

ACDA5014 ADVANCED CHEMISTRY OME FINAL EXAM

73.5

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SHOW ALL WORK. USE CORRECT UNITS AND SIGNIFICANT DIGITS. YOU MAY SHOW YOUR WORK ON THE BACK OF THE SHEET BUT INDICATE YOUR ANSWER ON THE FRONT.

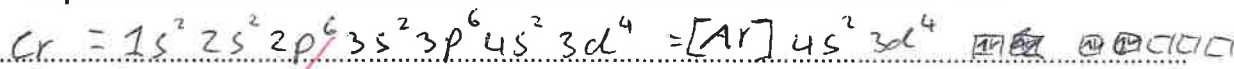
PERIODIC TABLE AND REFERENCE DATA CAN BE TORN OFF OF THE EXAM

THERE ARE 11 QUESTIONS, 100 POINTS TOTAL (PLUS 1 EXTRA CREDIT). TIME 120 min

QUESTION 1:

For each of the following statements determine if it is true or false. Justify your answer.

1. (2p) Chromium metal (atomic number 24) produces silver-white colour in a standard flame test as a result of the excitation of valence electrons. Chromium atom has 4 unpaired electrons in the outermost shells that can be excited in such test.



~~False~~ True

True as shown in the electron configuration diagram the outer shell ~~electrons~~ would have 4 valence electrons.

2. (2p) In ammonia, NH_3 , which is used in the industrial production of ammonium nitrate, the bond angle between a nitrogen atom and two hydrogen atoms is 120° .

Nitrogen has 3 electrons missing from its outer shell so when bonded with 3 hydrogen to form ammonia the bond/lp would be 3/0 resulting in a 120° degree bond angle, hence ~~True~~ False

3. (2p) In 1 L of 1.5 M solution of NaCl there is 87.8 g of table salt.

$$1.5 = \frac{mol}{L} = \frac{mol}{1} = mol$$

$$NaCl = 23 + 35.45 = 58.45 g/mol$$

$$58.45 \times 1.5 = 87.675g \text{ assuming rounded values were used this is true.}$$

4. (2p) Ideal gas equation describes well the behaviour of gases when the pressure and temperature of this gas tend to 0 atm and 0 K, respectively.

False the ideal gas equation can be used for any temperature and pressure as long as the gas is assumed to be ideal.

5. (2p) Activation energy of nitrocellulose and RDX is 86 kJ/mol and 199 kJ/mol, respectively. RDX is less stable than nitrocellulose.

2p
~~False, nitrocellulose has a lower activation energy than RDX, so it is more stable.~~
False ✓ RDX has a higher activation energy so is more stable.

6. (2p) Hess's Law states that the enthalpy change for a chemical reaction is independent of the route taken.

2p
True ✓ The enthalpy is only determined by reactants and products not the route taken from one to another.

7. (2p) For a hypothetical reaction $A + B \rightarrow C$ that is a second order in A, doubling the concentration of A will double the rate of the overall reaction.

2p
False ✓ If A is second order then rate of reaction would be $k[A]^2$ so doubling A would mean 4 times rate of reaction.

8. (2p) All combustion reactions are exothermic.

2p
True ✓ Combustion is the process by which heat is given out so therefore exothermic.

9. (2p) According to the kinetic theory of gases which leads to the ideal gas law, one of the assumptions is that when the gas particles collide, they lose their kinetic energy.

2p
False, ideal gas law states that all collisions are perfectly elastic so no energy is lost.

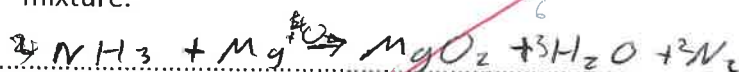
10. (2p) The rate of decomposition of the explosive material decreases when the temperature increases.

2p
False ✓ The rate of decomposition is directly related to temperature so increase temperature mean increase decomposition.

QUESTION 2:

When ammonium nitrate and magnesium metal are mixed in a stoichiometric ratio, they form a pyrotechnic composition that decomposes to form magnesium oxide, water vapour and nitrogen gas.

- a) (2p) Write a balanced equation showing all products for the decomposition of this mixture.



