## Topics in the June 2009 Exam Paper for CHEM1101

Click on the links for resources on each topic.

2009-J-2:

• Nuclear and Radiation Chemistry

2009-J-3:

- Wave Theory of Electrons and Resulting Atomic Energy Levels
- Liquid Crystals

2009-J-4:

• Shape of Atomic Orbitals and Quantum Numbers

2009-J-5:

- Periodic Table and the Periodic Trends
- Filling Energy Levels in Atoms Larger than Hydrogen
- Bonding MO theory (polar bonds)

2009-J-6:

• Bonding - MO theory (larger molecules)

2009-J-7:

• Band Theory - MO in Solids

2009-J-8:

- Lewis Structures
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2009-J-9:

- Chemical Equilibrium
- Equilibrium and Thermochemistry in Industrial Processes

2009-J-10:

• Chemical Equilibrium

2009-J-11:

- Gas Laws
- Thermochemistry
- First and Second Law of Thermodynamics

2009-J-12:

- Gas Laws
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2009-J-13:

• Chemical Equilibrium

2009-J-14:

• Types of Intermolecular Forces

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2009-J-15:

• Electrochemistry

• Scholars think that a parchment scroll recently found in the Middle East could have originated from the same group responsible for the Dead Sea Scrolls. If a modern piece of parchment has an activity of  $4.0 \times 10^{-4}$  Ci g<sup>-1</sup>, calculate the expected activity of the recently discovered scroll if it originated 2100 years ago.

The <sup>14</sup>C age of a sample is given by:

<sup>14</sup>C age = 8033 
$$\ln\left(\frac{A_0}{A_t}\right)$$
 years

If the <sup>14</sup>C age is 2100 years and its initial activity,  $A_0 = 4.0 \times 10^{-4}$  Ci g<sup>-1</sup>,

2100 years = 8033 
$$\ln\left(\frac{4.0 \times 10^{-4} \text{ Ci g}^{-1}}{A_0}\right)$$

$$A_{\rm t} = 3.1 \times 10^{-4} \, {\rm Ci} \, {\rm g}^{-1}$$

Answer:  $A_t = 3.1 \times 10^{-4} \text{ Ci g}^{-1}$ 

•  ${}^{11}$ C is an unstable isotope of carbon. Which force within the  ${}^{11}$ C nucleus is responsible for its instability? Explain.

<sup>11</sup>C has 6 protons but only 5 neutrons. Stable nuclei for the lighter elements have approximately equal numbers of neutrons and protons. <sup>11</sup>C has too many protons relative to neutrons within the nucleus.

Electrostatic repulsion between protons destabilises the nucleus.

Which force is responsible for the greater stability of the <sup>12</sup>C isotope compared to the <sup>11</sup>C isotope? Explain.

<sup>12</sup>C has 6 protons and 6 neutrons. The one extra neutron compared to <sup>11</sup>C increases the strength of the strong nuclear force between all nucleons (protons and neutrons). This overcomes the electrostatic repulsion of the protons and results in a stable nucleus.

Marks

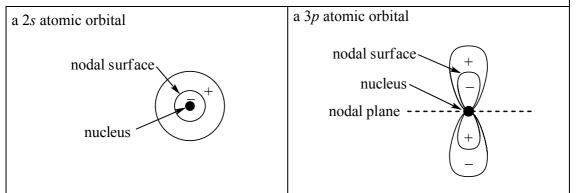
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Marks • In an electron microscope, to what minimum velocity must the electrons in the beam 2 be accelerated in order to achieve a better spatial resolution (*i.e.*, have a shorter wavelength) than a visible light microscope? Assume an average wavelength of visible light of 500 nm. The wavelength of the electrons must be shorter than 500 nm. The de Broglie wavelength  $\lambda$  associated with a particle of mass *m* travelling with a velocity *v* is given by:  $\lambda = \frac{h}{mv}$  or  $v = \frac{h}{m\lambda}$ Hence, the velocity required for a wavelength of 500 nm =  $500 \times 10^{-9}$  m is:  $v = \frac{6.626 \times 10^{-34} \text{ J s}}{(9.1094 \times 10^{-31} \text{ kg})(500 \times 10^{-9} \text{ m})} = 1 \times 10^3 \text{ m s}^{-1}$ Better resolution requires a shorter wavelength and so the velocity must be higher than this value. Answer:  $1 \times 10^3$  m s<sup>-1</sup> • Sketch the arrangement of molecules in a nematic phase and a smectic phase of a 2 liquid crystal. nematic phase smectic phase С A N// ////// N// //////

