

ACDA5014 ADVANCED CHEMISTRY OME FINAL EXAM

Student No. 1910566

NAME THOMAS BESWICK

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.

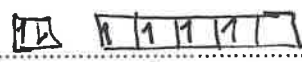
PERIODIC TABLE AND REFERENCE DATA CAN BE TORN OFF OF THE EXAM

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

QUESTION 1:

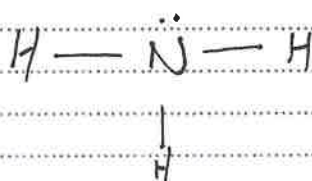
For each of the following statements determine if it is true or false. Justify your answer.

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 - $Cr = [Ar] 4s^2 3d^4$ 
valence electrons displayed above as 4 unpaired.

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° .

FALSE.



Due to the lone pair the angle will be $< 120^\circ$

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

TRUE. $\rightarrow M = \frac{\text{moles solute}}{\text{L solution}}$ $NaCl = 23 + 35 = 58 \text{ g/mol}$

$$M = \frac{1.5 \text{ mol}}{1 \text{ L}} = 1.5 \text{ M} \quad \frac{1.5 \text{ L}}{1} = \frac{87.8}{58} = 1.5 \text{ mol}$$

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.

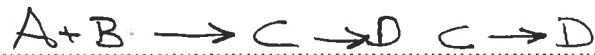
FALSE - Ideal gas equation is used when n , number of moles and R , gas constant are constant. Temperature, pressure and volume are all variables.

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 ✓ - Activation energy is required to begin the reaction to gain products. RDX requires 113 kJ/mol more energy to activate, therefore more stable.

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

3p
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
FALSE ✓ - As B will be the limiting reactant of the reaction therefore increasing A will not speed the reaction up.

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

3p
TRUE ✓ - As the combustion process gives off energy to the environment, hence why combustion gives off heat. ✓

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.

0p
TRUE ✓ - Conservation of energy states that during collisions energy is shared with each other and redirected with heat/light energy emitted due to lost kinetic energy.

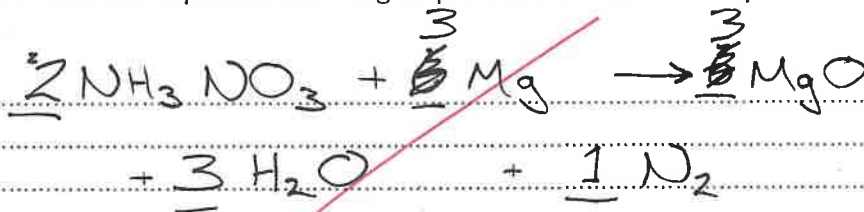
10. (2p) The rate of decomposition of the explosive material decreases when the temperature increases.

2p
FALSE ✓, the rate of decomposition increases with temperature.

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



$$-(2 \times 365) \\ = -730$$

$$+(3 \times 601) + (3 \times 242) \\ = 1803 + 726 \\ = 2529$$

Products - Reactants

$$\Delta_{\text{rxn}} H = -2529 - 730 = -3259 \text{ kJ}$$

$$\text{for one mole} = -1629.5 \text{ kJ}$$

Exothermic due to negative energy value means energy is given off to environment

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

TNT equivalence:

$$\frac{Q_{\text{exp}}}{Q_{\text{TNT}}} = \frac{-1629.5}{2.8}$$

$$\text{NH}_4\text{NO}_3 \\ = 79 \text{ g/mol}$$

$$n = \frac{m}{M} = \frac{1}{79} = 0.012 \text{ mol}$$

$$\frac{Q_{\text{exp}}}{Q_{\text{TNT}}} = \frac{20.62}{2.8} = 7.36$$

$$-1629.5 \times 0.012 \text{ mol} = 20.62 \text{ kJ/g}$$

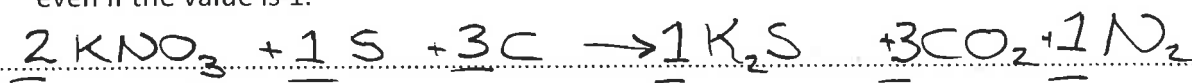
7.36 x more heat produced against TNT

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 ?