N-1-2-4

N-2-4

H-3-6-12

H-2-6-12

Mg-1

Mg-1

O-2-5-8

O-3-5-8

$6\text{H}_2\text{O} + 2\text{N}_2$

~~Answer = $2\text{NH}_3 + \text{Mg} + 5$~~

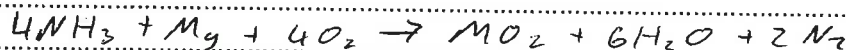
Answer = $4\text{NH}_3 + \text{Mg} + 4\text{O}_2 \rightarrow \text{MgO}_2 +$

- b) (3p) Using the standard heats of formation listed below, calculate the heat of reaction for molar quantities of the reactants. Is this process exothermic or endothermic? Explain

Ammonium nitrate (solid) -365 kJ/mol

Magnesium oxide (solid) -601 kJ/mol

Water (gas) - 242 kJ/mol



$(-601 + (-242 \times 6)) - (4 \times 365)$

$= -2053 - 1460$

$= -2053 + 1460$

$= -593 \text{ kJ/mol}$

$\therefore$ Exothermic reaction

- c) (3p) How does the heat of reaction from this reaction compare with 2.8 kJg⁻¹ provided by one gram of TNT.

$4 \times 14 + 12 \times 3 + 24 + 8 \times 16$

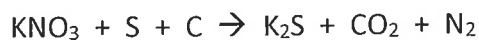
$= 220 \text{ g/mol}$

$\frac{593}{220} = 2.7 \text{ kJg}^{-1}$

It is therefore slightly less than that of TNT. ✓

QUESTION 3:

A simple chemical equation for the combustion of gun powder can be written as:



- a) (1p) Balance this equation using the smallest integer coefficients. Include all coefficients even if the value is 1.



- b) (4p) Assuming that the reaction above can be carried out at STP, how many grams of CO_2 are formed from the decomposition of 45 g of KNO_3 ?

$$\text{KNO}_3 = 39 + 14 + (3 \times 16) = 101 \text{ g/mol}$$

$$\text{CO}_2 = 12 + (2 \times 16) = 44 \text{ g/mol}$$

$$x = \frac{3}{2} \quad \frac{45}{101} \times \frac{3}{2} = 0.742 \text{ moles of CO}_2$$

$$0.742 \times 44 = 32.64 \text{ g of CO}_2$$

- c) (4p) How many litres of gas products would form from the decomposition of 45 g of potassium nitrate at STP?

$$\text{molar gas volume} = 22.4 \text{ dm}^3$$

$$0.742 \text{ moles of CO}_2 + \text{N}_2$$

$$\text{N}_2 = 28 \text{ g/mol}$$

$$x_{\text{N}_2} = \frac{1}{2} \quad \frac{45}{101} \times \frac{1}{2} = 0.25 \text{ moles of N}_2$$

$$(0.742 + 0.25) \times 22.4 = 22.16 \text{ dm}^3 \text{ of gas}$$

- d) (3p) 45 g KNO_3 at STP is heated to 100 degC and the pressure is reduced to 700 mmHg. What is the new volume of the gases?

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Assume STP is at 760 mmHg at 0 deg C

$$\frac{700}{760} \times 101325 = 93325.7 \text{ Pa}$$

$$101325$$

$$\frac{93325.7 \times 22.16}{273} = \frac{93325.7 \times x}{373}$$

$$\frac{373 \times 101325 \times 22.16}{273 \times 93325.7} = 3.29 \text{ m}^3 \text{ or } 32.9 \text{ dm}^3 \text{ of gas}$$

QUESTION 4:

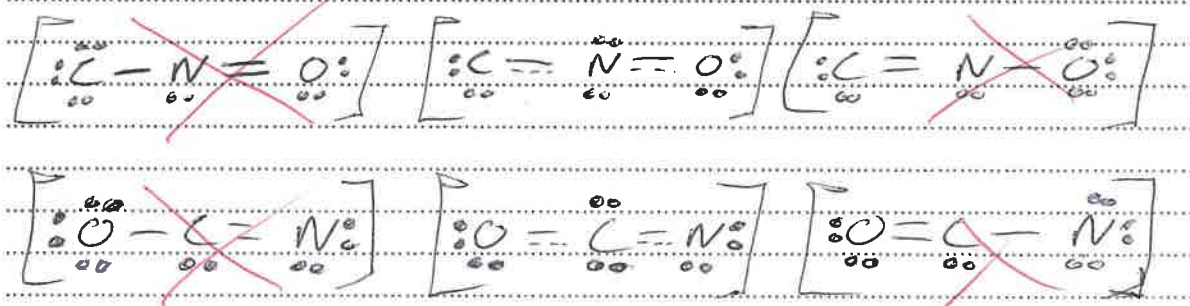
(4p) The normal boiling point is 100°C for H_2O and -33.3°C for NH_3 , even though the two molecules have almost identical atomic weights. Explain this difference in terms of intermolecular forces, using narrative or cartoons or both.

Due to the relative sizes of both Oxygen and Nitrogen Oxygen has a slightly stronger atomic force. This force is also only having to keep two bonds in place instead of 3. This results in NH_3 having a lower boiling point as the forces between the atoms are lower.

QUESTION 5:

Mercury (II) fulminate $\text{Hg}(\text{CNO})_2$ is a primary explosive whereas mercury (II) cyanate $\text{Hg}(\text{OCN})_2$ is not explosive in nature.

a) (3p) Draw all resonance structures, three for each anion, fulminate (N is a central atom) and cyanate (C is a central atom).



b) (3p) Explain in terms of formal charges why fulminate is explosive and cyanate is not

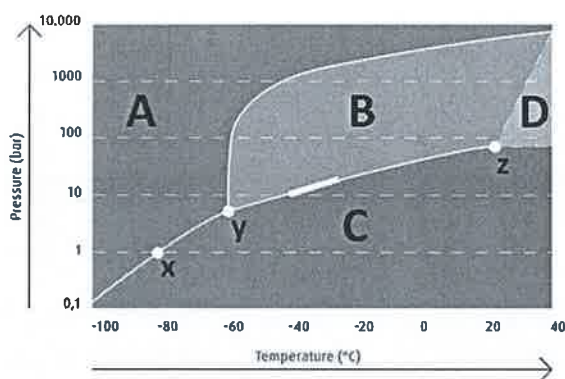
Due to the electron structure of fulminate it is easier to separate electrons causing the rapid degradation and detonation, whereas cyanate will not give up its electrons as easily preventing a chain reaction therefore rendering it non-explosive.

- c) (2p) What would be the other reason to explain explosive character of mercury fulminate?

It contains all the necessary elements to be a mono molecular explosive (CNO), a fuel C an oxidiser O and nitrogen N to produce high energy output.

QUESTION 6:

The phase diagram of carbon dioxide, CO_2 , is shown below:



- a) (2p) Identify each area of the plot:

A: Solid region

B: Liquid region

C: gaseous region

D: Superfluid region

- b) (1.5p) Give the names of points x, y and z:

point x: vapourisation point

point y: triple point

point z: Sublimation point

- c) (0.5p) Which phase can exist at SATP? ... gas

- d) (0.5p) If a sample of this substance is cooled from -45°C to -85°C at a pressure of 100 bar, what phase change will occur? ... Solid

- e) (0.5p) What name is given to the change from phase C to phase B?

Condensation

- f) (1p) What are the boiling and freezing points of this substance at 50 bar?

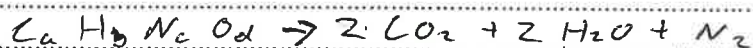
freezing = -60°C boiling = 30°C

- g) (1p) Estimate the conditions of a critical point. ... Low temperature and high pressure

QUESTION 7:

Some high explosives have the general formula $C_a H_b N_c O_d$. The oxidiser (O) and the fuel (C, H) are present in the same molecule. Nitrogen atoms are present so that there is a highly exothermic production of hot N_2 gas.

