#### Topics in the November 2007 Exam Paper for CHEM1101

Click on the links for resources on each topic.

2007-N-2:

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

2007-N-3:

Nuclear and Radiation Chemistry

2007-N-4:

- Wave Theory of Electrons and Resulting Atomic Energy Levels
- Shape of Atomic Orbitals and Quantum Numbers

2007-N-5:

• Bonding - MO theory (larger molecules)

2007-N-6:

- Lewis Structures
- VSEPR

2007-N-7:

• Wave Theory of Electrons and Resulting Atomic Energy Levels

2007-N-8:

- Thermochemistry
- First and Second Law of Thermodynamics

2007-N-9:

- First and Second Law of Thermodynamics
- Electrolytic Cells

2007-N-10:

• Chemical Equilibrium

2007-N-11:

• Equilibrium and Thermochemistry in Industrial Processes

2007-N-12:

Marks • In the spaces provided, explain the meanings of the following terms. You may use an 4 equation or diagram where appropriate. (a) Hund's rule When occupying orbitals with equal energy, the lowest energy configuration is the one with the maximum number of unpaired electrons with parallel spins. (b) node A point plane or surface where a wavefunction, such as an atomic or molecular orbital, changes sign. In the node, the wavefunction is zero. (c) lyotropic liquid crystal A concentration-dependent anisotropic liquid phase formed within a solvent as a result of the shape of the solute molecules plus intermolecular forces. (d) electron affinity The energy evolved by the process  $A(g) + e^{-} \rightarrow A^{-}(g)$ . A negative energy change means means that energy is evolved by this process and the anion is more stable than the neutral atom. A *positive* energy change means that the reverse process evolves energy and the atom is more stable than the anion. 2 Sketch the following wave functions as lobe representations. Clearly mark all nodal ٠ surfaces and nuclear positions. a  $\pi$  molecular orbital a 2s atomic orbital spherical orbital nodal plane passes through both nuclei between the lobes spherical node nuclei nucleus

CHEM1101 2007-N-3 November 2007 Marks • Balance the following nuclear reactions by identifying the missing nuclear particle or 3 nuclide.  $^{60}_{29}\mathrm{Cu} \rightarrow \left[ \begin{array}{c} ^{60}_{28}\mathrm{Ni} \\ ^{60}_{28}\mathrm{Ni} \end{array} \right] + {}^{0}_{+1}\mathrm{e}$  $_{26}^{55}$ Fe +  $_{-1}^{0}$ e  $\rightarrow _{25}^{55}$ Mn  $^{28}_{14}\text{Si} + ^{2}_{1}\text{H} \rightarrow ^{29}_{15}\text{P} +$  ${}^{1}_{0}n$ Calculate the following properties of the <sup>13</sup>N nuclide, given that its half-life 3 ٠ is 9.96 minutes. (a) the decay constant in  $s^{-1}$ 9.96 minutes corresponds to  $(9.96 \times 60.0) = 598$  s. The half life is related to the decay constant,  $\lambda$ , by  $\lambda = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{598} = 1.16 \times 10^{-3} \text{ s}^{-1}$ Answer:  $\lambda = 1.16 \times 10^{-3} \text{ s}^{-1}$ (b) the molar activity in Ci  $mol^{-1}$ The activity, A, is related to  $\lambda$  by  $A = \lambda N$  where N is the number of nuclei. The activity of a mole is thus:  $A = \lambda N = (1.16 \times 10^{-3}) \times (6.022 \times 10^{23}) = 6.98 \times 10^{20} \text{ Bg mol}^{-1}$ As 1 Bq =  $3.70 \times 10^{10}$  Bq, this corresponds to:  $A = 6.98 \times 10^{20} \text{ Bq mol}^{-1} = \frac{6.98 \times 10^{20}}{3.70 \times 10^{10}} \text{ Ci mol}^{-1} = 1.89 \times 10^{10} \text{ Ci mol}^{-1}$ Answer:  $1.89 \times 10^{10}$  Ci mol<sup>-1</sup>

• Calculate the energy (in J) and the wavelength (in nm) expected for an emission associated with an electronic transition from n = 4 to n = 2 in the Be<sup>3+</sup> ion.

