

ACDA5014 ADVANCED CHEMISTRY OME FINAL EXAM

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DATE: May 19, 2022

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

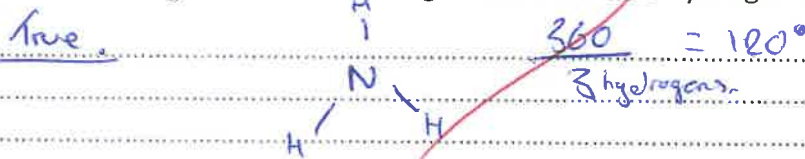
QUESTION 1:

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.

True. Chromium is ~~Ar~~ $4s^2 3d^4$ 
4 electrons from a possible 10.

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° .



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

$$NaCl = 23 + 35.4 = 58.4g$$

$$M = \frac{mol}{L} = 1.503$$

$$\frac{87.8}{58.4} = \frac{58.4}{87.8} = 0.665$$

$$\frac{87.8}{58.4} = 1.503 mol$$

$$M = \frac{1.503}{1} = 1.5032$$

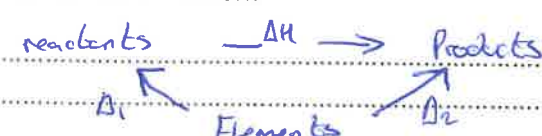
4. (2p) Ideal gas equation describes well the behaviour of gases when the pressure and temperature of this gas tend to 0 atm and 0 K, respectively.

False. 1 atm + 273 K.

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 is less stable + insensitive as it activates easier. The higher activation energy indicates more energy required to decompose.

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

2p True.  True. ✓

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.

1p incorrect. ✓
 $2 + 1 \rightarrow 3$
 $4 + 1 \rightarrow 5$
 $8 + 1 \rightarrow 9$

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

0 incorrect. Some combustions can absorb energy in order to burn further.

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.

1p incorrect. Collisions increase particle velocity/energy.

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

2p incorrect. It increases with temperature as the energy required is being overcome by a greater magnitude.

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.



4 Hydrogens

3 Oxygens

2x Nitrogens

2p

- 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

$$\text{Ammonium Nitrate} = 1 \text{ mol} = -365 \quad 1 \text{ mol} = 80 \text{g}$$

$$\frac{-365}{80} = -4.5625 \text{ kJ/g}$$

$$\text{Magnesium Oxide} = 56 \text{g} = \frac{-601}{56} = -10.7 \text{ kJ/g}$$

$$\text{MgO}_2$$

$$\text{Water (g)} = 33 \text{g} = \frac{-242}{33} = -7.33 \text{ kJ/g}$$

1p

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

All three exothermic reactions give off more ^{heat} energy than 1g of TNT during their reactions.

likely due to the amount of oxygen + the metal in the case of Mg.

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 ?

$$\begin{aligned} \text{C} &= 12 \\ \text{O} &= 16 \times 2 = 32 \\ \hline &44 \end{aligned}$$

$$34.98\text{g}$$

$$\begin{array}{r} \text{K} \quad 39 \\ \text{N} \quad 14 \\ \text{O} \quad 16 \times 3 \\ \hline 85 \end{array} \quad \begin{array}{r} 45 \\ \hline 85 \end{array} \quad \approx 0.53\text{mol}$$

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

$$\frac{101}{45} = 2.24\text{ mol of KNO}_3 \quad = 2.24 \times 22.4 = 50.28\text{L}$$

- 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?

$$\begin{array}{lll} 1\text{ atm} & P_1 = 760 & P_2 = 700 \\ 273\text{K} & V_1 = 50.28 & V_2 = \\ & T_1 = 273 & T_2 = 373 \end{array}$$

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

$$\begin{aligned} \text{K} &= 39 \\ \text{N} &= 14 \\ \text{O}_3 &= 48 \\ \hline 101 \end{aligned}$$

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.

op Liquid H_2O will be dipole-dipole forces between a positive end of one atom and the negative end of another.

Gas NH_3 will be London dispersion forces, which are weak forces between molecules close together.

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.