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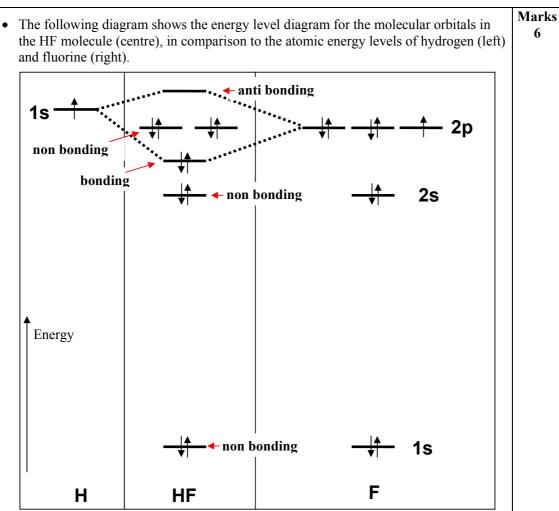
Marks • Sketch the following wavefunctions using lobe representations. Clearly mark all nodal surfaces, nuclear positions and the relative sign (+ or -) of the wavefunction within the lobes.



Explain the significance of (a) the lobes, (b) the nodes and (c) the sign of the wavefunction, in terms of the probability of finding an electron at a given point in space relative to the nucleus.

- (a) The lobes define the volume within which there is a certain probability (e.g. 95 %) of finding the electron.
- (b) The nodes represent surfaces where there is zero probability of finding the electron. Alternatively (and equivalently), they are the surfaces where the sign of the wavefunction changes.
- (c) The sign of the wavefunction is not relevant to the probability of finding the electron. The probability distribution depends on the square of the wavefunction, which is always positive.

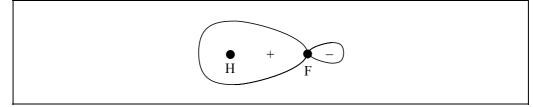
• Explain the trends in the periodic table, in the i.e. Discuss the trend	terms of the	eir electron	ic configur	ations.	the second $+ e^- \rightarrow A$		Marks 3
Element	Li	Be	В	С	Ν		
$\Delta H$ (in kJ mol <sup>-1</sup> )	-60	+241	-27	-122	+8		
The electron configu its outer shell. There energy orbital does extra electron suffici repulsion that occur negative.	e is space in not to be o iently to co	n the 2 <i>s</i> or ccupied. T ompensate	bital for a he nuclear for the ext	nother electro charge of tra electro	ctron so a l Li holds o n – electro	higher onto the n	
The electron configu extra electron would occupation of it is en of Be compared to L	l have to g ergetically	o into the 2	2 <i>p</i> orbital.	This has a	higher en	ergy and	
The electron configure in its 2p orbital. The proton in the B nucles situation in Be. As the electron, the addition The electron configure 2p orbitals. The extra proton in the C nucles compared to the situate the other 2p electron	extra elec eus means ne extra ele nal electro tration of ( ra electron eus means lation in B	tron is bei that an ele ectron can on – electro C is [He] 2 is being a that an ele . As the ex	ng added t ectron is fa have a spi on repulsio $s^2 2p^2$ . It h dded to th ectron is e tra electro	to the same avourable in parallel n is minim as 2 unpai e same sul ven more f on can have	e subshell. compared with the o nal. red electro bshell. The favourable e a spin pa	The extra to the ther 2 <i>p</i> ons in its extra rallel with	
The electron configues $2p$ orbitals. An addite and this leads to a late $\Delta H$ is positive.	tional elect	tron has to	pair its sp	oin with on	e of these	electrons	
• Briefly explain the fo	llowing co	ncepts and	their electr	onic origin	s.		2
(a) paramagnetism							
Paramagnetism is th field. It is occurs to magnetism when the	the presen	ce of unpa	ired electi				
(b) polar bond							
If the electron densit atoms, a polar bond electronegativities.	•			-	•		



Add the ground state electron configuration to the diagrams for all three species using the arrow notation for electron spin.

Label the orbitals of HF according to whether they are bonding, non-bonding, or antibonding.

Sketch the  $\sigma$ -bonding orbital showing the position of the atomic nuclei.



