CH101 GENERAL CHEMISTRY I MID TERM EXAMINATION

FALL SEMESTER 2008

Wednesday 22 October 2008: 1900 – 2100

Attempt all SIX questions
A copy of the periodic table is supplied

Some important constants

$$h = 6.626 \times 10^{-34} \text{ J s} \qquad c = 2.998 \times 10^8 \text{ m s}^{-1}$$
$$m_e = 9.109 \times 10^{-31} \text{ kg} \qquad N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$
$$1\ eV = 1.602 \times 10^{-19} \text{ J}$$

1. (i) Comment on the accuracy and precision of the following set of replicate measurements, if the accepted (real) value is 0.0919.

0.0902; 0.0884; 0.0886; 0.100 (2 points)

(ii) Calculate the length of the sides of a cubic volume occupied by a single benzene molecule (molar mass of benzene = 78.114 g mol^{-1}, density of benzene = 0.8765 g cm^{-3}). (4 points)

[1 Å $\equiv 10^{-8}$ cm]

(iii) Calculate the mass of potassium hydroxide (KOH) contained in 25.30 ml of 0.102 M (mol l^{-1}) solution. Show working.

[molar masses (g mol^{-1}): H = 1.008, O = 15.999, K = 39.098] (3 points)

1. (i) Mean value = 0.918 (1 point), hence accuracy high (good) (1 point), but precision low (poor) (because of scatter or wide range: 0.0884 – 0.100) (1 point).

(ii) Molar volume = volume occupied by 1 mol of molecules = 78.114 (g/mol)/0.8765 (g/cm^3)

= 89.12 cm^3/mol

Volume occupied by one molecule = 89.12 (cm^3/mol)/6.022 x 10^{23} (/mol) = 1.48 x 10^{-22} cm^3

This is equivalent to a cube of sides $^3\sqrt{}$(1.48 x 10^{-22}) cm^3 = 6.20 x 10^{-8} cm or 6.20 Å (4 points for this result with reasonable working)

(iii) Number of moles = $\dfrac{25.30}{1000}$ x 0.102 mol

Since mass (g) = mol x molar mass (g/mol) and molar mass = 56.105 g/mol,

mass = $\dfrac{25.30}{1000}$ x 0.102 x 56.105 = 0.145 g

(3 points if this or equivalent method gives the above result)

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2. (i) Calculate the maximum wavelength of electromagnetic radiation needed to eject electrons from the surface of tungsten, which has a work function of 7.29 x 10^{-19} J. (6 points)

(ii) If the maximum speed of electrons emitted from the tungsten surface is 2.00 x 10^6 m s^{-1}, calculate the wavelength of the incident radiation. (6 points)

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2. (i) This involves the photoelectric equation, $E_{max} = \frac{1}{2}m_e v_e^2 = h\nu - w$, where w is the work function (7.29×10^{-19} J) representing the minimum energy (and hence maximum wavelength) of photons required for photoelectric effect.

$E(min) = 7.29 \times 10^{-19}$ J $= hc/\lambda(max)$; $\lambda(max) = \dfrac{(6.626 \times 10^{-34} \text{ Js})(2.988 \times 10^8 \text{ ms}^{-1})}{7.29 \times 10^{-19} \text{ J}}$

$= \underline{2.72 \times 10^{-7} \text{ m (272 nm)}}$

(Give 6 points for clear method that gives above result)

(ii) Maximum energy of electrons ejected by impact of photons of wavelength λ is given by,

$E_{max} = \frac{1}{2}m_e v_e^2 = \frac{1}{2}(9.109 \times 10^{-31} \text{ kg})(2.00 \times 10^6 \text{ m/s})^2$

$= 18.2 \times 10^{-19}$ J $= hc/\lambda - w$

Hence, $hc/\lambda = 25.5 \times 10^{-19}$ J

$\lambda = \dfrac{(6.626 \times 10^{-34} \text{ Js})(2.988 \times 10^8 \text{ ms}^{-1})}{25.5 \times 10^{-19} \text{ J}}$

$= \underline{0.779 \times 10^{-7} \text{ m (77.9 nm)}}$

(Give 6 points for clear method that gives above result)