Be<sup>3+</sup> has one electron and so the equation below can be used with Z = 4 to calculate the orbital energies,  $E_n = -Z^2 E_R \left(\frac{1}{n^2}\right)$ 

The energies of the n = 4 and n = 2 levels are therefore,

$$E_{n=4} = -(4)^2 E_R \left(\frac{1}{4^2}\right) = E_R$$
 and  $E_{n=2} = -(4)^2 E_R \left(\frac{1}{2^2}\right) = 4E_R$ 

The energy associated with emission from n = 4 to n = 2 is the difference between the energy of these two levels:

$$\Delta E = E_{n=2} - E_{n=4} = 4E_R - E_R = 3E_R = 3 \times (2.18 \times 10^{-18}) = 6.54 \times 10^{-18} \text{ J}$$

The energy is related to the wavelength,  $\lambda$ , by E =  $\frac{hc}{\lambda}$ :

$$\lambda = \frac{hc}{E} = \frac{(6.634 \times 10^{-34}) \times (2.998 \times 10^8)}{6.54 \times 10^{-18}} = 3.04 \times 10^{-8} \text{ m} = 30.4 \text{ nm}$$

Energy:  $6.54 \times 10^{-18}$  J Wavelength:  $3.04 \times 10^{-8}$  m or 30.4 nm

• What two properties do electrons in atoms have which lead to discrete energy levels? Explain your answer.

All particles have wave-like properties with momentum given by  $mv = \frac{h}{2}$ .

The wavelengths that are possible for an electron are limited because the electron has restricted motion due to its attraction to the positive nucleus.

• What is the % transmission of a sample measured in an atomic absorption spectrometer to have an absorbance of 0.5?

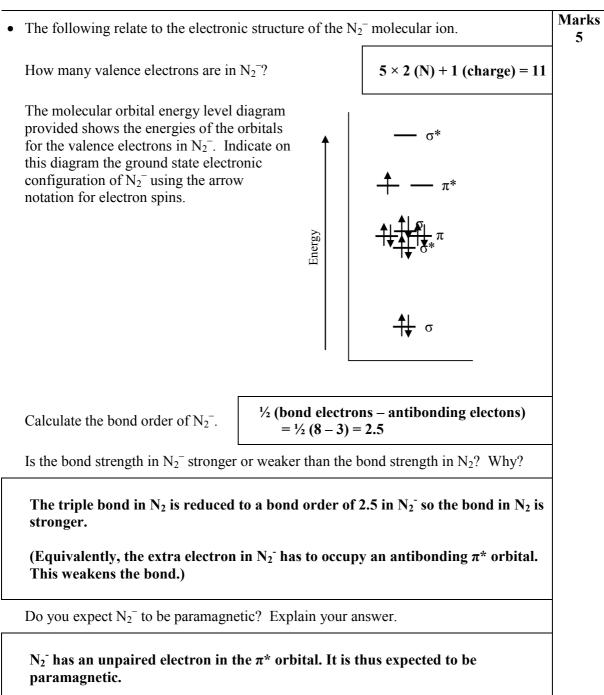
2

The absorbance, A, is related to the intensity of the incident light,  $I_0$ , and the transmitted light, I, by  $A = -\log_{10}\left(\frac{I}{I_0}\right)$ If A = 0.5, then the fraction transmitted is  $\frac{I}{I_0} = 10^{-0.5} = 0.3$  or 30%

If 
$$A = 0.5$$
, then the fraction transmitted is  $\frac{I}{I_0} = 10^{-0.5} = 0.3$  or 30%

Answer: 30%

2



		nowing the number of valence ele hape of each of the following sp		Marks 7
Formula	Total number of valence electrons	Lewis structure	Geometry of species	
H <sub>2</sub> O	8	н	V-shaped or bent	
PCl <sub>3</sub>	26	$\begin{array}{c} \vdots & \vdots & \vdots \\ \vdots & \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\$	trigonal pyramdial	
COS	16	∴o==c=s:́	linear	
ICl <sub>3</sub>	28	$: \underbrace{Cl}_{i} : $	T-shaped	