• Explain what is meant by the term "band gap". In a solid, there are very many energy levels for the electrons. Each "band" is made up of a large set of energy levels. If these sets are separated in energy, then there is a "band gap". Commonly, "band gap" refers to the energy difference between the top energy level in the conductance band and the bottom energy level valence band. It is small in conductors (e.g. metals) and large in insulators (e.g. diamond). The band gap of the semiconductor gallium(II) sulfide is 2.53 eV. What range of wavelengths (in nm) would you expect this material to absorb? As 1 eV =  $1.602 \times 10^{-19}$  J, 2.53 eV is equivalent to:  $(2.53 \times 1.602 \times 10^{-19})$  J =  $4.053 \times 10^{-19}$  J This is the smallest energy it will absorb. Using  $E = \frac{hc}{\lambda}$ , this corresponds to a wavelength of:  $\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{4.053 \times 10^{-19} \text{ J}} = 4.90 \times 10^{-7} \text{ m} = 490. \text{ nm}$ As 2.53 eV is the smallest energy it will absorb, this corresponds to the longest wavelength it will absorb. It will absorb wavelengths shorter than 490. nm.

For reference, the relationship between colours and wavelengths is as follows:

	violet	blue	green	yellow	orange	red	
400	) 45	50 49	0 50	50 5 <u>9</u>	63	0 70	0 nm

Predict the colour of a single crystal of GaS according to a human observer when it is illuminated with white light. Explain your answer.

From above, it will absorb wavelengths shorter than 490. nm, corresponding to the absorption of violet-blue light. The human observer will see white light with these colours removed: the complementary colour will be yellowy orange.

Marks 4 What is the bond order of the N–O bonds?

The bond order is an average over

the resonance structures: 1.5

:C]

			ne number of valence el n of the following specie	
Molecule name	Chemical formula	Number of valence electrons	Lewis structure	Geometry of species
e.g. water	H <sub>2</sub> O	8	н <sup>сос</sup> н	bent
carbonate ion	CO3 <sup>2-</sup>	24	$\begin{bmatrix} \vdots \vdots$	trigonal planar
chlorine trifluoride	CIF3	28	:F: :F-CI: :F:	T-shaped

• Consider the following reaction at equilibrium.

CH<sub>3</sub>OH(g)  $\iff$  CO(g) + 2H<sub>2</sub>(g)  $K_c = 1.30 \times 10^{-2}$ 

What is the concentration of CO(g) when  $[CH_3OH(g)] = 3.49 \times 10^{-1}$  M and  $[H_2(g)] = 1.76 \times 10^{-1}$  M?

The equilibrium constant for the reaction is given by:  $K_{eq} = \frac{[CO(g)][H_2(g)]^2}{[CH_3OH(g)]} = 1.30 \times 10^{-2}$ When  $[CH_3OH(g)] = 3.49 \times 10^{-1}$  M and  $[H_2(g)] = 1.76 \times 10^{-1}$  M,  $[CO(g)] = \frac{K_{eq}[CH_3OH(g)]}{[H_2(g)]^2} = \frac{(1.30 \times 10^{-2})(3.49 \times 10^{-1})}{(1.76 \times 10^{-1})^2}$  M = 0.146 M Answer: 0.146 M

• Explain briefly the chemical principles behind a) froth flotation, or b) electrorefining.

Froth flotation is a technique to separate a mineral from unwanted dirt and rocks. The crude ore is crushed to a fine powder and then treated with water to produce a slurry. A surfactant that selectively coats the mineral, thus making it more hydrophobic, is added and the mixture agitated and aerated. The mineral attaches to the air bubbles and floats to the surface (as a froth) where it is collected before undergoing further refining.

Electrorefining is a technique for purifying a metal, *e.g.* copper. An electrolytic cell consisting of a pure copper cathode and an impure copper anode is constructed. A voltage is selectively applied so that noble metals (less electropositive than Cu) do not dissolve. When operating, the current causes the impure copper anode to dissolve, including metal impurities more electropositive than copper. The noble metals do not dissolve and form a sludge. Only pure copper is deposited at the cathode - the more electropositive metals stay in solution as cations.

2

Marks

Marks • Solid NH<sub>4</sub>HS in placed in an evacuated container at 25 °C and the following 3 equilibrium is established. NH<sub>4</sub>HS(s)  $\checkmark$  NH<sub>3</sub>(g) + H<sub>2</sub>S(g)  $\Delta H^{\circ} = +93 \text{ kJ mol}^{-1}$ At equilibrium, some solid NH4HS remains in the container. Predict and explain each of the following. (a) The effect on the equilibrium partial pressure of  $NH_3$  gas when additional solid NH<sub>4</sub>HS is introduced into the container. The equilibrium constant is given by  $K_p = [NH_3(g)][H_2S(g)]$ . It does not include the concentration of the solid as this is a constant during the reaction. If extra solid is introduced, it does not change the concentration of the solid and there is no effect on the equilibrium. The solid is not included in the equilibrium constant so changing the amount present has no effect on the equilibrium. (b) The effect on the amount of solid NH<sub>4</sub>HS present when the volume of the container is decreased. Decreasing the volume of the container will increase the partial pressure of both gases. The reaction will move to the left to reduce the overall pressure. The amount on solid will therefore increase. (c) The effect on the amount of solid NH<sub>4</sub>HS present when the temperature is increased. The reaction is endothermic, as  $\Delta H^{\circ}$  is positive. If the temperature is increased, the reaction will move to the right to absorb the extra heat. The amount of solid will therefore decrease.

