Topics in the June 2006 Exam Paper for CHEM1101

Click on the links for resources on each topic.

2006-J-2:

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

2006-J-3:

- Nuclear and Radiation Chemistry

2006-J-4:

- Bonding - MO theory (larger molecules)

2006-J-5:

- Wave Theory of Electrons and Resulting Atomic Energy Levels
- Lewis Structures
- VSEPR

2006-J-6:

- Gas Laws
- Thermochemistry

2006-J-7:

- Thermochemistry
- First and Second Law of Thermodynamics

2006-J-8:

- Thermochemistry
- First and Second Law of Thermodynamics

2006-J-9:

- Chemical Equilibrium
- Equilibrium and Thermochemistry in Industrial Processes

2006-J-10:

- Material Properties (Polymers, Liquid Crystals, Metals, Ceramics)
- Types of Intermolecular Forces

2006-J-11:

- Electrochemistry

2006-J-12:

- Nitrogen Chemistry and Compounds

Marks 6

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

(a) Hund's rule

There is lower repulsion between electrons with parallel spins. When filling orbitals of equal energy, the lowest energy arrangement has the maximum number of unpaired electrons with parallel spins.

(b) electron affinity

The energy, E_a, required to detach an electron from the singly charged negative ion of an atom or molecule:

$$X^- \rightarrow X + e^-$$

(The sign convention for E_a is the opposite to most thermodynamic quantities: a positive electron affinity indicates that energy is *released* on going from atom to anion).

(c) nuclear fusion

The process by which multiple atomic particles join together to form a heavier nucleus, accompanied by the release of energy. For example:

$${}^{1}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He$$

(d) diamagnetic

Property of atoms or molecules with no unpaired electrons.

(e) p-type semiconductor

A semiconductor has electrical conductivity in between that of a metal and that of an insulator. A p-type semiconductor is obtained by adding a type of atoms to a semiconductor in order to increase the number of positive charge carrier. For example, doping a group 14 element such as Si with a group 13 element such as Ga leads empty orbitals slightly higher in energy than the conductance band. Electrons can be excited into these vacant orbitals leaving positive holes in the valance band to produce the primary conductance mechanism,

(f) π bond

A bond produced by the occupation of a π-bonding molecular orbital. This orbital is made by overlap of atomic orbitals, such as parallel p-orbitals, to produce a molecular orbital with a node along the internuclear axis. The electron density is in two lobes, above and below the internuclear axis.

Marks

- Balance the following nuclear reactions by identifying the missing nuclear particle or nuclide. **3**

$${}^{63}_{28}\text{Ni} \rightarrow {}^{63}_{29}\text{Cu} + \boxed{\mathbf{{}^{0}_{-1}\beta}}$$

$${}^{53}_{26}\text{Fe} + {}^{0}_{-1}\text{e} \rightarrow \boxed{\mathbf{{}^{53}_{25}Mn}}$$

$${}^{28}_{14}\text{Si} + {}^{2}_{1}\text{H} \rightarrow {}^{1}_{0}\text{n} + \boxed{\mathbf{{}^{29}_{15}P}}$$

- Calculate the energy (in J) and the wavelength (in nm) of the photon of radiation emitted when the electron in Be^{3+} drops from an n = 3 state to an n = 2 state. **3**

As Be^{3+} has one electron, the equation $E_n = \frac{-E_R Z^2}{n^2}$ where $E_R = 2.18\times10^{-18}$ J can be used. Beryllium has Z = 4. The energies of the n = 3 and n =2 levels are:

$$E_2 = \frac{-E_R(4)^2}{(2)^2} = -4E_R \quad \text{and} \quad E_3 = \frac{-E_R(4)^2}{(3)^2} = -\frac{16}{9}E_R = 1.78E_R$$

The separation is (4 - 1.78)E_R = 2.22E_R = 2.22 × (2.18 × 10^{-18}) = 4.84 × 10^{-18} J.

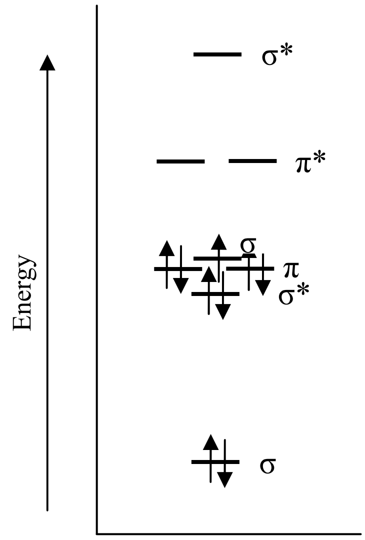
$$\text{As } E = \frac{hc}{\lambda},\ \lambda = \frac{hc}{E} = \frac{(6.626\times10^{-34})\times(2.998\times10^{8})}{(4.84\times10^{-18})} = 4.10\times10^{-8}\ \text{m} = 41.0\ \text{nm}$$

Energy: **4.84 × 10^{-18} J**	Wavelength: **4.10 ×10^{-8} m or 41.0 nm**

Marks 5

- The N_2^+ ion plays a role in the colourful display of the Northern Lights (the *Aurora Borealis*).