CHEM1101 2007-N-7 November 2007 Marks Ozone in the upper atmosphere absorbs light with wavelengths of 220 to 290 nm. 6 What are the frequency (in Hz) and energy (in J) of the most energetic of these photons? The energy, E, and frequency, v, are related to the wavelength,  $\lambda$ , of light by  $E = \frac{hc}{2}$  and  $v = \frac{c}{2}$  respectively. As energy is inversely proportional to wavelength, the most energetic of these photons has the shortest wavelength,  $\lambda = 220$  nm =  $220 \times 10^{-9}$  m. Hence,  $\mathbf{E} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{(220 \times 10^{-9} \text{ m})} = 9.0 \times 10^{-19} \text{ J}$  $v = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{220 \times 10^{-9} \text{ m}} = 1.4 \times 10^{15} \text{ Hz}$ Energy: **9.0** × **10**<sup>-19</sup> J Frequency:  $1.4 \times 10^{15}$  Hz Carbon-carbon bonds form the backbone of nearly every organic and biological molecule. The average bond energy of the C–C bond is 347 kJ mol<sup>-1</sup>. Calculate the wavelength (in nm) of the least energetic photon that can break this bond. A bond energy of 347 kJ mol<sup>-1</sup> corresponds to a bond energy per molecule of

 $E = \frac{347 \times 10^{3}}{6.022 \times 10^{23}} \frac{J \text{ mol}^{-1}}{\text{molecules mol}^{-1}} = 5.76 \times 10^{-19} \text{ J molecule}^{-1}$ As  $E = \frac{hc}{\lambda}$ , the corresponding wavelength is:  $\lambda = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})(2.998 \times 10^{8})}{(5.76 \times 10^{-19})} = 3.45 \times 10^{-7} \text{ m} = 345 \text{ nm}$ Wavelength:  $3.45 \times 10^{-7} \text{ m}$  or 345 nm

Compare this value to that absorbed by ozone and comment on the ability of the ozone layer to prevent C–C bond disruption.

345 nm is not blocked by ozone, so C–C bond disruption is still possible even with the presence of the ozone layer. Hence one still needs to wear sunblock creams.

Normal table sugar is pure sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>(s). Give the equation for the complete combustion of sucrose.

Marks 9

# $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$

A standard can (375 mL) of soft drink contains 795 kJ of energy. Assume the only ingredients are water and sucrose and that the energy obtained from sucrose by the body is the same as that obtained by combustion. Tagatose,  $C_6H_{12}O_6$ , is a low-calorie sweetener with a calorific value to humans of only 6.2 kJ g<sup>-1</sup>. On a weight for weight basis, it is 92% as sweet as sucrose. What mass of tagatose would be needed to produce a 375 mL can of drink with the same sweetness as a standard soft drink?

Data:

 $\Delta_{f} H^{\circ} (C_{12}H_{22}O_{11}(s)) = -2221.7 \text{ kJ mol}^{-1}$  $\Delta_{f} H^{\circ} (CO_{2}(g)) = -393.5 \text{ kJ mol}^{-1}$  $\Delta_{f} H^{\circ} (H_{2}O(1)) = -285.8 \text{ kJ mol}^{-1}$ 

The molar mass of sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> is:  $M_{sucrose} = 12 \times 12.01 (C) + 22 \times 1.008 (H) + 11 \times 16.00 (O) = 342.296 \text{ g mol}^{-1}$ As  $\Delta_{rxn} H^0 = \sum m \Delta_f H^0$  (products)  $-\sum n \Delta_f H^0$  (reactants), the  $\Delta_{comb} H^0$  (sucrose) is given by:  $\Delta_{comb} H^0 = \sum m \Delta_f H^0 (products) - \sum n \Delta_f H^0 (reactants)$  $= (12\Delta_{f}H^{0}(CO_{2}(g)) + 11\Delta_{f}H^{0}(H_{2}O(l)))$  $-(\Delta_{f} H^{0}(C_{12}H_{22}O_{11}(g)) + 12\Delta_{f} H^{0}(O_{2}(g)))$  $=(12 \times -393.5 + 11 \times -285.8) - (-2221.7 + 12 \times 0) = -5644.1 \text{ kJ mol}^{-1}$ 795 kJ As a standard can generates 795 kJ of energy, it must contain 5644.1 kJ mol<sup>-1</sup> 0.141 mol of sucrose. Using the molar mass from above, this corresponds to a mass of: mass = number of moles  $\times$  molar mass = 0.141  $\times$  342.296 = 48.2 g As tagatose only has 92% of the sweetness of sucrose, more is required to match the sweetness provided by sucrose: mass of tagatose required =  $\frac{48.2}{0.92}$  = 52.4 g

