Topics in the June 2012 Exam Paper for CHEM1001

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- Stoichiometry

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- Lewis Model of Bonding
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Atomic Energy Levels

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• First Law of Thermodynamics

Marks

2

• Complete the following table.

Name	Formula
calcium nitride	Ca ₃ N ₂
carbon tetrabromide	CBr ₄
iron(III) oxide	Fe ₂ O ₃
sulfuric acid	H ₂ SO ₄

• Explain why relative atomic masses are not always close to an integer. For example, copper has a reported value of 63.54.

Many elements consist of isotopes, *i.e.* atoms with different numbers of neutrons and hence different atomic masses. The atomic mass of each isotope is close to an integer value. The relative atomic mass of an element is calculated using all these different isotopic masses and their relative percentages.

• Analysis of a black-coloured mineral called pitchblende returned the following percentage composition by weight: 84.80% uranium and 15.20% oxygen. What is the empirical formula of this compound?

The mineral contains 84.80% U and 15.20% O.

	U	0
percentage	84.80	15.20
divide by atomic mass	$\frac{84.80}{238.03} = 0.356$	$\frac{15.20}{16.00} = 0.950$
divide by smallest value	1	2.67

The ratio of U : O is 1 : 2.67. The simplest whole number ratio can be obtained by multiplying this by 3 to give U : O equal to 3 : 8.

The empirical formula is U₃O₈.

Answer: U₃O₈

• Complete the following table, including resonance structures where appropriate. The central atom is underlined.

Marks
6

central atom is underlined.					
Species	Lewis structure(s)	Is the molecule polar?			
COCl ₂		yes			
<u>C</u> S ₂	∴s=c=s:	no			
<u>N</u> Br ₃	:Br $-$ N $-$ Br: :Br $:$	yes			
<u>S</u> O ₂	: <u>;</u> ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	yes			

• What is resonance? Give at least one example.

When two or more Lewis structures can be drawn for a molecule, the true structure is none of the structures that is drawn, but a type of average made up of all the resonance contributors. Some structures may contribute more than others.



For example, in NO_3^- , the ion does not contain 1 double and 2 single bonds, but is an average of the three structures shown. All of the N-O bonds are exactly the same length and the energy of the true structure is lower than the theoretical energy for any one of the given structures. This energy difference is known as resonance stabilisation energy. 2

Marks • Balance the following equation: 3 $NH_3(g) + O_2(g) \rightarrow NO(g) + H_2O(l)$ $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$ Calculate the mass of NH₃ required to produce 140. g of water. The molar mass of H₂O is: molar mass = $[2 \times 1.008 \text{ (H)} + 16.00 \text{ (O)}] \text{ g mol}^{-1} = 18.016 \text{ g mol}^{-1}$ Hence, the number of moles of water produced is: number of moles = mass / molar mass = $(140. \text{ g}) / (18.016 \text{ g mol}^{-1}) = 7.771 \text{ mol}$ From the balanced equation, 4 mol of NH₃ will produce 6 mol of H₂O. Hence, to produce 7.771 mol of H₂O so: number of moles of $NH_3 = (4/6) \times 7.771 \text{ mol} = 5.18 \text{ mol}$ The molar mass of NH₃ is: molar mass = $[14.01 (N) + 3 \times 1.008 (H)]$ g mol⁻¹ = 17.034 g mol⁻¹ The mass of NH₃ in 5.18 mol is therefore: mass = number of moles \times molar mass = (5.18 mol) \times (17.034 g mol⁻¹) = 88.2 g Answer: 88.2 g • Describe Rutherford's experiment that showed atoms consisted of a concentrated positive charge with a high mass. Make sure you discuss the observations and the conclusions drawn.

A stream of positively charged alpha particles was fired at a thin sheet of gold foil. Most of the particles passed straight through or were slightly deflected, but the occasional one was reflected back towards the source.

The conclusion drawn was that atoms consist of mostly empty space with a small, dense, positively charged nucleus.

2

Name

1s orbital

 $2p_x$ orbital

3d subshell

2nd shell

0 and 1

Marks

6

• For a single atom, complete the following table. If more than one quantum number is possible, give all correct possibilities.

all correct possibilities.Maximum number of
electrons containedQuantum numbersnl212121

2

2 I 3 2

• The σ -bonding in two plausible structures of ozone, O₃, is shown below. Complete each structure by adding electrons and/or π -bonds as appropriate.

3

10

8

Which of these geometries does ozone adopt? Give reasons for your answer.