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the N_2^+ ion. Indicate on this diagram the ground state electronic configuration of N_2^+ using the arrow notation for electron spins.



Calculate the bond order of N_2^+.

Bond order = ½ (7 – 2) = 2.5

Indicate the lowest energy electron excitation in this ion by identifying the initial and final states of the electron undergoing the excitation.

The lowest energy excitation corresponds to the electron moving from π → σ

The line at 3914 Å (391.4 nm) in the emission spectrum of the *Aurora Borealis* is due to N_2^+ returning to its ground state. Calculate the energy gap (in eV) between the molecular orbitals involved in this transition.

As $E = \frac{hc}{\lambda}$**, the line corresponds to an energy of:**

$$E = \frac{(6.626\times10^{-34})\times(2.998\times10^{8})}{(391.4\times10^{-9})} = 5.075\times10^{-19}\ \text{J}$$

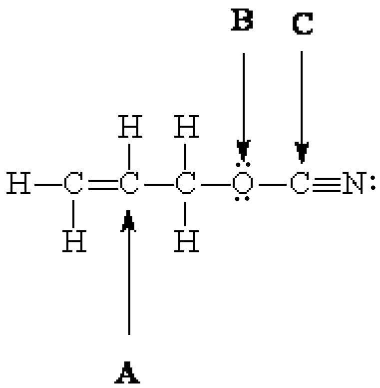
As 1 eV = 1.602×10^{-19} J, this corresponds to:

$$E = 5.075 \times 10^{-18} =, \frac{5.075\times10^{-19}}{1.602\times10^{-19}} = 3.172\ \text{eV}$$

Answer: **3.172 eV**

Marks

• With respect to the molecule sketched below, answer the following questions concerning the selected atoms indicated by arrows as **A**, **B** and **C**. **3**



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	**0**	**3**	**trigonal planar**
B	**2**	**2**	**bent**
C	**0**	**2**	**linear**

• Identify two factors that explain the origin of the discrete energy levels of electrons in atoms? **2**

- **The wave-like nature of electrons**
- **The restricted motion of the electrons caused by the electrostatic attraction of the nucleus**

Marks

- At room temperature and pressure (RTP), 1 mole of an ideal gas occupies 24.45 L. Calculate the molar volume of the same ideal gas in the stratosphere, where the pressure is 0.020 atm and the temperature is 200 K. **2**

Using the ideal gas equation, PV = nRT, the volume of 1 mole of gas at P = 0.020 atm and T = 200 K is:

$$V = \frac{nRT}{P} = \frac{1\times(0.08206)\times(200)}{(0.020)} = 820\,L = 8.2\times10^{2}\ L$$

Answer: **820 L= 8.2 × 10^2 L**

- Two blocks of metal, as shown in the table below, are placed in intimate contact in an insulated environment. **4**

Metal	Iron	Copper
Mass (g)	30.0	20.0
Initial T (°C)	0.0	100.0
c (J g^{-1} K^{-1})	0.450	0.387

In which direction will the heat flow? Write "from Fe to Cu" or "from Cu to Fe".

As the copper is at a higher initial temperature, heat will flow from Cu to Fe

What is the final temperature of the system?

Heat will flow until the temperatures are equal. The heat lost by the copper is equal to the heat gained by the iron. The heat is related to the temperature change by the equation, q = m × c × ΔT.

The heat lost by the copper in going from 100.0 °C to the final temperature T_f is:

$$q = m_{Cu} \times c_{Cu} \times \Delta T = 0.387 \times 20.0 \times (100.0 - T_f).$$

The heat gained by the iron in going from 0.0 °C to the final temperature T_f is:

$$q = m_{Fe} \times c_{Fe} \times \Delta T = 0.450 \times 30.0 \times (T_f - 0.0).$$

Setting the two heat changes to be equal gives:

$$0.387 \times 20.0 \times (100.0 - T_f) = 0.450 \times 30.0 \times (T_f - 0.0) \text{ or } 774 - 7.74T_f = 13.5\,T_f$$