A gaseous hydrocarbon is found to contain 85.6 % carbon and 17.4 % hydrogen by mass. A 10.0 L sample of this gas has a mass of 23.78 g at 1.00 atm and 298 K. Show that the hydrocarbon is butane, C<sub>4</sub>H<sub>10</sub>.

From the percentages:		
	С	Н
percentage	85.6	17.4
divide by atomic mass	$\frac{85.6}{12.01} = 7.13$	$\frac{17.4}{1.008} = 17.3$
divide by smallest value	1	2.44

The ratio 1 : 2.44 is consistent with the empirical formula C<sub>2</sub>H<sub>5</sub>.

Alternatively, using the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(10.0 \text{ L})}{(0.08206 \text{ L} \text{ atm} \text{ K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 0.409 \text{ mol}$$

As this has a mass of 23.78 g, the molar mass, corresponding to 1 mol, is:

molar mass =  $\frac{\text{mass}}{\text{number of moles}} = \frac{23.78 \text{ g}}{0.409 \text{ mol}} = 58.1 \text{ g}$ 

The molar mass of  $C_4H_{10}$  is  $(4 \times 12.01 + 10 \times 1.008)$  g mol<sup>-1</sup> = 58.12 g mol<sup>-1</sup>, which is again consistent with the experimental data.

Using the data below, calculate the heat generated when this quantity of butane is burnt in air.

 $\Delta_{\rm f}H^{\circ}$ : C<sub>4</sub>H<sub>10</sub>(g) –126 kJ mol<sup>-1</sup>, CO<sub>2</sub>(g) –394 kJ mol<sup>-1</sup>, H<sub>2</sub>O(l) = –286 kJ mol<sup>-1</sup>

The combustion reaction is:

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

Using  $\Delta_{rxn}H^\circ = \Sigma m \Delta_f H^\circ$  (products) -  $\Sigma n \Delta_f H^\circ$  (reactants), the enthalpy of this reaction is:

$$\Delta_{\text{comb}}H^{\circ} = (4\Delta_{\text{f}}H^{\circ}(\text{CO}_{2}(\text{g}) + 5\Delta_{\text{f}}H^{\circ}(\text{H}_{2}\text{O}(\text{l})) - (\Delta_{\text{f}}H^{\circ}(\text{C}_{4}\text{H}_{10}(\text{g}))$$
  
= [(4 × -394 + 5 × -286) - (-126)] kJ mol<sup>-1</sup> = -2880 kJ mol<sup>-1</sup>

Hence, for 0.409 mol, the enthalpy change is:

 $\Delta_{\text{comb}}H^{\circ} = (-2880 \text{ kJ mol}^{-1}) \times (0.498 \text{ mol}) = -1180 \text{ kJ}$ 

Answer: 1180 kJ

Marks

5

• A radiator generates 150 J to heat up air inside a sealed container with volume of 2.00 L and initially at 25 °C and atmospheric pressure. What will be the pressure inside the container after heating?

Assume that air is composed of 80 % nitrogen and 20 % oxygen by volume.

Molar heat capacities:  $N_2$  29.14 J K<sup>-1</sup> mol<sup>-1</sup> and  $O_2$  29.38 J K<sup>-1</sup> mol<sup>-1</sup>

Using the ideal gas law, the number of moles in 2.00 L of air at 25 °C ( = 298.0 K) at atmospheric pressure is:

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(2.00 \text{ L})}{(0.08206 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1})(298.0 \text{ K})} = 0.0818 \text{ mol}$$

The temperature change,  $\Delta T$ , is related to the heat change, q, through,

$$q = n C_p \Delta T$$
 or  $\Delta T = \frac{q}{nC_p}$ 

The ideal gas law shows that the number of moles is directly proportional to the volume. The molar heat capacity of air is therefore the average of individual molar heat capacities:

$$C_{\rm p}({\rm air}) = 0.80C_{\rm p}({\rm N}_2) + 0.20C_{\rm p}({\rm O}_2) = [(0.80 \times 29.14) + (0.20 \times 29.38)] \,{\rm J}\,{\rm K}^{-1}\,{\rm mol}^{-1}$$
  
= 29.19  ${\rm J}\,{\rm K}^{-1}\,{\rm mol}^{-1}$ 

Hence,

$$\Delta T = \frac{q}{nC_p} = \frac{150 \text{ J}}{(0.0818 \text{ mol})(29.19 \text{ J} \text{ K}^{-1} \text{ mol}^{-1})} = 62.8 \text{ K}$$

As the initial temperature is 298 K and the air is being heated, the final temperature is (298.0 + 62.8) K = 360.8 K.

