in the number of moles of gas (per mole of TNT consumed) for each of these two processes?

For process (i), the change in the number of moles of gas, Δn, is:

$$\Delta n = n(\text{moles of gaseous products}) - n(\text{moles of gaseous reactants})$$
$$= ((12 + 3 + 5) - (0))\ \text{mol} = 20\ \text{mol}$$

As (i) involves 2 mol of TNT, Δn = 10 mol per mole of TNT

Answer: **(i) 10 mol**

For process (ii), the change in the number of moles of gas, Δn, is:

$$\Delta n = n(\text{moles of gaseous products}) - n(\text{moles of gaseous reactants})$$
$$= ((14 + 5 + 3) - ({}^{21}/_2))\ \text{mol} = {}^{23}/_2\ \text{mol}$$

As (i) involves 2 mol of TNT, $\Delta n = \frac{1}{2} \times {}^{23}/_2$ mol per mole of TNT

Answer: **(ii) ${}^{23}/_4$ mol**

Which of these two processes releases more energy into the surroundings?

Data: $\Delta_fH°(\text{TNT}) = 6.9$ kJ mol^{-1} $\Delta_fH°(CO(g)) = -111$ kJ mol^{-1}
$\Delta_fH°(CO_2(g)) = -393$ kJ mol^{-1} $\Delta_fH°(H_2O(g)) = -242$ kJ mol^{-1}

Using $\Delta_rH° = \Sigma\, m\Delta_fH°(\text{products}) - \Sigma\, m\Delta_fH°(\text{reactants})$, the enthalpy change for reaction (i) can be written as

$$\Delta_rH° = [12\Delta_fH°(CO(g))] - [2\Delta_fH°(C_7H_5N_3O_6(s))]$$
$$= ([12 \times -111] - [2 \times 6.9])\ \text{kJ mol}^{-1} = --1346\ \text{kJ mol}^{-1}$$

ANSWER CONTINUES ON THE NEXT PAGE

Similarly. the enthalpy change for reaction (ii) can be written as

$$\Delta_r H° = [14\Delta_f H°(CO_2(g)) + 5\Delta_f H°(H_2O(g))] - [2\Delta_f H°(C_7H_5N_3O_6(s))]$$
$$= ([14 \times -393 + 5 \times -242] - [2 \times 6.9])\ \text{kJ mol}^{-1} = -6726\ \text{kJ mol}^{-1}$$

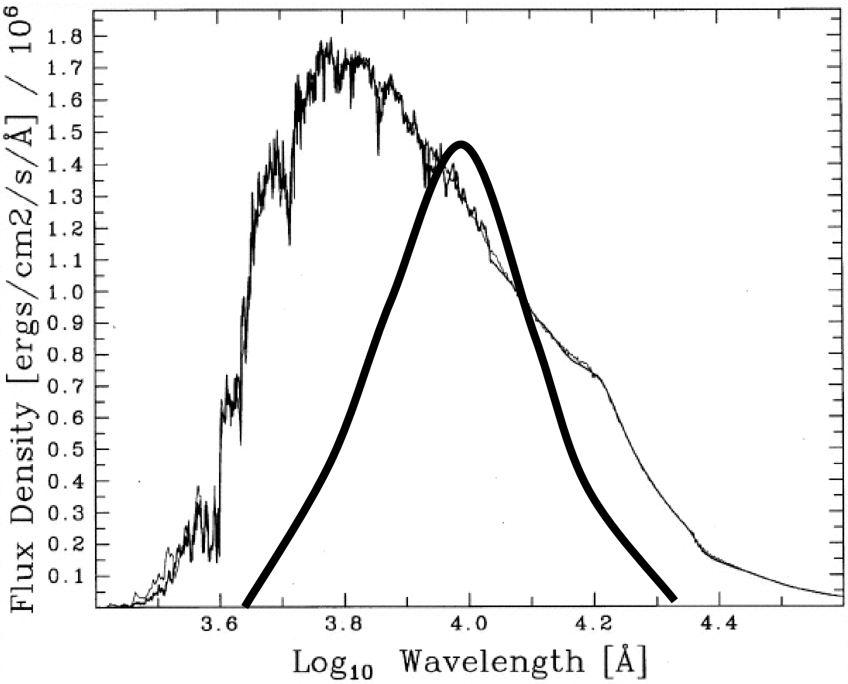
$\Delta_f H°(N_2(g))$, $\Delta_f H°(H_2(g))$ and $\Delta_f H°(C(s)$ all represent formation of the elements from their standard states and are all zero.