3. (i) Identify, with a brief explanation, the orbital whose wave function is given by

$$\Psi_{n,l,m} = \frac{\sqrt{2}}{81\sqrt{\pi}} \; a_0^{-3/2} \left(6 - \rho\right) \rho \; e^{-\rho/3} \cos\theta$$

(5 points)

(ii) Complete the table below by filling in the gaps. The first row is completed as an example. (5 points)

Label	n	l	No. of orbitals	Radial nodes	Angular nodes
3d	3	2	5	0	2
	5	0			0
5f		3		1	
	7	4			

(iii) Palladium is predicted by the Aufbau Principle to be paramagnetic, but is in fact diamagnetic. Write the predicted and actual electron configurations that explain these facts. You may use short hand noble gas configurations for core electrons. (2 points)

(iv) Write the electron configuration of Sc and Sc$^+$, given that they are both paramagnetic. You may use short hand noble gas configurations for core electrons. (2 points)

(i)

1 nodal sphere at $\rho = 6$ $n = 3$

$l = 1$, 1 angular node

$$\Psi_{n,l,m} = \frac{\sqrt{2}}{81\sqrt{\pi}}\, a_0^{-3/2}\,(6 - \rho)\,\rho\, e^{-\rho/3}\cos\theta$$

$n = 3$

Highest power in ρ = 2: $n = 3$

No trig term in ϕ: $m = 0$ (points along z axis)

Orbital is 3p$_Z$ ($\Psi_{3,1,0}$)   **(5 points for identity and rationalization as above)**

(ii)

| Label	n	l	No. of orbitals	Radial nodes	Angular nodes
3d	3	2	5	0	2
5s	5	0	**1**	**4**	0
5f	**5**	3	**7**	1	**3**
7g	7	4	**9**	**2**	**4**

(1/2 point for each correct entry = 5 total))

(iii)

Predicted electronic configuration of Pd (Z = 46) is [Kr]4d^{8}5s^2 (paramagnetic)

Actual electronic configuration is [Kr]4d^{10} (diamagnetic)   **(2 points)**

(iv) Sc (Z = 21) is [Ar]3d^{1}4s^2 (paramagnetic)

Sc$^+$ is [Ar]3d^{1}4s^1 (paramagnetic)   **(2 points)**

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4. (i) Calculate the potential energy of either electron in the atomic arrangement for helium shown below.

He (nucleus)

2.00 Å   2.00 Å

e ←→ e
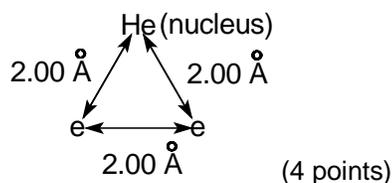
2.00 Å   (4 points)

(ii) Using an electron-nucleus distance of 2.00 Å (as in (i) above), sketch a better atomic arrangement for helium that gives the lowest total potential energy and calculate the potential energy of either electron. (4 points)

3

Generally, V = $\dfrac{14.40\ q_1 q_2}{r}$ **(q_1, q_2 are in units of electronic charge and r is in Å)**

V for either electron = V(attractive) + V(repulsive)

= $\dfrac{14.40\ eVÅ\ (+2)(-1)}{2.00\ Å}$ + $\dfrac{14.40\ eVÅ\ (-1)(-1)}{2.00\ Å}$

= -7.20 eV   **(4 points for this result and reasonable clarity)**

(ii) Best arrangement is

e⁻   He(2+)   e⁻
←——————→ ←——————→   **(Linear)**
2.00 Å   2.00 Å
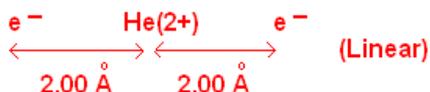
This time V = $\dfrac{14.40\ eVÅ\ (+2)(-1)}{2.00\ Å}$ + $\dfrac{14.40\ eVÅ\ (-1)(-1)}{4.00\ Å}$