- a) (4p) For an unknown explosive of general formula $C_a H_b N_c O_d$ and a molar mass of 152 g/mol, determine the coefficients a , b , c and d if 152 g of this material decomposes to form 44.8 dm^3 of CO_2 , 44.8 dm^3 of H_2O , and 22.4 dm^3 of N_2 .



$$1 \text{ mole gas} = 22.4 \text{ dm}^3$$

A
H
N
O

$$C = 2$$

$$H = 4$$

$$N = 2$$

$$O = 6$$

$$a = 2$$

$$b = 4$$

$$c = 2$$

$$d = 6$$

- b) (2p) Which of the produced gases will move fastest and explain why?

The H_2O will move the fastest due to being the lightest molecule

$$18 < 44 \text{ or } 28 \text{ g/mol}$$

- c) (2p) For the explosive determined in a) calculate the per cent by mass of oxygen.

$$\frac{2 \times 12}{(2 \times 12) + (4 \times 1) + (2 \times 14) + (6 \times 12)} \times 100 = 63\%$$

- d) (3p) The oxygen balance of an explosive is the mass of oxygen either in excess (the balance is positive) or in deficit (the balance is negative) of that required for complete oxidation of C and H. The oxygen balance is expressed as a percentage of the molar mass of the explosive. Calculate the oxygen balance for explosive with the formula determined in part a).

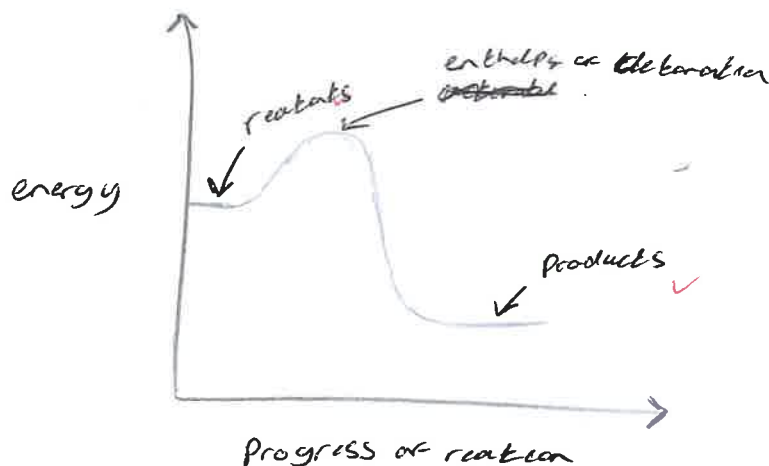
$$OB = \frac{16}{128} \times [6 - (2 \times 2) - (\frac{4}{2})] \times 100 = 0$$

$$MW = 2 \times 12 + 4 + 2 \times 14 + 6 \times 12 = 128$$

QUESTION 8:

An explosive, RDX has an enthalpy of detonation of $-1106 \text{ kJ mol}^{-1}$.

- a) (3p) Sketch the reaction profile ("energy" vs. "progress of reaction") showing the reactants, products, activated complex, enthalpy of detonation and the activation energy



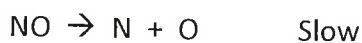
- b) (2p) The activation energy for the explosive detonation of RDX is 199 kJ mol^{-1} whereas the activation energy for the explosive detonation of mercury fulminate is 105 kJ mol^{-1} . Define the term activation energy and hence comment on the relative stability of these two explosives.

2p

Activation energy is the energy needed to cause an explosive to detonate. Therefore as mercury fulminate has a lower activation energy it is easier to ignite making it more sensitive.

QUESTION 9:

Nitrous oxide, NO_2 , is a common propellant for rocket motors. The proposed mechanism for the formation of NO_2 is shown below:



a) (2) Write the overall chemical equation for the reaction with the above mechanism.