The combustion reaction releases more energy.

Answer: **combustion reaction**

Estimate the surface temperature of the star Arcturus from its emission spectrum shown in the figure below.

Marks 3



The wavelength at the maximum, λ, is related to the temperature, *T*, by Wien's displacement law:

$$T = \frac{2.898 \times 10^6}{\lambda}$$

where λ is in nm. The maximum is at approximately 3.8. This corresponds to a wavelength of:

$$\lambda = 10^{3.8} \times 10^{-10}\ \text{m} \quad \text{(since the scale is a } \log_{10} \text{ scale and } 1\ \text{Å} = 10^{-10}\ \text{m)}$$
$$= 6.3 \times 10^{-7}\ \text{m} = 630\ \text{nm}$$

Hence, the temperature of the star is approximately:

$$T = \frac{2.898 \times 10^6}{630}\ \text{K} = 4600\ \text{K}$$

Given the broadness of the peak, which is exasperated by the $\log_{10}$ scale, this value is very approximate.

Answer: **~4600 K**

On the figure above, sketch the broad emission spectrum of a red giant, clearly showing the emission maximum and the overall intensity.

Red giants have (relatively) low surface temperature. A Wien's law predict an inverse relationship between the temperature and maximum, the spectrum is shifted to the right (i.e. towards longer wavenlengths). Because they are a cooler, the intensity will also be lower. See sketch above.

Marks 6

- A calorimeter containing 300.0 mL of water at 25 °C was calibrated as follows. A 1000.0 W heating coil was run for 10.0 s, after which time the temperature had increased by 7.5 °C. Calculate the heat capacity of the empty calorimeter. The specific heat of water is 4.184 J K^{-1} g^{-1}.

With a power of 1000.0 W = 1000.0 J s^{-1}, the amount of heat generated by the coil is:

$$q = (1000.0 \text{ J s}^{-1}) \times (10.0 \text{ s}) = 1.00 \times 10^3 \text{ J}$$

As the density of water at 25 °C is 0.997 g mL^{-1}, 300.0 mL of water corresponds to:

$$\text{mass of water} = m = \text{density} \times \text{volume} = (0.997 \text{ g mL}^{-1}) \times (300.0 \text{ mL}) = 299 \text{ g}$$

The heat required to heat this quantity of water by 7.5 °C is:

$$q = c_{H_2O} \times m_{H_2O} \times \Delta T = (4.184 \text{ J K}^{-1} \text{ g}^{-1}) \times (299 \text{ g}) \times (7.5 \text{ K}) = 9380 \text{ J}$$

The remaining heat, (1.00×10^3 – 9380) J = 620 J, is used to heat the calorimeter. This also increases in temperature by 7.5 °C so the heat capacity of the calorimeter is:

$$c_{\text{calorimeter}} = \frac{q}{\Delta T} = \frac{620 \text{ J}}{7.5} = 82 \text{ J K}^{-1}$$

Answer: **82 J K^{-1}**

A solution containing 0.040 mol Ag^+(aq) was mixed with a second solution containing 0.050 mole Br^-(aq) in this calorimeter, causing AgBr(s) to precipitate. The temperature increased by 2.4 °C. Given the solubility product constant is K_{sp}(AgBr) = 5×10^{-13} M^2 , calculate the equilibrium concentrations of Ag^+(aq) and Br^-(aq) present in the final solution of volume 320 mL.

To calculate the equilibrium constants of Ag^+(aq) and Br^-(aq), a reaction table can be used, with x representing the number of moles which do *not* precipitate:

	Ag^+(aq)	Br^-(aq)	$\rightleftharpoons$	AgBr(s)
initial (mol)	0.040	0.050		0
final (mol)	x	$0.010 + x$		$0.040 - x$

The concentrations in the final solution of volume 320 mL are therefore:

$$[Ag^+(aq)] = \frac{x \text{ mol}}{0.320 \text{ L}} \quad \text{and} \quad [Br^-(aq)] = \frac{(0.010 - x) \text{ mol}}{0.320 \text{ L}}$$

Hence, the solubility product is:

ANSWER CONTINUES ON THE NEXT PAGE

$$K_{sp} = [Ag^+(aq)][Br^-(aq)] = \left(\frac{x}{0.320}\right)\left(\frac{0.010 - x}{0.320}\right) = 5 \times 10^{-13}$$

K_{sp} is very small, x is tiny and so 0.010 – x ~ 0.010. This approximation gives:

$$\left(\frac{x}{0.320}\right)\left(\frac{0.010}{0.320}\right) = 5 \times 10^{-13}$$

or

$$[Ag^+(aq)] = \left(\frac{x}{0.320}\right) = (5 \times 10^{-13}) \times \left(\frac{0.320}{0.010}\right)\ \text{M} = 1.6 \times 10^{-11}\ \text{M}$$

$$[Br^-] = \frac{0.010}{0.320}\ \text{M} = 0.031\ \text{M}$$

$[Ag^+(aq)]$: **1.6×10^{-11} M**	$[Br^-(aq)]$: **0.031 M**

Calculate the enthalpy of solution of AgBr(s).

As the final solution has a volume of 320 mL, its mass is:

$$\text{mass} = \text{density} \times \text{volume} = (0.997\ \text{g mL}^{-1}) \times (320\ \text{mL}) = 319\ \text{g}$$

The heat produced causes the temperature of this mass of solution and the calorimeter to rise by 2.4 °C:

$$\begin{aligned} q &= (c_{H_2O} \times m_{H_2O} \times \Delta T) + (c_{\text{calorimeter}} \times \Delta T) \\ &= ((4.184\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (319\ \text{g}) \times (2.4\ \text{K})) + ((82\ \text{J K}^{-1}) \times (2.4\ \text{K})) \\ &= 3400\ \text{J} \end{aligned}$$

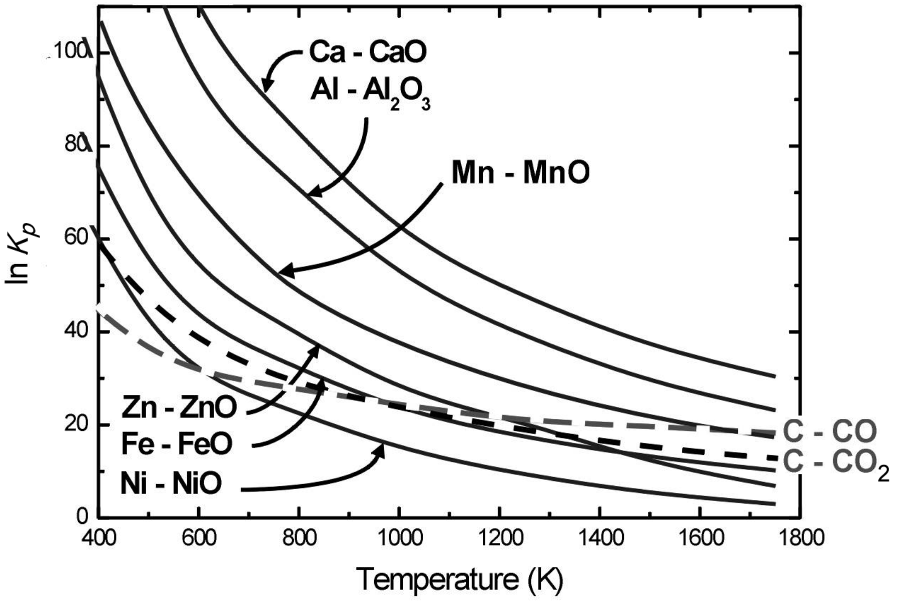
This corresponds to the heat given out in the precipitation of 0.040 mol of AgBr(s). As the precipitation is exothermic, the heat of solution is endothermic:

$$\text{heat of solution} = +\frac{3400\ \text{J}}{0.040\ \text{mol}} = +85\ \text{kJ mol}^{-1}$$

Answer: **$+85\ \text{kJ mol}^{-1}$**

Marks 4

- Use the figure below to help answer the following.



Write a balanced equation for the smelting of one of these metal oxides with coke in which a major product is CO_2. Give the approximate temperature range over which this reaction is spontaneous and state what happens outside this temperature range.