Ozone adopts the non-cyclic structure. The cyclic structure is very strained with bond angles of 60° instead of 109.5°, making it very unstable. In contrast, the second structure is stabilised by resonance.



Ozone does not contain 1 double and 1 single bond. Both the O-O bonds are exactly the same length and true structure is a sort of average of the two Lewis structures shown. The energy of the true structure is lower than the theoretical energy for either of the given structures. This energy difference is known as resonance stabilisation energy.

2012-J-6 June 2012 Marks • Describe the differences between a 1s atomic orbital and a 2s atomic orbital. 2 1s orbital is smaller, closer to the nucleus, has a lower energy and has 0 nodes. 2s orbital is larger, further from the nucleus, has a higher energy and has 1 node. Both orbitals are spherical. • Complete the following table. 3 Full electron configuration Species $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$ gallium atom

P³⁻ $1s^2 2s^2 2p^6 3s^2 3p^6$ $1s^2 2s^2 2p^6 3s^2 3p^6$ K^+

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

22/01(a)



•	A galvanic cell has the following cell reaction:	Marks			
	$D(s) + 2Zn^{2+}(aq) \rightarrow 2Zn(s) + D^{4+}(aq)$ $E^{\circ} = 0.18 V$	0			
	Write the overall cell reaction in shorthand cell notation.				
	$D(s) D^{4+}(aq) Zn^{2+}(aq) Zn(s)$				
	Is the reaction spontaneous? Why?				
	Yes. E° is positive and hence ΔG° is negative.				
	Which electrode is the anode? D				
	Write the equation for the half-reaction that occurs at the anode?				
	$D(s) \rightarrow D^{4+}(aq) + 4e^{-}$				
	What is the standard reduction potential of the D^{4+}/D redox couple?				
	The two half equations are:				
	$D(s) \rightarrow D^{4+}(aq) + 4e^{-} \qquad E^{\circ}_{\text{oxidation}} (D^{4+}/D)$ $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s) \qquad E^{\circ}_{\text{reduction}} (Zn^{2+}/Zn)$				
where $E^{\circ}_{\text{oxidation}} (D^{4+}/D) + E^{\circ}_{\text{reduction}} (Zn^{2+}/Zn) = 0.18$ V. From the standard reduction potential for $Zn^{2+}(aq)$ is -0.76 V. Therefore:					
	$E^{\circ}_{\text{oxidation}} (D^{4+}/D) = (0.18 - (-0.76)) \text{ V} = 0.94 \text{ V}$				
	The standard reduction potential for the D^{4+}/D redox couple is the reverse of this:				
	$E^{\circ}_{\rm reduction} (D^{4+}/D) = -0.94 {\rm V}$				
	Answer: -0.94 V				
	ANSWER CONTINUES OVER THE PAGE	-			



Marks • A 120.0 g piece of copper is heated to 80.0 °C before being added to 150.0 mL of 3 water at 25.0 °C. What is the final temperature of the mixture? The specific heat capacity of copper is $0.385 \text{ J g}^{-1} \text{ K}^{-1}$ and the specific heat capacity of water is 4.18 J g^{-1} K⁻¹. The copper will cool down and the water will heat up when the two are mixed. The final temperature, $T_{\rm f}$, will be the same for both. For the copper, $q_{\text{copper}} = m c \Delta T = (120.0 \text{ g}) \times (0.385 \text{ J g}^{-1} \text{ K}^{-1}) \times \Delta T_{\text{copper}}$ For the water, $q_{\text{water}} = m c \Delta T = (150.0 \text{ g}) \times (4.18 \text{ J g}^{-1} \text{ K}^{-1}) \times \Delta T_{\text{water}}$ As the heat lost by the copper is gained by the water, $q_{water} = -q_{copper}$: $(150.0 \text{ g}) \times (4.18 \text{ J g}^{-1} \text{ K}^{-1}) \times \Delta T_{\text{water}} = -(120.0 \text{ g}) \times (0.385 \text{ J g}^{-1} \text{ K}^{-1}) \times \Delta T_{\text{conner}}$ or $627 \times \Delta T_{water} = -46.2 \times \Delta T_{conner}$ Using $\Delta T_{water} = (T_f - 25.0)$ °C and $\Delta T_{copper} = (T_f - 80.0)$ °C gives: $T_{\rm f} = 28.8 \,{}^{\rm o}{\rm C}$ Answer: 28.8 °C • H^+ is reduced to H_2 in an electrochemical cell. What is the total charge transferred 5 when a current of 2 A is passed through the cell for 20 minutes? Total charge = current × time = $(2 \text{ A}) \times (20 \times 60 \text{ s}) = 2400 \text{ C} = 2000 \text{ C}$ (to 1 s.f.) Answer: 2000 C

What amount of H₂ (in mol) is produced under these conditions?