Answer: **52.4** g

## ANSWER CONTINUES ON THE NEXT PAGE

How much energy will a person obtain from this reduced-calorie can of soft drink?

As tagatose has a calorific value of 6.2 kJ g<sup>-1</sup>, 52.4 g will provide:

energy obtained = 52.4 g × 6.2 kJ g<sup>-1</sup> = 330 kJ

Answer: 330 kJ

Marks • Indicate the relative entropy of each system in the following pairs of systems. 2 Use: ">", "<", or "=".  $CO_2(g)$ >  $CO_2(s)$  $O_2(g) + H_2O(l)$ >  $O_2(aq)$ hexane,  $C_6H_{14}(g)$ > pentane,  $C_5H_{12}(g)$ >  $3O_2(g)$  $2O_3(aq)$ • An electrolytic cell contains a solution of MCl<sub>3</sub>. A total charge of 3600 C is passed 3 through the cell, depositing 0.65 g of the metal, M, at the cathode. What is the identity of the metal, M? A charge of 3600 C corresponds to: number of moles of electrons =  $\frac{\text{charge}(C)}{\text{Faraday's constant}(C \text{ mol}^{-1})} = \frac{3600}{96485} \text{ mol}$  $= 0.037 \, mol$ As the metal, M, has a +3 charge in MCl<sub>3</sub>, three moles of electrons are required to reduce each mole of  $M^{3+}$ . The number of moles of M deposited is therefore: number of moles of M =  $\frac{0.037}{3}$  mol = 0.012 mol As 0.012 mol has a mass of 0.65 g, the atomic mass of M must be:  $\frac{\text{mass}}{\text{number of moles}} = \frac{0.65 \,\text{g}}{0.012 \,\text{mol}} = 52 \,\text{g mol}^{-1}$ atomic mass =-----This corresponds to chromium. Answer: Chromium

Marks

5

• Water (1.00 mol) was placed in an otherwise empty container with a fixed volume of 100 L. The container was heated to 1705 K, at which temperature the following equilibrium was established.

$$2H_2O(g)$$
  $\implies$   $2H_2(g) + O_2(g)$   $K_p = 1.89 \times 10^{-9}$  atm

Calculate  $K_c$  for this reaction at 1705 K.

For a reaction involving a change in the number of moles of gas of  $\Delta n$ ,  $K_p$  and  $K_c$  are related by:

 $K_{\rm p} = K_{\rm c}({\rm RT})^{\Delta n}$ 

In this reaction, 2 mol of gas  $\rightarrow$  3 mol of gas and hence  $\Delta n = 1$ . Thus,

$$K_{\rm p} = K_{\rm c}({\rm RT})^1$$
 or  $K_{\rm c} = \frac{K_{\rm p}}{{\rm RT}} = \frac{1.89 \times 10^{-9}}{(0.08206) \times (1705)} = 1.35 \times 10^{-11}$ 

$$K_{\rm c} = 1.35 \times 10^{-11}$$

Determine the amount of O<sub>2</sub> (in mol) in the container at equilibrium at 1705 K.