Between 400 – 950 K, the Ni – NiO lines is below the C – CO_2 line and hence the oxide will be reduced by coke to produce CO_2:

$$2NiO(s) + C(s) \rightarrow 2NI(l) + CO_2(g)$$

Below 400 K, it appears that the Ni – NiO will be above the C – CO_2 line so this reduction will not occur.

Above 950 K, the C – CO line is higher than the C – CO_2 line so the reduction produces CO_2. (Any CO_2 produced would be reduced by C to produce CO.)

Over what temperature range can ZnO be reduced by Fe? What other metal could be used instead to increase the temperature range in which metallic Zn was produced?

The Zn – ZnO line falls below the Fe – FeO line at approximately 1450 K and reduction of ZnO by Fe will thus occur above this temperature.

The Zn – ZnO line is below the Ca – CaO, Al – Al_2O_3 and Mn – MnO lines over the entire temperature range of the diagram and so Ca, Al or Mn could be used to reduce ZnO at these temperatures.

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks 5

Estimate the partial pressure of CO that would be expected at equilibrium in the smelting of ZnO by coke at 1500 K.

At 1500 K,

$C + \frac{1}{2}O_2 \rightarrow CO$ $\ln K_p(1) \sim 21$

$Zn + \frac{1}{2}O_2 \rightarrow ZnO$ $\ln K_p(2) \sim 14$

Hence, for:

$ZnO + C \rightarrow Zn + CO$

$K_p = p(CO) = K_p(1) / K_p(2)$

or

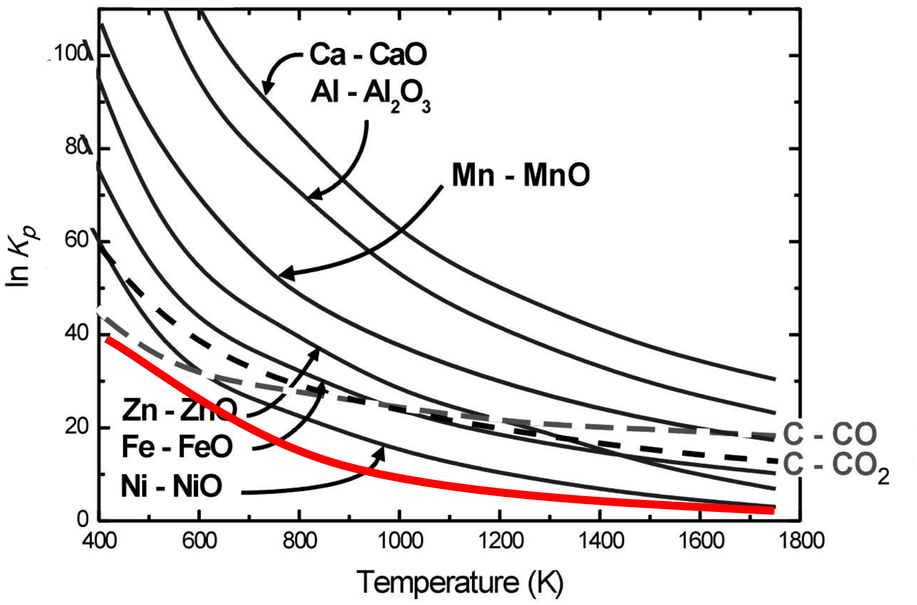
$\ln K_p = \ln(K_p(1)/K_p(2)) = \ln K_p(1) - \ln K_p(2) = 21 - 14 = 7$

$K_p \sim 10^3$ **and hence** $p(CO) \sim 1000$ **atm**

Metallic copper is produced by smelting chalcopyrite, $CuFeS_2(s)$, directly in oxygen to produce iron oxides and SO_2. Write a balanced equation for this reaction, and sketch the $\ln K_p$ *versus* temperature curve for Cu-CuO on the diagram on page 24. Clearly label the curve you have drawn.

$CuFeS_2(s) + {}^5/_2O_2(g) \rightarrow Cu(s) + FeO(s) + 2SO_2(g)$

The $\ln K_p$ curve for Cu – CuO lies below Fe – FeO at all temperatures. A *sketch* (in bold / red) is shown below.



Marks 4

- A voltaic cell consists of Zn^{2+}/Zn and Cu^{2+}/Cu half cells with initial concentrations of $[Zn^{2+}]$ = 1.00 M and $[Cu^{2+}]$ = 0.50 M. Each half cell contains 1.00 L of solution.