The equation for the reduction of H^+ to H_2 is:

 $2H^+(aq) + 2e^- \rightarrow H_2(g)$

The number of moles of electrons in 2000 C is:

moles of electrons = total charge / Faraday's constant = 2000 C / 96485 C mol⁻¹ = 0.02 mol

ANSWER CONTINUES ON THE NEXT PAGE

Two moles of electrons is required for each mole of H ₂ . Hence the number of moles of H ₂ is half of this: number of moles of H ₂ = $(1/2) \times 0.02$ mol = 0.01 mol				
	Answer: 0.01 mol			
What volume would this gas occupy at 25 °C and 90 kPa?				
As 1 atm = 101.3 kPa, 90 kPa corresponds to: pressure = (90 / 101.3) atm = 0.89 atm				
Using the ideal gas equation, $PV = nRT$: V = nRT / P $= (0.01 \text{ mol}) \times (0.08206 \text{ atm L K}^{-1} \text{ mol}^{-1}) \times ((25 + 273) \text{ K}) / (0.89 \text{ atm})$ = 0.3 L				
	Answer: 0.3 L			

Marks

4

• Consider the following reaction.

 $SO_2(g) + NO_2(g) \implies SO_3(g) + NO(g)$

An equilibrium mixture in a 1.00 L vessel was found to contain $[SO_2(g)] = 0.800$ M, $[NO_2(g)] = 0.100$ M, $[SO_3(g)] = 0.600$ M and [NO(g)] = 0.400 M. If the volume and temperature are kept constant, what amount of NO(g) needs to be added to the reaction vessel to give an equilibrium concentration of NO₂(g) of 0.300 M?

From the chemical equation,

 $K_{eq} = \frac{[SO_3(g)][NO(g)]}{[SO_2(g)][NO_2(g)]}$

As the original mixture is at equilibrium:

 $K_{\rm eq} = \frac{[{\rm SO}_3({\rm g})][{\rm NO}({\rm g})]}{[{\rm SO}_2({\rm g})][{\rm NO}_2({\rm g})]} = \frac{(0.600)(0.400)}{(0.800)(0.100)} = 3.00$

This equilibrium is now disturbed by the addition of x M of NO(g). To reestablish equilibrium, the reaction will shift to the left by an unknown amount y. The reaction table for this is:

	SO ₂ (g)	$NO_2(g)$		SO ₃ (g)	NO(g)
initial	0.800	0.100	1	0.600	0.400 + x
change	+y	+y		-y	- <u>v</u>
equilibrium	0.800 + y	0.100 + y		0.600 - y	0.400 + <i>x</i> - y

As $[NO_2(g)] = 0.300$ M at the new equilibrium, y = (0.300 - 0.100) M = 0.200 M. Hence, the new equilibrium concentrations are:

$$\begin{split} [SO_2(g)] &= (0.800 + 0.200) \text{ M} = 1.000 \text{ M} \\ [NO_2(g)] &= 0.300 \text{ M} \\ [SO_3(g)] &= (0.600 - 0.200) \text{ M} = 0.400 \text{ M} \\ [NO(g)] &= (0.400 + x - 0.200) \text{ M} = (0.200 + x) \text{ M} \end{split}$$

As the system is at equilibrium,

 $K_{\rm eq} = \frac{[{\rm SO}_3(g)][{\rm NO}(g)]}{[{\rm SO}_2(g)][{\rm NO}_2(g)]} = \frac{(0.400)(0.200+x)}{(1.000)(0.300)} = 3.00$

Solving this gives x = 2.05 M. As the reaction is carried out in a 1.00 L container, this is also the number of moles required.

