

ACDA5014 ADVANCED CHEMISTRY OME FINAL EXAM

NAME Frazer Graham 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.

- 2p 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, chromium has six electrons in its outer shell?~~
False, chromium has 5 unpaired electrons as the s-shell does not fill. $[Ar] 4s^1 3d^5$ $\uparrow \uparrow \uparrow \uparrow \uparrow$ ✓

- 2p 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° .

NH_3 False, the bond angle is less than 180° because the lone pair & polarity squashes to a tetrahedral shape. ✓

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

$M = \frac{\text{Mass solute}}{\text{L solution}}$ $1.5 \times 1 = 1.5M$
 $35.5 + 23 = 58.5 \text{ MM}$ $1.5M \times 58.5MM = 87.75g$
True! ✓

- 1p 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.

$PV = nRT$
False, ✓ ideal gas equation cannot be used for extreme pressure environments. why?

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, ✓ RDX is ~~more~~ ^{less sensitive} ~~more stable~~ requiring more energy to reach the activation energy for the reaction.

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

2p

True, ✓ the enthalpy change will remain constant the only factor is which direction to determine if it's negative or positive.

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

True, ✓ a second order means any increase will square the rate of reaction.

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

2p

True, ✓ combustion releases energy from the bonds to create smaller stable molecules.

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, ✓ the conservation of momentum means that energy is transferred & cannot be destroyed.

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

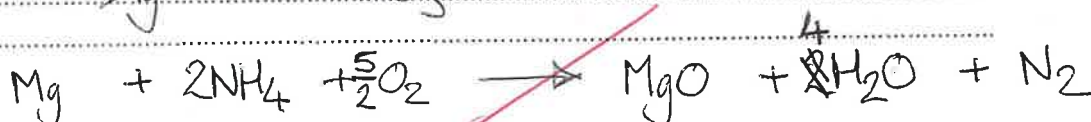
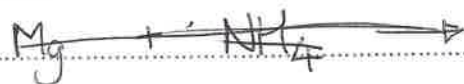
2p

False, ✓ $V = kT + C$ therefore when temperature increase the rate of decomposition increase.

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.



- 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

$$(2 \times 365) + (-601) + (4 \times -242) = -839 \text{ kJ}$$

The process is exothermic because the energy is negative showing it is being released.

$$\text{kJ/mol} \times 2 \text{ mols} = \text{kJ}$$

$$\text{m} = \text{g}$$

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

$$839 \text{ kJ} \quad 24 + 14 + 4 = 42 \text{ g}$$

$$839 \text{ J} \div 42 \text{ g} = 19.97 \text{ kJ/g}$$

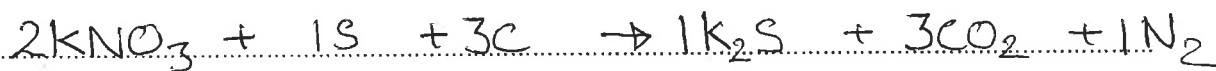
The energy released from ammonium nitrate & Magnesium is greater than the energy released from TNT!

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 ? 1 atm & 298 K

$$\begin{array}{l} \text{KNO}_3 \\ \text{CO}_2 \quad 39 + 14 + (3 \times 16) = 101 \text{ MM} \\ 45 \div 101 = 0.45 \text{ moles} \end{array}$$

$$\frac{\text{CO}_2}{0.45 \text{ KNO}_3} = \frac{3}{2} \rightarrow \frac{3}{2} \times 0.45 = 0.68 \text{ moles of CO}_2$$

$$12 + (2 \times 16) = 44 \text{ MM}$$

$$44 \times 0.68 = 30 \text{ g of CO}_2$$

- c) (4p) How many litres of gas products would form from the decomposition of 45 g of potassium nitrate at STP? Nitrogen + CO_2

$$\text{CO}_2 = 0.68 \text{ moles}$$

$$\frac{\text{N}_2}{0.45 \text{ KNO}_3} = \frac{1}{2} \times 0.45 = 0.23 \text{ moles N}_2$$

$$(22.4 \times 0.23) + (22.4 \times 0.68) = 20.38 \text{ L}$$

- 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?

$$T_1 = 298 \text{ K}$$

$$T_2 = 373 \text{ K}$$

$$P_1 = 1 \text{ atm}$$

$$P_2 = \frac{700}{760} \times 1 \text{ atm} = 0.92 \text{ atm}$$

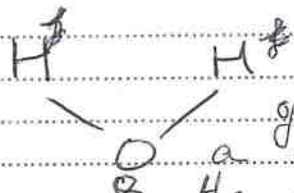
$$V_1 = 20.38 \text{ L}$$

$$\frac{V_1 P_1 T_2}{T_1 P_2} = \frac{20.38 \text{ L} \times 1 \times 373}{298 \times 0.92} = 27.73 \text{ L}$$

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.