= -10.80 eV   **(4 points for this result and reasonable clarity)**

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5. (i) Sketches of the radial distribution function $r^2[R_{n\ell}]^2$ for three orbitals from the same n level are shown below.
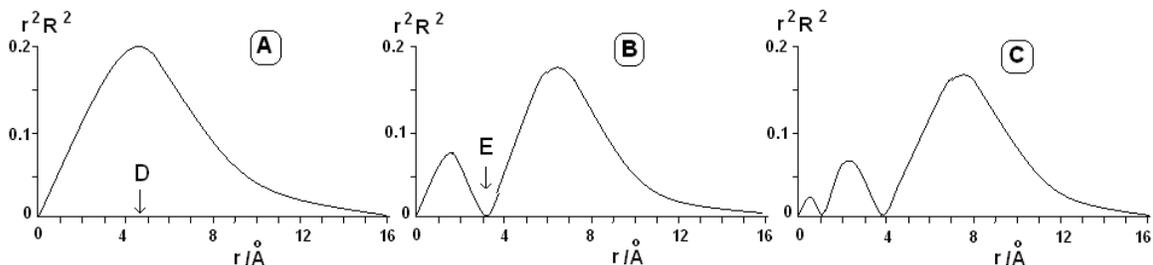
(a) Which of A, B or C correspond to (a) $r^2[R_{n0}]^2$ (b) $r^2[R_{n1}]^2$ (c) $r^2[R_{n2}]^2$? (3 points)

(b) What is the distance D in plot A? (1point)

(c) What occurs at distance E in plot B? (1 point)

(d) Which orbital experiences the greatest nuclear charge? (1 point)

(e) Which plot is derived from a radial function that is proportional to $r^2 e^{(-r/3a_0)}$? (1 point)

(f) Which of A, B or C has m values –1, 0, +1? (1 point)

(g) Identify the orbitals represented by A, B and C. (2 points)

(ii) Identify the period 3 element that possesses the ionization energies (in kJ mol^{-1}) in the table below. Give an explanation. (3 points)

IE$_1$	IE$_2$	IE$_3$	IE$_4$	IE$_5$	IE$_6$
1012	1903	2910	4956	6278	22,230

(iii) Explain how and why the atomic radius varies on proceeding from Li to F; and going from Li to Cs.   (5 points)

(i) (a)   (a) C   (b) B   (c) A   (3 points)

(b) n^2a_0 (1 point)

(c) nodal sphere (radial node or spherical node)   (1 point)

(d) C (1 point)

(e) A (1 point)

**(f) B (1 point)**

**(g) A is 3d; B is 3p; C is 3s (2 points)**

(ii) IE_6 is much larger than the others, suggesting loss of an electron from a filled shell (that is, IE_6 corresponds to the electronic configuration of Ne ($1s^2 2s^2 2p^6$). Hence original atom is of element 5 electrons along period 3: P ([Ne]$3s^2 3p^3$). (3 points for correct deduction and reasonable argument)

(iii) Li to F: atomic radius decreases because electrons are being added to the same shell (n = 2). Additional electrons do not sufficiently shield each other from additional charges on nucleus: Z_{eff} increases. (2.5 points for argument like this)

Li to Cs: atomic radius increases. On proceeding down group 1, electrons are added in complete shells (n = 2 to n = 6), thereby effectively shielding the outer electrons: Z_{eff} decreases. (2.5 points for argument like this)

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6. (i) Write Lewis diagram resonance structures for imidofulminic acid (HCNNH), showing all non-zero formal charges. Is it possible to write a Lewis structure for this molecule that has all zero formal charges on its atoms?   (4 points)

(ii) Although the inert gases are generally unreactive, Kr and Xe will form compounds in the right conditions. Three reactions of inert gas compounds are shown below, (A) – (C).

(A) $3XeF_4 + 6H_2O \rightarrow XeO_3 + Xe + 12HF + 3/2O_2$

(B) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

(C) $KrF_2 + AsF_5 \rightarrow KrF^+ AsF_6^-$
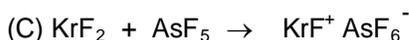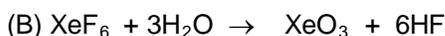
Classify reactions (A) – (C) as redox or acid-base reactions.   (3 points)

(iii) Sulfides react with aqueous nitric acid according to the unbalanced ionic equation below.