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

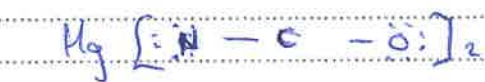
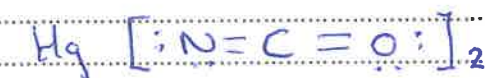
C = 6
N = 7
O = 8



$$\text{Formal Ch} = (8 + 8 + 8) - 24 = 24$$

$$-(6 + 7 + 8) = 21$$

$$\text{FC} = [23]$$



$$8 + 8 + 8 = 24$$

$$7 + 6 + 8 = 21$$

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

Formal Charge of Central atom

$$\text{N} = 8 - 7 = 1$$

$$\text{C} = 8 - 6 = 2$$

Nitrogen being a deficient central atom will want to react + release H_2 Gas. Nitrogen will react exothermally whereas the carbon will not.

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

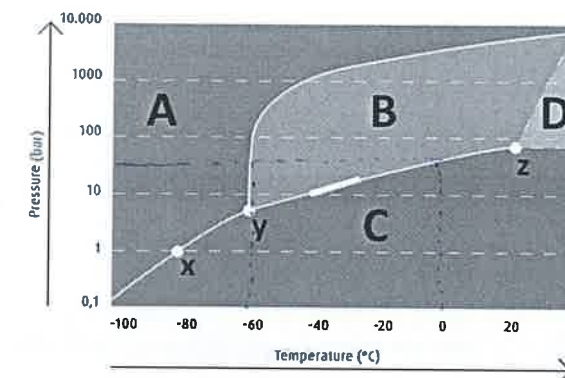
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QUESTION 6:

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



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

15 A: Solid State

B: Liquid State

C: Gas State

D: Vaporising

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

point x:

point y: Melting Point

point z: Boiling Point

c) (0.5p) Which phase can exist at SATP? All ?

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?

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

condensation

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

freezes @ -60°C boils @ 0°C

g) (1p) Estimate the conditions of a critical point.

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 dm³ of CO_2 , 44.8 dm³ of H_2O , and 22.4 dm³ of N_2 .



$$\frac{44.8}{22.4} = 2 CO_2 \quad \frac{44.8}{22.4} = 2 H_2O \quad \frac{22.4}{22.4} = 1 N_2$$

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

~~Hydrogen gas~~ or the Nitrogen as it is the lightest

~~28g N₂~~
~~44g CO₂~~
~~36g H₂O~~

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

$$\text{Oxygen Balance} = \frac{16}{152} \times \left(8 - (2 \times 2) - \frac{4}{2} \right) \times 100$$

$$= -20.42\%$$

- 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).

$$\text{Total MM} = 152g$$

$$\begin{array}{r} 2 \times 12 \\ + 4 \times 1 \\ + 2 \times 14 \\ + 6 \times 16 \\ \hline 152 \end{array} = 96$$