Hence, T_f = 36.4 °C

Answer: **36.4 °C**

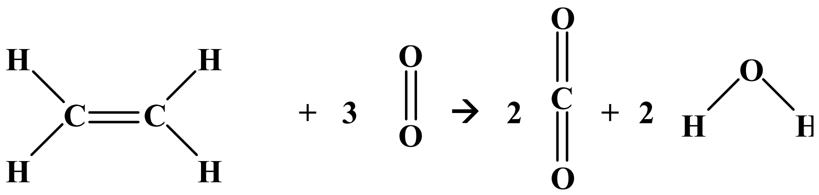
Marks
5

- Calculate the molar enthalpy of combustion of ethylene (C_2H_4) using bond dissociation energies.

Data:

Bond	Bond enthalpy (in kJ mol^{-1})	Bond	Bond enthalpy (in kJ mol^{-1})
C–H	413	C=C	614
O–H	467	C=O	799
		O=O	498

The combustion reaction is: $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$



$\Delta H = \{ [\Delta_{atom}H (C_2H_4)] + 3 \times [\Delta_{atom}H (O_2)] \} - \{2 \times [\Delta_{atom}H (CO_2)] + 2 \times \Delta_{atom}H (H_2O)] \}$

$= \{[614 (C=C) + 4 \times 413 (C\text{-}H)] + 3 \times [498 (O=O)] \} - \{2 \times [2 \times 799 (C=O)] + 2 \times [2 \times 467)] \} = (3760) – (5064) = -1304$ kJ mol^{-1}

Answer: **-1304 kJ mol^{-1}**

The heat of combustion of ethane (C_2H_6) is –1560 kJ mol^{-1}, while that of ethanol (C_2H_5OH) is –1367 kJ mol^{-1}. Comment on which of ethylene, ethane and ethanol is the most efficient fuel.

The molar masses of ethane, ethene and ethanol are:

molar mass of ethane is (2 × 12.01 (C)) + (6 × 1.008 (H)) = 30.068
molar mass of ethene is (2 × 12.01 (C)) + (4 × 1.008 (H)) = 28.052
molar mass of ethanol is (2 × 12.01 (C)) + (6 × 1.008 (H)) + (16.00 (O))= 45.068

The best comparison of the fuel efficiencies are the heats of combustion per gram:

$$\Delta_{comb}H \text{ (ethane)} = -1560 \text{ kJ mol}^{-1} = \frac{-1560}{30.068} = -51.9 \text{ kJ g}^{-1}$$

$$\Delta_{comb}H \text{ (ethene)} = -1304 \text{ kJ mol}^{-1} = \frac{-1304}{28.052} = -46.5 \text{ kJ g}^{-1}$$

$$\Delta_{comb}H \text{ (ethanol)} = -1367 \text{ kJ mol}^{-1} = \frac{-1367}{46.068} = -29.7 \text{ kJ g}^{-1}$$

On this basis, ethane is the most efficient and ethanol is the least efficient.

Marks 5

- Silicon tetrachloride ($SiCl_4$) is produced annually on a kilotonne scale for making transistor-grade silicon. It can be made directly from the elements (reaction 1), or, more cheaply, by heating sand and graphite with chlorine gas (reaction 2). If water is present, some $SiCl_4$ may be lost in an unwanted side-reaction (reaction 3).

  - $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(g)$
  - $SiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow SiCl_4(g) + 2CO(g)$
  - $SiCl_4(g) + 2H_2O(g) \rightarrow SiO_2(s) + 4HCl(g)$ $\Delta H° = –139.5$ kJ mol$^{–1}$

  Calculate the heats of reaction of reactions 1 and 2.

Compound	$\Delta H°_f$ / kJ mol$^{–1}$
$SiO_2(s)$	-910.9
$HCl(g)$	-92.3
$H_2O(g)$	-241.8
$CO(g)$	-110.5

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

$$\Delta_{rxn}H^o(1) = \Delta_f H^o(SiCl_4(g))$$

$$\Delta_{rxn}H^o(2) = [\Delta_f H^o(SiCl_4(g)) + 2\Delta_f H^o(CO(g))] - [\Delta_f H^o(SiO_2(s))]$$

$$\Delta_{rxn}H°(3) = [\Delta_f H°(SiO_2(s)) + 4\Delta_f H°(HCl(g))] - [\Delta_f H°(SiCl_4(g)) + 2\Delta_f H°(H_2O(g))]$$