$S^{2-} + NO_3^- \rightarrow SO_4^{2-} + NO$
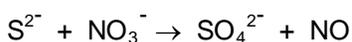
Write balanced ionic oxidation and reduction half equations and hence a fully balanced ionic redox equation for this reaction. (7 points)

(i)

$$H-\overset{\overset{\displaystyle\cdot\cdot}{\cdot\cdot}}{\underset{}{C}}=\overset{+}{N}=\overset{\overset{\displaystyle\cdot\cdot}{}}{N}-H \quad\longleftrightarrow\quad H-C\equiv\overset{+}{N}-\overset{\overset{}{}}{\underset{\displaystyle\cdot\cdot}{N}}-H$$
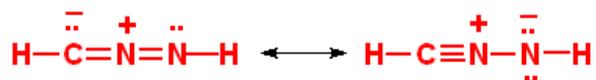
(3 points)

No, it is not possible to write a Lewis structure with all zero formal charges for the molecule, without breaking the octet rule. (1 point)

(ii) (A) Redox   (B) Acid-base   (C) Acid-base   (3 points)

(iii) In this reaction sulfide (S^{2-}) is oxidized to sulfate (SO_4^{2-}) and nitrate (NO_3^-) is reduced to nitric oxide (NO) in *aqueous acidic* solution.

Oxidation half equation: $S^{2-} + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 8e^-$

Reduction half equation: $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$

To balance the number of electrons on each side, multiply top equation by 3 and bottom equation by 8. Adding these gives the full ionic redox equation:

$3S^{2-} + 8H^+ + 8NO_3^- \rightarrow 3SO_4^{2-} + 4H_2O + 8NO$

(7 points for argument like this to give the above result)

CH101 GENERAL CHEMISTRY I END OF TERM EXAMINATION
Wednesday 17 December 2008
19.00 – 21.00
Attempt all 8 questions. Each question is worth 15 points
Write your answers in the boxes provided

1. (i) Use Pauling's atomic hybridization theory to sketch the bonding in the carbodiimide molecule (HN=C=NH), clearly showing the hybridization mode of the carbon and nitrogen atoms and all σ and π bonds. (9 points)

(ii) If the H-Cl bond is 18.0% ionic and the HCl molecule has a dipole moment of 1.109 D, determine the bond length of H-Cl in Å. Show working. (6 points)

(i)
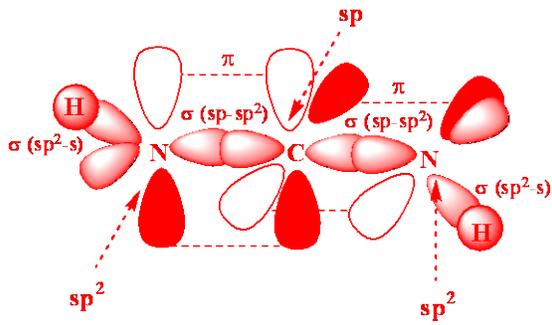
(or equivalent sketch) (9 points)

(ii)

$$\mu\,(\text{Debye}) = \frac{R(\overset{\circ}{A})\,\delta}{0.2082\,(\overset{\circ}{A}/\text{Debye})}$$

i.e. $1.109 = \dfrac{R(\overset{\circ}{A})\,0.18}{0.2082}$, from which $R = 1.28\ \overset{\circ}{A}$

(or equivalent working) (6 points)

2. (i) (a) Use the VSEPR theory to determine the shape of the nitronium ion (NO_2^+) and the nitrite ion (NO_2^-) and determine the hybridization on the nitrogen atom in each molecule. (6 points)

(b) Write the major Lewis resonance structures for nitrogen dioxide (NO_2) and, on the basis of this and your answer to part (a), suggest the likely hybridization of N in NO_2 and the likely shape of the NO_2 molecule. (4 points)

(ii) Use the VSEPR theory to sketch the geometry of the BrF_4^- ion and indicate whether or not the molecule is distorted. (5 points)

(i) (a) Sketches
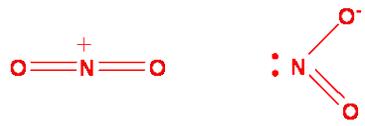
(2 x 1 points)