$$\text{KNO}_3 = 101 \text{ g/mol} \quad n = \frac{m}{MM} = \frac{45}{101} = 0.45 \text{ mol}$$

$$2 \text{ mol KNO}_3 = 3 \text{ mol CO}_2$$

$$n_{\text{CO}_2} = 0.45 \times \frac{3 \text{ mol CO}_2}{2 \text{ mol KNO}_3} = 0.675 \text{ mol CO}_2$$

$$\text{CO}_2 = 44 \text{ g/mol}$$

$$M = n \times MM = 0.675 \times 44 = \underline{\underline{29.7 \text{ g CO}_2}}$$

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

$$\text{KNO}_3 = 101 \text{ g/mol} \quad n = \frac{m}{MM} = \frac{45}{101} = 0.45 \text{ mol}$$

$$2 \text{ mol KNO}_3 = 5 \text{ mol gas} \quad \text{1 mol gas} = 22.4 \text{ L at STP}$$

$$n_{\text{gas}} = 0.45 \times \frac{5}{2} = 1.125 \text{ mol gas}$$

$$1.125 \times \frac{22.4}{1} = \underline{\underline{25.2 \text{ L}}}$$

Gas produced at STP.

- 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?

$$45 \text{ g KNO}_3 = 0.45 \text{ mol}$$

$$P_2 = 700 \text{ mmHg} = 0.92 \text{ atm}$$

$$T_1 = 0^\circ\text{C} \quad T_2 = 100^\circ\text{C}$$

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

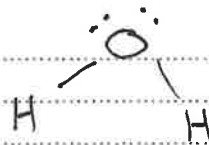
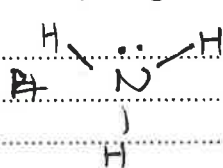
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{1 \times 25.2 \times 373}{273 \times 0.92}$$

$$= \underline{\underline{37.42 \text{ L}}}$$

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

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.

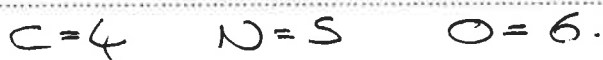
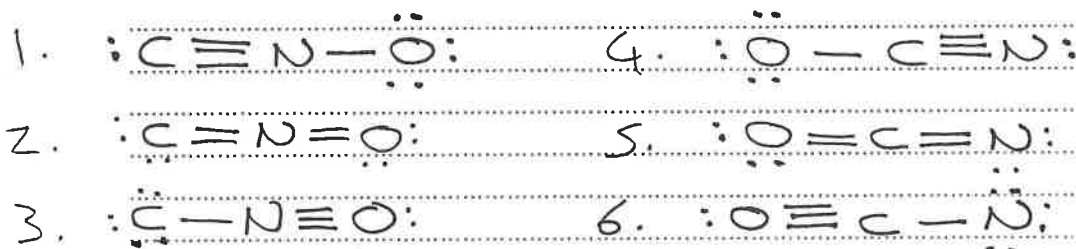


Despite H_2O and NH_3 being similar, they differ in boiling points due to the hydrogen bonds formed in H_2O . These are stronger than any IMF bonds found in standard liquids and allow H_2O to remain in liquid form at much higher temperatures.

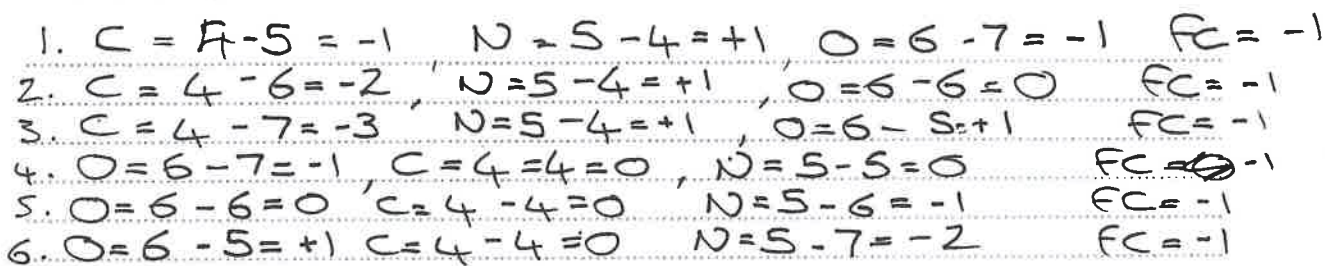
QUESTION 5:

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).