Finally, at this temperature, the ideal gas gives the pressure as:

$$P = \frac{nRT}{V} = \frac{(0.0818 \text{ mol})(0.08206 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1})(360.8 \text{ K})}{(2.00 \text{ L})} = 1.21 \text{ atm}$$

If this heated air is injected into a balloon, it will rise. Use the ideal gas equation to explain why this happens.

From the ideal gas law,  $\frac{n}{V} = \frac{P}{RT}$ . As the density is proportional to  $\frac{n}{V}$ , this shows that the density is inversely proportional to the temperature. The heated air has a lower density than the air in the atmosphere.

• Fe<sub>2</sub>O<sub>3</sub> can be reduced by carbon monoxide according to the following equation.

 $Fe_2O_3(s) + 3CO(g) \implies 2Fe(s) + 3CO_2(g)$   $K_p = 19.9 \text{ at } 1000 \text{ K}$ 

At 1000 K, what are the equilibrium partial pressures of CO and  $CO_2$  if the only gas initially present is CO at a partial pressure of 0.978 atm?

The reaction table is:

	Fe <sub>2</sub> O <sub>3</sub> (s)	3CO(g)	+	2Fe(s)	3CO <sub>2</sub> (g)
initial / atm	-	0.978		-	0
change / atm		-3 <i>x</i>			+3x
equilibrium / atm		0.978 - 3x			3 <i>x</i>

The solids do not appear in the equilibrium constant expression and do not need to be considered. The equilibrium constant in terms of partial pressures,  $K_p$ , is given by:

$$K_{\rm p} = \frac{p(\rm CO_2)^3}{p(\rm CO)^3} = \frac{(3x)^3}{(0.978 - 3x)^3} = 19.9$$

Hence,

$$\frac{(3x)}{(0.978-3x)} = (19.9)^{1/3} = 2.71$$
  

$$3x = (2.71)(0.978 - 3x) = 2.65 - 8.13x \text{ or } 11.1x = 2.65 \text{ or } x = 0.238$$
  
From the reaction table,  

$$p(\text{CO}) = (0.978 - 3x) \text{ atm} = 0.264 \text{ atm}$$

 $p(CO_2) = 3x$  atm = 0.714 atm

p(CO) = 0.264 atm

 $p(CO_2) = 0.714$  atm

• Explain the trend in the following table in terms of the type and size of intermolecular forces.

Substance	Boiling point (°C)
CH <sub>3</sub> CH <sub>3</sub>	-89
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-1
CH <sub>3</sub> CH <sub>2</sub> –O–CH <sub>2</sub> CH <sub>3</sub>	35
CH <sub>3</sub> CH <sub>2</sub> OH	78
H <sub>2</sub> O	100

CH<sub>3</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> have weak dispersion forces only, so have the lowest boiling points. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> has more atoms, so more dispersion forces and hence the higher boiling point of the two.

CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> is similar in size to CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, but has dipole-dipole forces as well due to the presence of polar C-O bonds. Thus, the boiling point of CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> is higher than that of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>.

CH<sub>3</sub>CH<sub>2</sub>OH and H<sub>2</sub>O have strong intermolecular H-bonds due to the presence of H atoms bonded to electronegative O atoms. Their boiling points are thus higher.

Water has 2 H atoms and 2 lone pairs on O capable of H-bonding so can form on average 4 H-bonds per molecule. Ethanol just one H so can only form 1 Hbond per molecule. Water this has the higher boiling point.

There are two isomers with the molecular formula C<sub>4</sub>H<sub>10</sub>.

butane

2-methylpropane

ĭ<sup>™</sup>, C<H<sub>2</sub> CH<sub>3</sub>

Discuss which isomer will have the greater intermolecular forces.

Both molecules have weak dispersion forces only. Butane has the greater dispersion forces as it has a greater surface area that can interact with other molecules. 2-Methylpropane is ball-like in structure with a smaller surface area will prevents close approach of the bonds.