Answer: 2.05 mol

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks Rank the following compounds in order of increasing boiling point? Justify your 3 answer. CH₃CH₂OCH₂CH₃, CH₃OH, CH₄, CH₃CH₃, CH₃CH₂OH $CH_4 < CH_3CH_3 < CH_3CH_2OCH_2CH_3 < CH_3OH < CH_3CH_2OH$ Only weak dispersion forces act in CH₄ and CH₃CH₃. The bigger molecule has more interactions and hence the higher b.p. CH₃CH₂OCH₂CH₃ is a bigger molecule than CH₄ and CH₃CH₃, so has more dispersion forces. It also has dipole-dipole forces due to the polarised C-O bonds. CH₃OH and CH₃CH₂OH have hydrogen bonds due to the very electronegative O atom bonded to the H atom. These H-bonds are much stronger than the dispersion and dipole-dipole forces in the other compounds and hence these two compounds have the highest boiling points. CH₃CH₂OH has more dispersion forces than CH₃OH, so it has the highest boiling point. Melting points of the hydrogen halides increase in the order HCl < HBr < HF < HI. 2 Explain this trend. There are two competing intermolecular forces at play: Dipole-dipole forces increase as the halogen becomes more electronegative (I < Br < Cl < F). Dispersion forces are dependent on the polarisability of the atoms and increase with the size of the halogen. Dispersion force dominate in HCl, HBr and HI and determines the order of their melting points. The dipole-dipole force in HF is so strong (due to the very small and very electronegative F atom) that it is given a special name - a hydrogen bond. This causes HF to have an anomalously high melting point, which just happens to lie between that of HBr and HI.

•	• Use average bond dissociation enthalpies given below to calculate the molar enthalpy change for the following chemical transformation:					Marks 6	
	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$						
		Bond	H–H	N–H	N=N		
		$\Delta H / \text{kJ mol}^{-1}$	436	391	945		
	The r	eaction requires:					
	 breaking 1 N=N and 3 H-H bonds and formation of 6 N-H bonds 						
	The e	nthalpy required to	break these l	oonds is:			
	ΔI	H (bond breaking) =	[945 (N≡N) + = +2253	- 3 × 436 (H-F 3 kJ mol ⁻¹	I)] kJ mol ⁻¹		
	Enth	alpy is <i>released</i> by m	aking the new	w bonds is:			
	ΔΙ	I (bond making) = -	[6 × 391 (N-H =	H)] kJ mol ⁻¹ = -2346 kJ mol	r ¹		
	The o	overall enthalpy cha	nge is therefo	re:			
	ΔΙ	<i>I</i> = [(+2253) + (-2340	6)] kJ mol ⁻¹ =	-93 kJ mol ⁻¹			
	Answer: -93 kJ mol ⁻¹						-
	What	is the standard enthat	lpy of formation	on, $\Delta_{\rm f} H^{\circ}$, of N	H ₃ (g)? -4	7 kJ mol ⁻¹	
	(Note: the reaction in the question produces 2 mol of NH ₃ so the enthalpy of formation is half of the enthalpy change of this reaction.)						
The standard enthalpy of formation of hydrazine, $N_2H_4(g)$ is +96 kJ mol ⁻¹ . Calculate the strength of the N–N single bond in hydrazine.							
	The s	tandard enthalpy of	formation of	f N ₂ H ₄ (g) corr	esponds to t	he reaction:	
	$N_2(g) + 2H_2(g) \rightarrow N_2H_4(g)$						
	This	reaction requires:					
	 breaking 1 N=N and 2 H-H bonds and formation of 4 N-H and 1 N-N bond 						
	The enthalpy required to break these bonds is:						
	ΔH (bond breaking) = [945 (N=N) + 2 × 436 (H-H)] kJ mol ⁻¹ = +1817 kJ mol ⁻¹						

The standard enthalpy of formation of N₂H₄(g) corresponds to the reaction:

 $N_2(g) + 2H_2(g) \rightarrow N_2H_4(g)$

This reaction requires:

- breaking 1 N=N and 2 H-H bonds and
- formation of 4 N-H and 1 N-N bond

The enthalpy required to break these bonds is:

 ΔH (bond breaking) = [945 (N=N) + 2 × 436 (H-H)] kJ mol⁻¹ = +1817 kJ mol⁻¹

Enthalpy is *released* by making the new bonds is:

 ΔH (bond making) = - [4 × 391 (N-H) + x (N-N)] kJ mol⁻¹ = - (1564 + x) kJ mol⁻¹

The overall enthalpy change is equal to the enthalpy of formation of N₂H₄:

 $\Delta_{\rm f}H = [(+1817) + -(1564 + x)] \text{ kJ mol}^{-1} = +96 \text{ kJ mol}^{-1}$

So

 $x = +157 \text{ kJ mol}^{-1}$

Answer: +157 kJ mol⁻¹

Suggest why the N–N single bond in hydrazine is much weaker than the N–H and H–H bonds. Hint: Draw its Lewis structure.

Each N atom in hydrazine has a lone pair of electrons and is the negative end of a dipole formed with the H atoms.

These lone pairs repel each other, weakening the bond.