What is the voltage of the cell at 20 °C after equilibrium has been reached?

E_{cell} = **0 V**

What are the concentrations of the Ni^{2+}(aq) and the Cu^{2+}(aq) ions at 20 °C after equilibrium has been reached?

The standard reduction half-cell reactions are (from the data sheet):

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = +0.34\ V$$
$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E° = -0.76\ V$$

As the Zn^{2+} / Zn value is the least positive, it is reversed and the reaction and cell potential are:

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq) \qquad E° = (+0.34\ V) + (+0.76\ V) = +1.10\ V$$

Using $E° = \frac{RT}{nF} \ln K$, the equilibrium constant for this 2 e^- process at T = 20 °C (= 20 + 273 K) is:

$$K = \exp\left(\frac{(1.10\ V) \times 2 \times (96485\ C\ mol^{-1})}{(8.314\ J\ K^{-1}\ mol^{-1}) \times (293\ K)}\right) = 6.97 \times 10^{37}$$

The equilibrium constant is so large that the reaction essentially goes to completion. As, initially, $[Zn^{2+}(aq)]_{initial}$ = 1.00 M and $[Cu^{2+}(aq)]_{initial}$ = 0.50 M, the latter is the limiting reagent and so:

$$[Zn^{2+}(aq)]_{equilibrium} = 1.50\ M \text{ and } [Cu^{2+}(aq)] = 0.00\ M$$

Alternatively, a reaction table can be constructed:

	Zn(s)	Cu^{2+}(aq)	$\rightleftharpoons$	Zn^{2+}(aq)	Cu(s)
initial		0.50		1.00	
change		$-x$		$+x$	
final		$0.50 - x$		$1.00 + x$	

Hence:

$$K = \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]} = \frac{1.00 + x}{0.50 - x} = 6.97 \times 10^{37}$$

As K is very large, $x \sim 0.5$ M.

$[Zn^{2+}]_{eq}$ = **1.5 M**	$[Cu^{2+}]_{eq}$ = **0.0 M**

	Marks
• Judging by the electrochemical series of standard reduction potentials, H^+(aq) should be reduced to H_2(g) by exposure to metallic Fe, which is oxidised to Fe^{2+}(aq). Why do we not see water on iron spontaneously generating hydrogen gas?	**2**

The standard electrode potentials correspond to reactants having standard concentrations – they refer to [H^+(aq)] = 1.0 M. Water has a pH close to 7 and so [H^+(aq)] = 10^{-7} M.

Also, there is a high overpotential associated with the formation of H_2(g) and so the standard electrode potential does not give the actual potential required to produce H_2(g).

• State the Second Law of Thermodynamics, and explain how an exothermic process in a closed system changes the entropy of the surroundings.	**4**

In any spontaneous process, the entropy of the universe always increases.

A closed system can exchange heat or work with its surroundings. An exothermic reaction releases heat, q, into the surroundings: $\Delta_{surr}S = q / T > 0$

The enthalpy of reaction defines the heat released into or absorbed from the surroundings at constant temperature and pressure.

The standard enthalpy and entropy of solution of poly(oxyethylene) in water are $\Delta H° = –7.8$ kJ mol$^{–1}$ and $\Delta S° = –31$ J K$^{–1}$ mol$^{–1}$. Use these data to predict whether the solubility of poly(oxyethylene) in water increases or decreases when the solution is warmed.

The surroundings receive 7.8 kJ mol^{-1} from this exothermic reaction. Hence:

$$\Delta_{surr}S° = (7.8 \times 10^3 \text{ kJ mol}^{-1}) / T$$

As $\Delta_{sys}S° = –31$ J K$^{–1}$ mol$^{–1}$, the total change in entropy is:

$$\Delta_{univ}S° = (–31 + 7800/T) \text{ J K}^{–1} \text{ mol}^{–1}$$

Spontaneous process occur when $\Delta_{univ}S°$ is positive:

- **At low T, the second term is large and dominates the first term. This leads to $\Delta_{univ}S° > 0$ and dissolution being favoured.**
- **At high T, the second term is small and the first term dominates. This leas to $\Delta_{univ}S° < 0$ and dissolution being unfavoured.**

Hence, the solubility decreases with temperature.