$$\left(\frac{96}{152} \right) \times 100 = 63\%$$

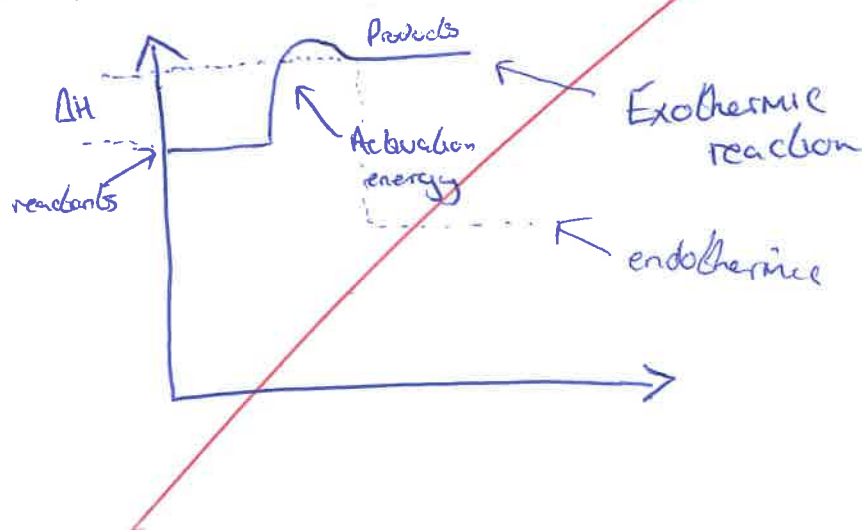
oxygen

Sorry!
Swap
2p

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

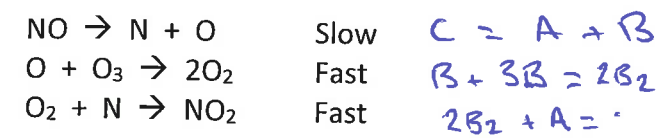
The Activation energy is the ~~req~~ amount of input required to overcome the bond strength of the composition + break it apart.

A lower activation energy means that a composition can be set off with less effort. A very low activation energy could result in accidental ignitions.

RDX has the higher Activation energy so it is more stable than mercury fulminate.

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

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

Slowest reaction is the rate determining step.

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

Slowest rate is the rate defining step.

2p

QUESTION 10:

(4p) A 500 g sample of TNT ($C_7H_5N_2O_6$) is burned in a bomb calorimeter containing 610 g of water at an initial temperature of 20.0 degC. 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 degC. Using these data, calculate the heat of combustion of TNT in kJ/mol. The specific heat of water is 4.184 J/g-degC.

$$Q = MC \Delta t$$

$$\begin{aligned} Q &= 500g \times 4.184 \times 23 \\ &= 0.5 \times 4.184 \times 296k \\ &= 619.2 kJ/mol. \end{aligned}$$

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.

1p

~~Calcium~~ The shortest wavelength = Barium

b) (3p) Write the full electron configuration for calcium and show the electrons in orbitals. For barium write the shorthand electron configuration ONLY.

3p

Calcium = $\overset{20}{\text{Ca}} = [\text{Ne}] 4s^2$

Orbital diagram for Calcium: $1s^2$ (up, down), $2s^2$ (up, down), $2p^6$ (three boxes, each up, down), $3s^2$ (up, down), $3p^6$ (three boxes, each up, down), $4s^2$ (up, down).

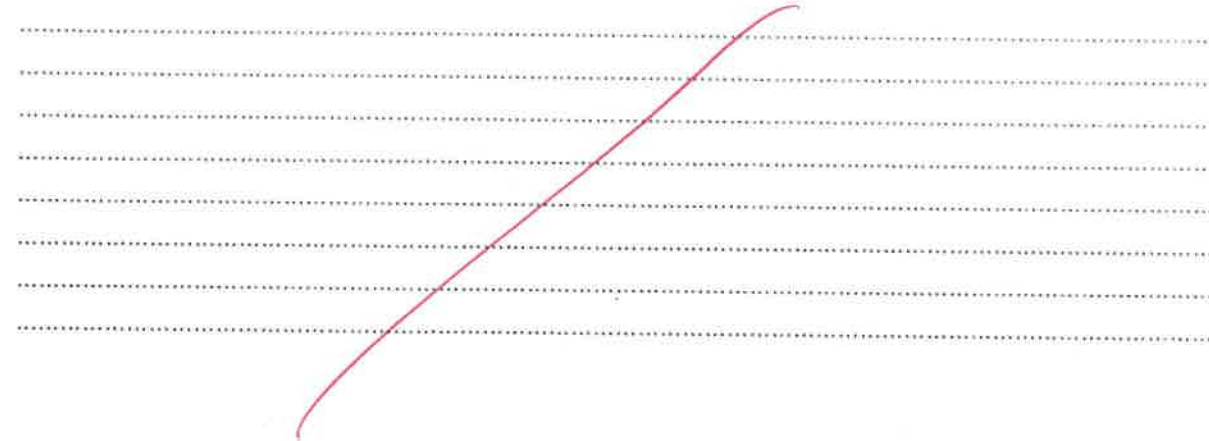
Barium = ~~[Kr]~~ $[\text{Xe}] 6s^2$

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

0p

The different colours depend on the wavelength emitted & where those wavelengths sit on the colour spectrum.

- 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.



EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleev?