As $\Delta_{rxn}H^o(3) = -139.5$ kJ mol^{-1}, using the tabulated values of $\Delta_f H^o$ for $SiO_2(s)$, $HCl(g)$ and $H_2O(g)$ gives:

$$-139.5 = [(-910.9) + (4 \times -92.3)] - [\Delta_f H°(SiCl_4(g)) + (2 \times -241.8)]$$

Hence, $\Delta_{rxn}H^o(1) = \Delta_f H^o(SiCl_4(g)) = -657$ kJ mol^{-1}.

$$\Delta_{rxn}H^o(2) = [(-657) + (2 \times -110.5)] - [(-910.9)] = +32.9 \text{ kJ mol}^{-1}$$

$\Delta H°_{(\text{reaction 1})}$ = **-657 kJ mol^{-1}**	$\Delta H°_{(\text{reaction 2})}$ = **+32.9 kJ mol^{-1}**

Write down the new reaction that is the sum of reactions 2 and 3. What is the heat of reaction for this new reaction?

$SiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow SiCl_4(g) + 2CO(g)$

$SiCl_4(g) + 2H_2O(g) \rightarrow SiO_2(s) + 4HCl(g)$

$2C(s) + 2Cl_2(g) + 2H_2O(g) \rightarrow 2CO(g) + 4HCl(g)$

$$\Delta_{rxn}H^o(2) = \Delta_{rxn}H^o(2) + \Delta_{rxn}H^o(3) = (+32.9) + (-139.5) = -106.6 \text{ kJ mol}^{-1}$$

Reaction: **$2C(s) + 2Cl_2(g) + 2H_2O(g) \rightarrow 2CO(g) + 4HCl(g)$**	$\Delta H°$ = **-106.6 kJ mol^{-1}**

Marks
2

- The thermal decomposition of lithium peroxide produces oxygen.

$$2Li_2O_2(s) \rightleftharpoons 2Li_2O(s) + O_2(g)$$

A 1.0 g sample of Li_2O_2 was placed in a closed container and heated to a temperature, where some, but not all, of the Li_2O_2 decomposes. The experiment is then repeated using a 2.0 g sample, heated to the same temperature in an identical container. How does the pressure of $O_2(g)$ produced vary between these two experiments? Explain.

The equilibrium constant for this reaction is given by:

$K_p = p_{O_2(g)}$ as all other reactants and products are solids.

As solid is left at the equilibrium point in both reactions, it does not enter the equilibrium expression and has no effect on the equilibrium constant.

The pressure of $O_2(g)$ will be a constant, equal to K_p.

Marks
4

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

$NaCl$, H_2, CH_4, H_2O, SiO_2

$H_2 < CH_4 < H_2O < NaCl < SiO_2$

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

The interactions between the molecules of H_2 and between the molecules of CH_4 are dispersion forces, involving induced dipole-induced dipole interactions. CH_4 is a larger molecule with more electrons so has a larger polarizability than H_2 and, as a result, has stronger dispersion forces and a higher melting point.

H_2O 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, H_2O has a higher melting point than CH_4.

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.

SiO_2(s) is a covalent network with very strong Si-O bonds that need to be broken to melt the solid. Hence, SiO_2 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.

Marks

- Balance the following redox equation in acidic medium. 4

$HBrO_3(aq) + Bi(s) \rightarrow HBrO_2(aq) + Bi_2O_3(s)$

$3HBrO_3(aq) + 2Bi(s) \rightarrow 3HBrO_2(aq) + Bi_2O_3(s)$

In an acidic medium, the $HBrO_3(aq)$ will be the pre-dominant species rather than the conjugate base $BrO_3^-(aq)$.

Which species is the oxidizing agent?	**$HBrO_3$**
Which element is reduced?	**Br**
What is the oxidation number of Br before the reaction?	**+V**
How many electrons does each Bi gain or lose?	**it loses 3 e^-**

- What is the role of the salt bridge in a voltaic cell and how is this accomplished? 4

The salt bridge completes the circuit by allowing electrical neutrality to be maintained via the movement of ions.

How is this role achieved in the lead acid battery?

The sulfuric acid solution provides H^+ and HSO_4^- ions to conduct the current. The reactants (Pb and PbO_2) and products ($PbSO_4$) are all solids so no physical separation other than initial placement is required.

Marks 4

- Identify four features of a compound that would make it a good explosive.

- **It should undergo a highly exothermic oxidation reaction**
- **The oxidant should be contained in the explosive**
- **A large number of moles of gas should be produced**
- **The explosion reaction should have a low activation energy but should be stable enough to be safely transportable.**

Generally, explosives are solids to maximize the volume increase on explosion and often contain nitrogen as this gives stable N_2(g) as a product, which tends to lead to highly exothermic oxidation.