Shape of NO_2^+ is __**linear**__. Shape of NO_2^- is __**bent**__. **(or V-shape) (2 x 1 points)**

Hybridization of N in NO_2^+ is __**sp**__. Hybridization of N in NO_2^- is __**sp²**__. **(2 x 1 points)**

(i) (b) Lewis structures of NO_2
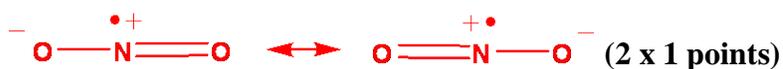
(2 x 1 points)

Hybridization of N **sp^2**.   Likely shape of NO_2 **bent** . **(or V-shape) (2 x 1 points)**

(ii) Sketch of BrF_4^-
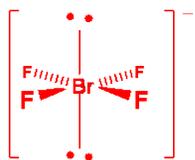
(square planar: - charge can be shown on Br) (4 points)

Distorted? (yes or no) **no** . **(1 point)**

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3. (i) Sketch molecular orbital energy diagrams for NO^+, NO and NO^-. (6 points)
   (ii) From the electron distributions in the MO energy diagrams, determine the bond order for each and determine whether each molecule is diamagnetic or paramagnetic. (3 points)
   (iii) Comment briefly on the relative stabilities of the three molecules. (2 points)
   (iv) Sketch the HOMO and LUMO for NO^+. (4 points)

(i) MO energy diagrams **(6 points)**
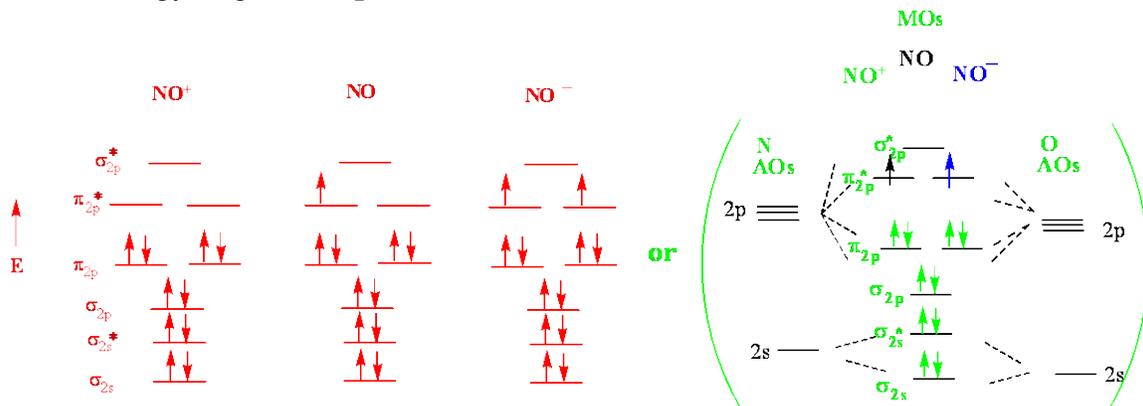
(ii) Bond orders? NO^+ (**3**)   NO (**2.5**) NO^- (**2**) **(1.5 points)**

Magnetism? NO^+ (**diamagnetic**) NO (**paramagnetic**) NO^- (**paramagnetic**) **(1.5 points)**

(iii) Comment: **Stability NO^+ > NO > NO^- or similar statement** **(2 points)**
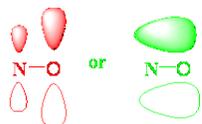
(iv) Sketches   HOMO   LUMO

(4 points)

4. Sketch the π molecular orbitals of the allyl cation ($CH_2=CH-CH_2^+$) in order of increasing energy and for each write a wave expression in terms of linear combinations of p-orbital wave functions. (15 points)

$\Psi_3 = c_A \Psi_A - c_B \Psi_B - c_A \Psi_C$

π_3^* (antibonding)

$\Psi_2 = c_A \Psi_A - c_A \Psi_C$

π_2 (non-bonding)

$\Psi_1 = c_A \Psi_A + c_B \Psi_B + c_A \Psi_C$

π_1 (bonding)

or similar diagram showing nodes and/or constructive and destructive interaction (or overlap)