As 1.00 mol of  $H_2O$  is initially present in a container with volume 100 L, the initial concentration of  $H_2O$  is:

concentration =  $\frac{\text{number of moles}}{\text{volume}} = \frac{1.00 \text{ mol}}{100 \text{ L}} = 0.0100 \text{ M}$ 

The reaction table, with  $[O_2(g)]_{equilibrium} = x$ , is:

	2H <sub>2</sub> O(g)	 2H <sub>2</sub> (g)	+	O <sub>2</sub> (g)
initial	0.0100	0		0
change	-2x	+2x		+ <u>x</u>
equilibrium	0.0100-2x	2x		X

Hence, 
$$K_{\rm c} = \frac{[{\rm H}_2({\rm g})]^2 [{\rm O}_2({\rm g})]}{[{\rm H}_2 {\rm O}({\rm g})]^2} = \frac{(2{\rm x})^2 ({\rm x})}{(0.0100 - 2{\rm x})^2} = 1.35 \times 10^{-11}$$

Although the amount of water initially present is quite small, the value of  $K_c$  is so very small that  $0.0100 - 2x \sim 0.0100$ . This approximation simplifies the expression so that:

$$K_{\rm c} = \sim \frac{4x^3}{(0.0100)^2} = 1.35 \times 10^{-11}$$
 or  $4x^3 = (0.0100)^2 \times (1.35 \times 10^{-11})$ 

Hence,  $x = [O_2(g)]_{equilibrium} = 6.96 \times 10^{-6} M$ 

### CHEM1101

#### 2007-N-10

## ANSWER CONTINUES ON THE NEXT PAGE

As this concentration of  $O_2$  is present in a 100 L container, the number of moles of  $O_2$  present is:

number of moles = concentration × volume =  $(6.96 \times 10^{-6} \text{ M}) \times (100 \text{ L})$ =  $6.96 \times 10^{-4} \text{ mol}$ 

Answer:  $6.96 \times 10^{-4}$  mol

Marks • Ammonia is produced industrially by the direct combination of nitrogen and 5 hydrogen. Write a balanced equation for the production of ammonia.  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  $\Delta_{\rm f} H^{\circ}$  for ammonia is -46 kJ mol<sup>-1</sup>. A typical ammonia plant operates at a pressure of 250 atm and a temperature of 400 °C. Briefly explain the operation of an ammonia plant and the rationale for these conditions. What other "tricks of the trade" are used to maximise the production of ammonia? Le Chatelier's principle predicts that: As the reaction is exothermic, high temperature favours the reactants (i) and low temperature should be used to maximize the amount of ammonia. (ii) As the reaction converts 4 mol of gas to 2 mol of gas, low pressure favours the reactants and high pressure should be used to maximize the amount of ammonia. However, the reaction is very slow at low temperatures and hence is run at an intermediate temperature of about 400 °C. The equilibrium is pushed further to the right by removing the ammonia as it is formed (it has a much lower boiling point than hydrogen and nitrogen). The use of a catalyst speeds up the reaction (in both directions) and reduces the need to increase the temperature.

• 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 concentration of  $Cu^{2+}$  ions at 20 °C after equilibrium has been reached?

The standard reduction reactions and potentials are:

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

The least positive is reversed leading to the overall reaction and standard cell potential:

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

At equilibrium, 
$$K = \frac{[Zn^{2+}(aq)]_{eq}}{[Cu^{2+}(aq)]_{eq}}$$
 and  $E^{\circ} = \frac{RT}{nF} \ln K$ 

So for this 2 electron reaction at 20 °C,

+1.10 = 
$$\frac{(8.314) \times (20 + 273)}{2 \times 96485} \ln K$$
 or  $K = 6.97 \times 10^{37}$ 

This value of K is so large that there will no virtually no  $Cu^{2+}$  left at equilibrium.

(The reaction table, with  $[Cu^{2+}(aq)]_{equilibrium} = x$ , is:

	Cu <sup>2+</sup> (aq)	Zn(s)	 Zn <sup>2+</sup> (aq)	+	Cu(s)
initial	0.50	large	1.00		large
change	-X	large	+x		large
equilibrium	0.50 – x	large	1.00 + x		large

Hence, 
$$K = \frac{[Zn^{2+}(aq)]_{eq}}{[Cu^{2+}(aq)]_{eq}} = \frac{(1.00 + x)}{(0.50 - x)} = 6.97 \times 10^{37}$$
 or  $x = 0.50$  M (within accuracy limits. Hence,  $[Cu^{2+}(aq)]_{eq} = 0.50 - 0.50 = 0.00$  M !)

$$[Cu^{2+}]_{eq} = 0.00 M$$