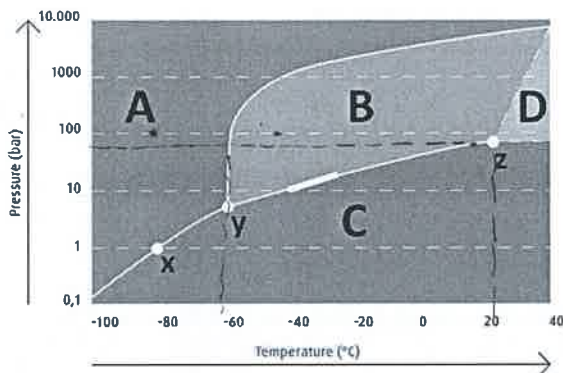
1p b) (3p) Explain in terms of formal charges why fulminate is explosive and cyanite is not



The most stable version is where lowest charge is on most electronegative (O) - for fulminate, this is the 4th structure where C & N are both not in charge and looking to gain/lose electron. For cyanite, this stable structure has C & N at 0, meaning they are stable. To summarise, fulminate's most stable structure is still looking to react to gain/lose electron.

The other characteristic is the bond energy between a central N atom and central C atom.

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



A: Solid

B: Liquid

C: Gas

D: Superheated gas

point x: Sublimation point at 1 atm

point y: ~~P Temp & pressure where all 3 states can exist~~ Critical point

point z: ~~.....~~

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

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

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?

Boiling: 20°C Freezing: -65°C ✓

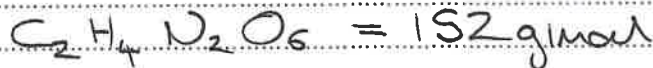
g) (1p) Estimate the conditions of a critical point. 7 bar, -60°C

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 . $22.4 \text{ dm}^3 = 1 \text{ mol gas}$
- $CO_2 = 2 \text{ mol}$ $H_2O = 2 \text{ mol}$ $N_2 = 1 \text{ mol}$

$$C = 2$$



$$O = 6$$

$$H = 4$$

$$N = 2$$

$$\frac{44.8 \text{ dm}^3}{22.4 \text{ dm}^3} = 2 \text{ mol gas}$$

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

$$N_2 = 28 \text{ g/mol}$$

$$H_2O = 18 \text{ g/mol}$$

$$CO_2 = 50 \text{ g/mol}$$

H_2O will move fastest according to Graham's law of ratios to molar mass and velocity

$$\text{Ratio of molar mass} = \frac{18}{28} = \sqrt{\frac{9}{14}}$$

$$\text{Ratio of } \sqrt{m} = \frac{3}{3.74}$$

$$\text{Ratio of velocity} = \frac{1}{(3/3.74)} = 1.24 \times \text{faster}$$

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

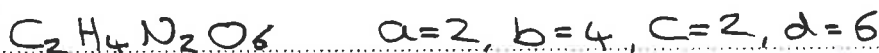
$$O_6 = 96 \text{ g/mol}$$

$$\frac{96}{152} = 0.63$$

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

$$0.63 \times 100 = \underline{63\% \text{ oxygen}}$$

- 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).