(3 x 3 points for sketch and 3 x 2 points for wave expressions)
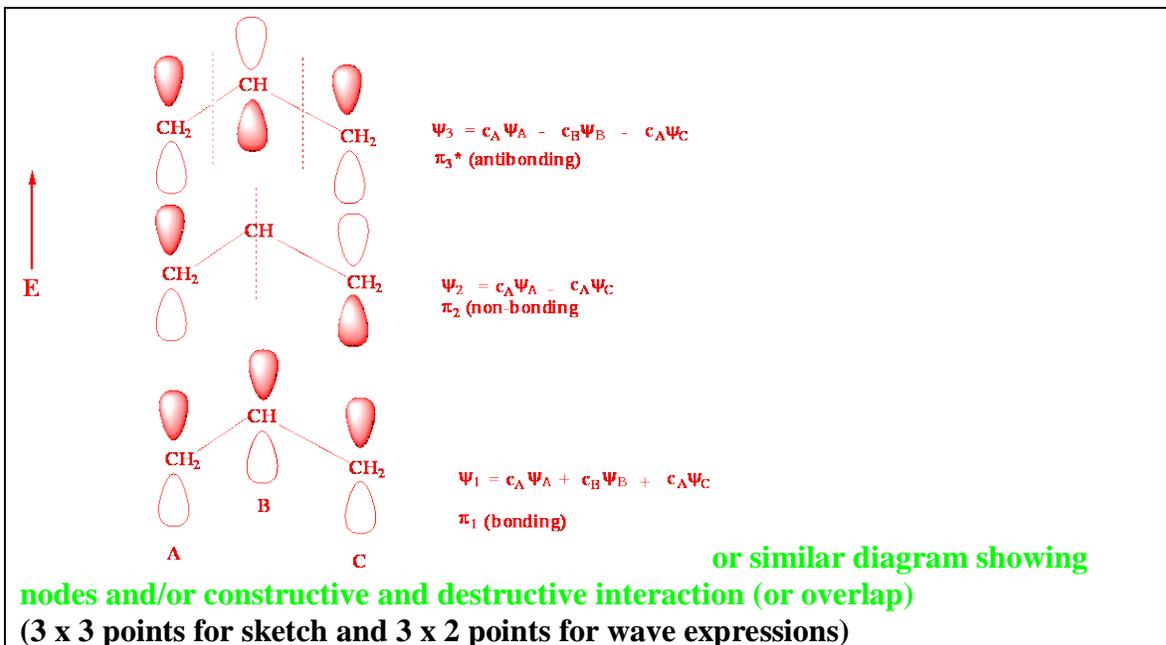
5. Suppose 1.00 mol of hydrogen gas is expanded reversibly from an initial volume of 10.0 L at 400 K to a final volume of 50.0 L, without changing the temperature. Assuming ideal behavior, determine the free energy change (ΔE), the enthalpy change (ΔH), the heat transferred (q) and the work done (w) for this process. Show working. (15 points)
[R = 8.315 J K^{-1} mol^{-1}]

Since this is an isothermal expansion ($\Delta T = 0$), $\underline{\Delta E = \Delta H = 0}$ **(2 points)**

For a reversible isothermal process,

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$= (1.00 \text{ mol})(8.315 \text{ J K}^{-1} \text{ mol}^{-1})(400 \text{ K}) \ln\left(\frac{50.0 \text{ L}}{10.0 \text{ L}}\right)$$

$$= \underline{-5353 \text{ J}} \quad \textbf{(9 points)}$$

From the first law of thermodynamics, q = -w

Hence, $\underline{q = 5353 \text{ J}}$ **(4 points)**

Give graded points for extent of working and also for equivalent method that gives the above answers

6. When 1.00 g of potassium chlorate ($KClO_3$) is dissolved in 50.0 g of water held in a Styrofoam calorimeter of negligible heat capacity, the temperature drops from 24.50 to 22.86 ^oC. Calculate q for water and ΔH^o for the process $KClO_3(s) \rightarrow K^+(aq) + ClO_3^-(aq)$. [Specific heat of water is 75.40 J K^{-1} mol^{-1}. Molar masses (g mol^{-1}): K = 39.1; Cl = 35.5; O = 16.0; H = 1.01] (15 points)