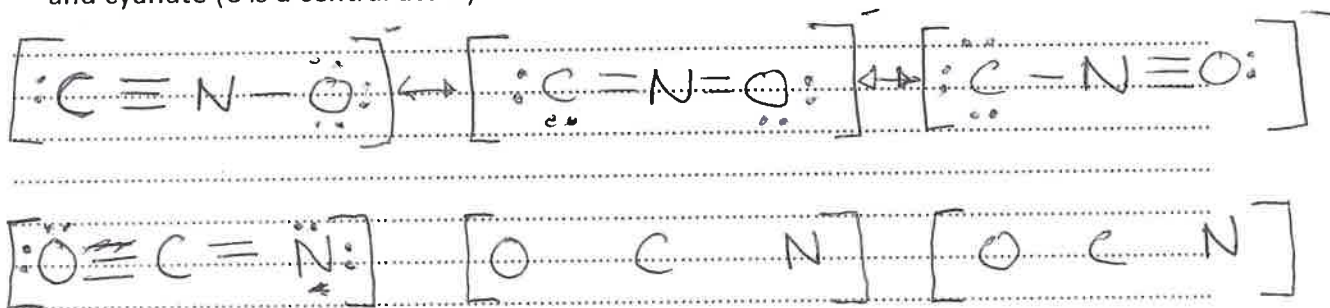
2p


 The reason due to difference is because of hydrogen bonding. Hydrogen bonding cause a dipole-dipole bond of H_2O which increases the energy required to break the molecule. NH_3 while it has hydrogen atoms, nitrogen is less electronegative & it's only lone pair of electrons makes it more difficult to polarise.

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).

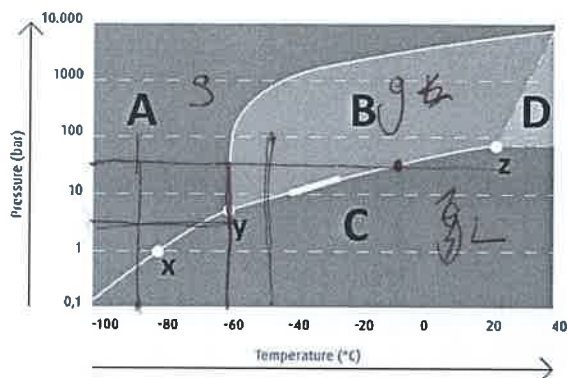


b) (3p) Explain in terms of formal charges why fulminate is explosive and cyanite is not

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

QUESTION 6:

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



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

2p

- A: Solid
B: High gas
C: Liquid
D: Super critical area

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

1p

- point x: Double point?
point y: Triple point
point z: Critical point

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

- 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? ~~Solidification~~ $L \leftrightarrow G \leftrightarrow S$

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

~~Vapourisation~~

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

-60°C freezing boiling point 10°C

- g) (1p) Estimate the conditions of a critical point 7.5 bar -60°C

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 .

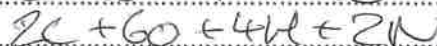
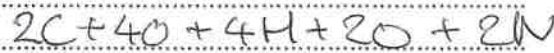
$$152 \text{ g/mol}$$

$$152 \div 152 = 1 \text{ mole}$$

$$44.8 \div 22.4 = 2 \text{ moles } CO_2$$

$$44.8 \div 22.4 = 2 \text{ moles } H_2O$$

$$22.4 \div 22.4 = 1 \text{ mole } N_2$$



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

$$H_2O = 18 \text{ MM} \quad H_2O = 18 \text{ mm gas}$$

$$CO_2 = 44 \text{ MM}$$

$$N_2 = 18 \text{ MM}$$

Both N_2 & $H_2O(g)$ will move at the faster speeds due to being lighter than the MM.

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

$$\frac{12 \times 2 + 1 \times 4 + 14 \times 2 + 16 \times 6}{24 + 4 + 28 + 96} = 152 \text{ MM} \quad \text{don't it was already given}$$

$$\frac{16}{152} \times \left[6 - (2 \times 2) - \left(\frac{4}{2} \right) \right] \times 100 = 0\% \quad \frac{96}{152} \times 100 = 63\%$$

- 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).