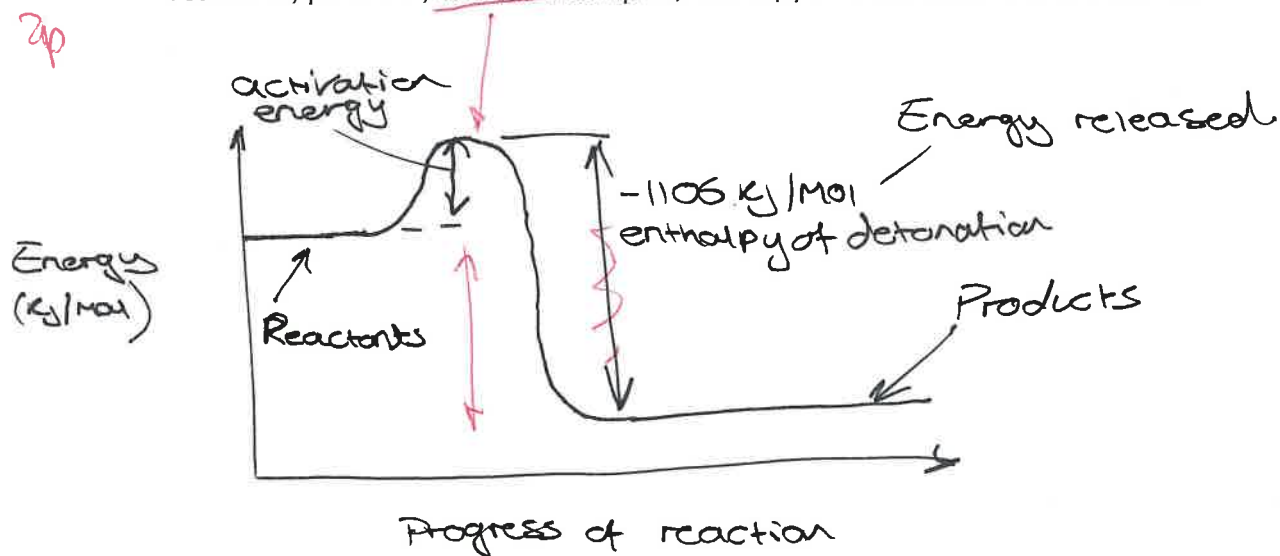


$$\frac{[6 - (2 \times 2) - (4/2)] \times 1600}{152} = \underline{\underline{0\%}}$$

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.

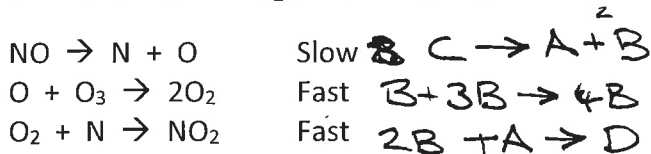
2p

Activation energy is the 'bump' in energy required for an explosive substance to begin decomposition.

In this example, RDX is more stable due to the higher activation energy. Mercury fulminate is easy (and more unstable) as it requires much less energy to activate.

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.

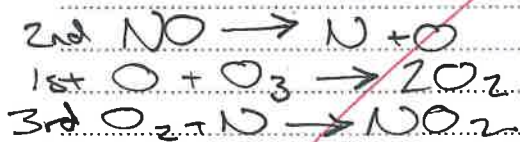


b) (4p) Three experiments were conducted to discover the initial rate of formation of NO_2 values as the concentrations of the reactants change. Use the data in the table below to determine the order of the reaction with respect to each reactant and write the rate law for the reaction

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

$$\text{NO, average} = (0.012 + 0.024 + 0.024) / 3 = 0.02 \text{ mol/L}$$

$$\text{O}_3, \text{ average} = (0.02 + 0.02 + 0.04) / 3 = 0.026 \text{ mol/L}$$



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

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

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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.

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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.

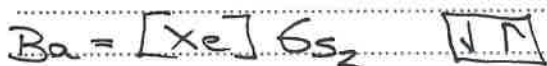
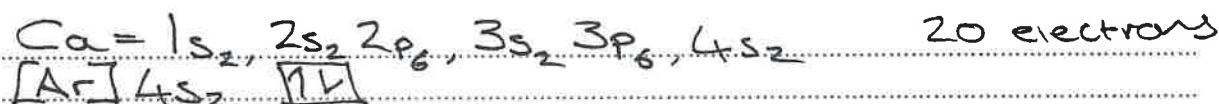
$$C = h \times v = 3 \times 10^8$$

Barium has the higher energy

$$\text{Barium} = \frac{3 \times 10^8}{554} = 541 \text{ kJ}$$

$$\text{Calcium} = \frac{3 \times 10^8}{616} = 487 \text{ kJ}$$

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.

These colours are emitted by the energy of the electrons moving layer to layer within the shell of an atom. With different atoms requiring different energy to enable this movement, various wavelengths are possible.

- 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.

Ba = ~~76~~ 56 protons

~~Mass~~ Neutrons = Atomic mass - protons

2p $^{132}\text{Ba} = 132 - 56 = 76 \text{ neutrons}$

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

EXTRA CREDIT (must give all three) 7

What are three elements predicted by Mendeleev?