Molar mass of water is 18.02 g mol^{-1} and molar mass of $KClO_3$ is 122.6 g mol^{-1}

q(water) = mass x specific heat x ΔT

$$= (50.00 \text{ g})\left(\frac{75.40 \text{ J K}^{-1} \text{ mol}^{-1}}{18.02 \text{ g mol}^{-1}} \right)(-1.64 \text{ K})$$

= -343.1 J   (9 points)

ΔH(reaction) = -q, scaled up to 1.00 mol: for 122.6 g of $KClO_3$

$$= (343.1 \text{ J}) \left(\frac{122.6 \text{ g mol}^{-1}}{1.00 \text{ g}} \right)$$

= <u>42,064 J mol^{-1}</u> or <u>42.064 kJ mol^{-1}</u> (6 points)

Give equivalent points for similar working, provided it is clear and precise

7. (i) Calculate the entropy change associated with the reversible expansion of 5.00 mol of an ideal monatomic gas at a constant temperature of 298.0 K from a pressure of 10.0 atm to 1.00 atm. Show working. (6 points)
(ii) Calculate the entropy change associated with the reversible adiabatic expansion of 5.00 mol of an ideal monatomic gas from a pressure of 10.0 atm to 1.00 atm, so that the temperature drops to 118.6 K, followed by reversible heating of the gas at constant pressure back to 298.0 K. Show working. (6 points)
(iii) Comment briefly on the results of (i) and (ii). (3 points)
[R = 8.315 J K^{-1} mol^{-1}]

8. Tungsten (VI) oxide can be reduced to tungsten by heating with carbon in an electric furnace:

$$2WO_3(s) + 3C(s) \rightarrow 2W(s) + 3CO_2(g)$$
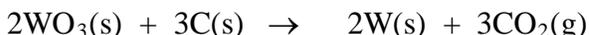
(i) If the standard Gibbs free energy of formation (ΔG^o_f) of $WO_3(s)$ and $CO_2(g)$ are –764.1 and –394.4 kJ mol^{-1}, respectively, calculate ΔG^o for the above reaction at STP (NTP) and comment briefly on its value. (6 points)

(ii) If the standard enthalpies of formation (ΔH^o_f) of $WO_3(s)$ and $CO_2(g)$ are –842.9 and –393.5 kJ mol^{-1} respectively and if the standard entropies (S^o) of $WO_3(s)$, $C(s)$, $W(s)$ and $CO_2(g)$ are 75.9, 5.7, 32.6 and 213.6 J mol^{-1} K^{-1}, respectively, determine the temperature at which the above reaction becomes feasible. Assume ΔH and ΔS do not vary much with temperature. (9 points)

(i) ΔG^o = (3 mol)(-394.4 kJ mol^{-1}) - (2 mol)(-764.1 kJ mol^{-1})

   = **345.0 kJ**   (3 points)

   The reaction is not feasible (spontaneous) at STP (NTP) (298 K) (3 points)

(ii) ΔH^o = (3 mol)(-393.5 kJ mol^{-1}) - (2 mol)(-842.9 kJ mol^{-1})

   = **505.3 kJ**   (3 points)

   ΔS^o = (2 mol)(32.6 J mol^{-1}K^{-1}) + (3 mol)(213.6 J mol^{-1}K^{-1})

   - (2 mol)(75.9 J mol^{-1}K^{-1}) - (3 mol)(5.7 J mol^{-1}K^{-1})

   = **537.1 J K^{-1}** (3 points)

   $\Delta G^o = \Delta H^o - T\Delta S^o$

   At the temperature at which the reaction becomes feasible (the "turn around" temperature), $\Delta G^o = 0$, hence $T\Delta S^o = \Delta H^o$

   Therefore $T = \dfrac{\Delta H^o}{\Delta S^o} = \dfrac{(505300 \text{ J})}{(537.1 \text{ J K}^{-1})}$

   All units need not be shown in working. Allow for variations

   = **940.8 K** (667.6 °C) (3 points)