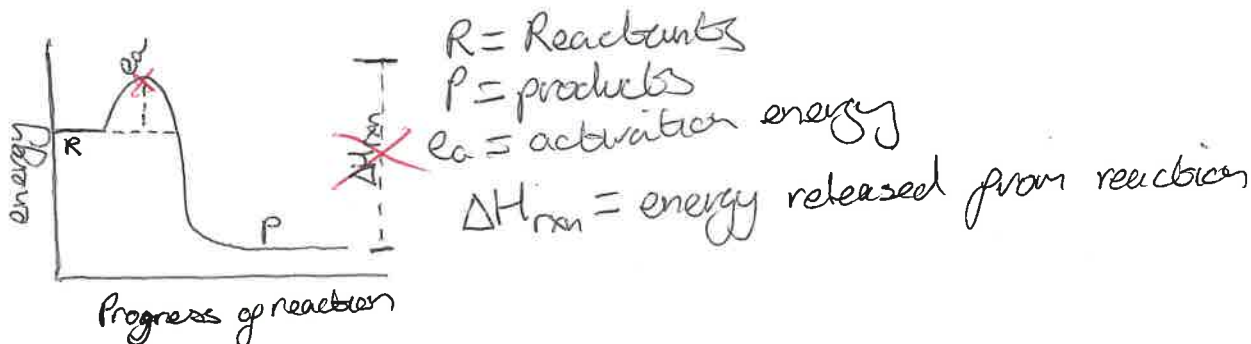
$$OB = \frac{16}{MW} \times \left[d - 2a - \left(\frac{b}{2} \right) \right] \times 100\%$$

$$\frac{16}{152} \times \left[6 - (2 \times 2) - \left(\frac{4}{2} \right) \right] \times 100 = 0\%$$

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

more

Activation energy is the energy required to break the bonds & allow the atoms to re-arrange to ~~smaller~~ stable molecules. While releasing // capturing energy. As RDX has a higher activation energy it is less sensitive to smaller stimuli making it more stable & safer to handle than Mercury fulminate.

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

It shows oxygen has no effect on the rate of reaction, while there is a 1:1 increase of rate of reaction from NO.

This supports by increasing concentration you will have a increase rate of reaction.

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.)

$$Q_{\text{system}} = -Q_{\text{surroundings}}$$

$$420 \times \Delta T$$

Q - system

$$4.184 \times 0.410 \text{ kg} \times 610 \text{ g} \times (23 - 20) = 109 \text{ kJ}$$

Assuming H_2O = calorimeter = 9

Heat

Calorimetry. $-Q_{\text{surrounding}}$

$$Q = HC \times \Delta T$$

$$420 \times 23 = 9960$$

$$109 \text{ kJ} = -9960$$

$$109 \text{ kJ} + 9960 \text{ J} = 118.96 \text{ kJ}$$

$$C_p \times M \times \Delta T$$

$$\Delta_{\text{comb}} H = 118.96 \text{ kJ}$$

Assuming T_1 of calorimeter = 20°C same as water.

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.

$$E = c \div \lambda = \nu$$

$$E = h \times \nu$$

$$E = h \times (c \div \lambda)$$

m p n

$$6.6 \times 10^{-34} \times (3.0 \times 10^8) \div (554 \times 10^{-9}) = 3.57 \times 10^{-19}$$

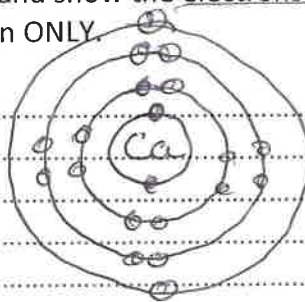
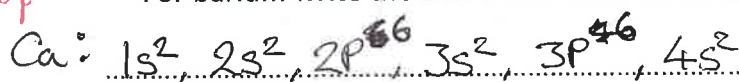
$$\text{Ba } (3.0 \times 10^8) \div (554 \times 10^{-9}) = 541 \times 10^6 \times 6.6 \times 10^{-34} = 3.57 \times 10^{-19}$$

$$\text{Ca } (3.0 \times 10^8) \div (616 \times 10^{-9}) = 487 \times 10^6 \times 6.6 \times 10^{-34} = 3.21 \times 10^{-19}$$

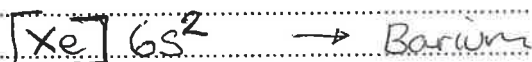
Barium has the higher energy.

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

For barium write the shorthand electron configuration ONLY.



s²
p⁴
d



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

The colours are from electrons absorbing energy & going to higher shells. Followed by falling to a lower shell emitting photons as they fall. The levels they fall correspond to a wavelength which can be colour.

- 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.

$$132 - 56 =$$

 ^{132}Ba ^{138}Ba

$$132 - 56 = 76$$

$$138 - 56 = 82$$

76 neutrons ✓

82 neutrons ✓

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleev?

~~Titanium, aluminium, zinc Zr~~