b) (4p) Three experiments were conducted to discover the initial rate of formation of NO_2 values as the concentrations of the reactants change. Use the data in the table below to determine the order of the reaction with respect to each reactant and write the rate law for the reaction

experiment	NO, mol/L	O_3 , mol/L	Initial rate, mol/L-s
1	0.012	0.020	0.102
2	0.024	0.020	0.204
3	0.024	0.040	0.204

$$\text{NO} = 0.012 \quad \text{rate} = 0.102 \quad \frac{0.204}{0.102} = 2$$

$$2\text{NO} = 0.024 \quad \text{rate} = 0.204 \quad \frac{0.204}{0.102}$$

$$2\text{NO} = 2 \text{ rate}$$

NO is first order

$$\text{O}_3 = 0.02$$

$$\text{rate} = 0.204$$

$$\frac{0.204}{0.204} = 1$$

$$2\text{O}_3 = 0.04$$

$$\text{rate} = 0.204$$

$$\frac{0.204}{0.204}$$

$$2\text{O}_3 = 0 \text{ rate}$$

O_3 is zeroth order

$$\text{rate} = k[\text{NO}]^1$$

c) (3) Calculate the value of the rate constant. What is the unit of k?

$$\text{rate} = k[\text{NO}]^1$$

$$0.102 = k \times 0.012$$

$$k = \frac{0.102}{0.012} = 8.5 \frac{\text{mol/L-s}}{\text{mol/L-s}}$$

d) (2p) How does the rate law support the mechanism of this reaction?

Rate law states a reaction is only as fast as its slowest component reaction.

This supports the mechanism as the breakdown of NO into $\text{N} + \text{O}$ is the slowest stage of the reaction so the rate will only ~~be~~ relate to that.

QUESTION 10:

(4p) A 500 g sample of TNT ($\text{C}_7\text{H}_5\text{N}_2\text{O}_6$) is burned in a bomb calorimeter containing 610 g of water at an initial temperature of 20.0°C . The heat capacity of the calorimeter is 420 J/degC . Once the reaction is completed final temperature of the water and calorimeter increased to 23.0°C . Using these data, calculate the heat of combustion of TNT in kJ/mol . The specific heat of water is 4.184 J/g-degC .

$$23 - 20 = 3$$

$$3 \times 420 + (3 \times 4.184 \times 610) = 8916.72 \text{ J}$$

$$\begin{aligned} \text{molar mass TNT} &= (7 \times 12) + (5 \times 1) + (2 \times 14) + (6 \times 16) \\ &= 213 \text{ g/mol} \end{aligned}$$

$$\frac{500}{213} = 2.35 \text{ moles}$$

$$\frac{8916.72}{2.35} = 3798.5 \text{ J/mol}$$

$$\text{or } \underline{\underline{3.8 \text{ kJ/mol}}}$$

QUESTION 11:

Many fireworks contain metal compounds that emit visible light. The colours given by barium and calcium compounds and their wavelengths are given in the table

metal	colour	Wavelength, nm
Barium	Green	554
Calcium	Orange-red	616

a) (3p) Which of these two colours has the higher energy? Show your calculations.

3p
green $\frac{c}{\lambda} = \nu$ $\frac{3 \times 10^8}{554 \times 10^{-9}} = 5.415 \times 10^{14}$

$E = h \times \nu$ $6.6 \times 10^{-34} \times 5.415 \times 10^{14} = 3.57 \times 10^{-19}$

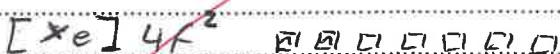
orange-red $\frac{3 \times 10^8}{616 \times 10^{-9}} = 4.87 \times 10^{14}$ ✓

$6.6 \times 10^{-34} \times 4.87 \times 10^{14} = 3.214 \times 10^{-19}$

∴ Green has the higher energy level

b) (3p) Write the full electron configuration for calcium and show the electrons in orbitals.

For barium write the shorthand electron configuration ONLY.



c) (2p) The colours seen are a result of the emission of visible light. State how these colours are produced.

2p
To change the orbital of an electron energy must be added to the system. when the electron drops back down to a lower energy state the extra energy is given off in the form of light. Depending on the initial energy input depends what determines the colour output.

- d) (2p) Two, out of six stable isotopes of barium are ^{132}Ba and ^{138}Ba . For each of these isotopes, determine the number of neutrons.

2p Ba has 56 protons

$$132 - 56 = 76 \text{ neutrons for } ^{132}\text{Ba}$$

$$138 - 56 = 82 \text{ neutrons for } ^{138}\text{Ba}$$

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleev?