

## ACDA5014 ADVANCED CHEMISTRY OME FINAL EXAM

NAME Peter Kennie (1910613) 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.

- 0p 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 - it is in group 6 so  $4s^2 3d^4$

- 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  $120^\circ$ .

False - there is a lone pair of electrons on the N atom  
so  $109.5^\circ$  ✓

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

$1.5 = \frac{\text{mol}}{1} \therefore 1.5 \text{ mol NaCl} \approx 87 \text{ g}$  - 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.

False - the equation breaks down towards 0 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 ✓ - RDX Requires more A.E. ∴ 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 reactants are broken down into their most basic components and reconstituted as the product regardless of how many steps.

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 ✓ -  $[A]^2 = A$  ~~2[A]~~  $= 4A$

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

2p  
True ✓ all combustion reactions give off energy.

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 ✓ - All collisions are perfectly elastic.

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

2p  
False ✓ - using Arrhenius equation  $k = Ae^{-\frac{E_a}{RT}}$

## 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

$$\text{Mg} \& \text{N}_2 = 0 \text{ kJ/mol} \quad \checkmark$$

$$2(-242) + 2(-601) - (2(-365)) = -956 \text{ kJ}$$

$$-956/2 = -478 \text{ kJ/mol}$$

It's negative: exothermic.  $\checkmark$

- c) (3p) How does the heat of reaction from this reaction compare with  $2.8 \text{ kJg}^{-1}$  provided by one gram of TNT.



$$90 \times n = g \quad n = 1 \therefore 1 \text{ mole} \sim 90 \text{ g}$$

$$\cancel{90 \text{ g}} = -478 \text{ kJ} \therefore 1 \text{ g} = \frac{-478}{90} = 5.31 \text{ kJg}^{-1}$$

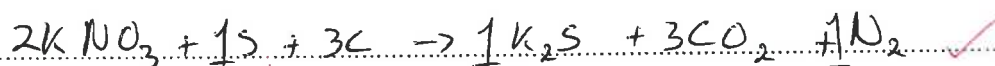
$$5.31 \text{ kJg}^{-1} > 2.8 \text{ kJg}^{-1} \quad 1 \text{ p}$$

## 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  $\text{CO}_2$  are formed from the decomposition of 45 g of  $\text{KNO}_3$ ?

$$45 \text{ g KNO}_3 \div 101 \text{ g/mol} = \frac{45}{101} = 0.4455 \text{ moles}$$

$$\text{Ratio KNO}_3 \rightarrow \text{CO}_2 \text{ is } 2:3 \therefore \frac{0.4455 \times 3}{2} = 0.67 \text{ moles CO}_2$$

$$0.67 \text{ mol CO}_2 \times 44 \text{ g/mol} = 0.67 \times 44 = 29.48 \text{ g CO}_2 \text{ produced}$$

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

$$45 \text{ g KNO}_3 = 0.4455 \text{ moles} \therefore \frac{0.4455}{2} \text{ K}_2\text{S moles} = 0.223 \text{ mol}$$

$$2(0.223) + 0.67 = 1.12 \text{ moles product}$$

$$1.12 \times 22.4 \text{ L/mol} = 25.09 \text{ L of gas products}$$

- d) (3p) 45 g  $\text{KNO}_3$  at STP is heated to 100 degC and the pressure is reduced to 700 mmHg. What is the new volume of the gases?

$$V_1 = 25.09 \text{ L} \quad P_1 = 760 \text{ mmHg} \quad T_1 = 273 \text{ K}$$

$$V_2 = ? \quad P_2 = 700 \text{ mmHg} \quad T_2 = 373 \text{ K}$$

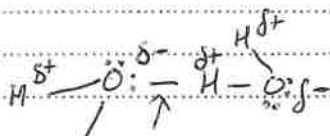
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \therefore \frac{P_1 V_1 T_2}{T_1 P_2} = V_2$$

$$V_2 = \frac{760 \times 25.09 \times 373}{273 \times 700} = 37.22 \text{ L}$$

## QUESTION 4:

(4p) The normal boiling point is  $100^{\circ}\text{C}$  for  $\text{H}_2\text{O}$  and  $-33.3^{\circ}\text{C}$  for  $\text{NH}_3$ , even though the two molecules have almost identical atomic weights. Explain this difference in terms of intermolecular forces, using narrative or cartoons or both.

$\text{H}_2\text{O}$  utilises the "Hydrogen bond" due to dipoles.



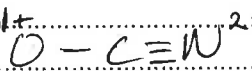
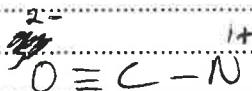
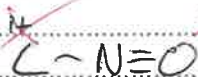
$\text{H}\delta^+ \text{H bond} - \text{intermolecular}$

$\text{NH}_3$  only utilises the London Dispersion force which is much weaker resulting in lower energies required to break the intermolecular forces.

## 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).



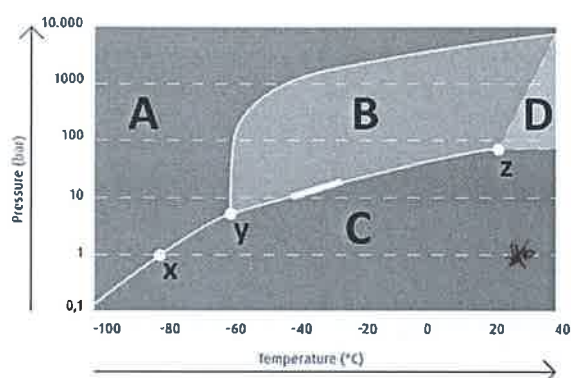
lone pairs?

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,  $\text{CO}_2$ , is shown below:



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

A: Solid

B: Liquid

C: Gas

D: Plasma

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

point x: Sublimation point at 1 bar

point y: Triple point

point z: Critical point

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

- d) (0.5p) If a sample of this substance is cooled from  $-45^\circ\text{C}$  to  $-85^\circ\text{C}$  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?

$B_p = 0^\circ\text{C}$   $F_p = -60^\circ\text{C}$  @ 50 bar

- g) (1p) Estimate the conditions of a critical point. 90 bar @  $20^\circ\text{C}$

## QUESTION 7:

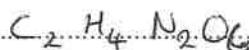
Some high explosives have the general formula  $C_a H_b N_c O_d$ . The oxidiser (O) and the fuel (C, H) are present in the same molecule. Nitrogen atoms are present so that there is a highly exothermic production of hot  $N_2$  gas.

- 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 dm<sup>3</sup> of  $CO_2$ , 44.8 dm<sup>3</sup> of  $H_2O$ , and 22.4 dm<sup>3</sup> of  $N_2$ .



$$\frac{44.8}{22.4} = 2 \quad \therefore \text{ratio} = 2 CO_2 + 2 H_2O + 1 N_2$$

$$a = 2 \quad b = 4 \quad c = 2 \quad d = 6$$



$$2C + 4O + 4H + 2O + 2N$$

$$2C + 6O + 4H + 2N$$

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

$$CO_2 - 44 \text{ mm}$$

$$H_2O - 18 \text{ mm}$$

$$N_2 - 28$$

$H_2O$  as it has the lowest mm.

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

$$6 \times O = 6 \times 16 = 96 \text{ mm}$$

$$1 \text{ mol} : 96 \text{ g } O$$

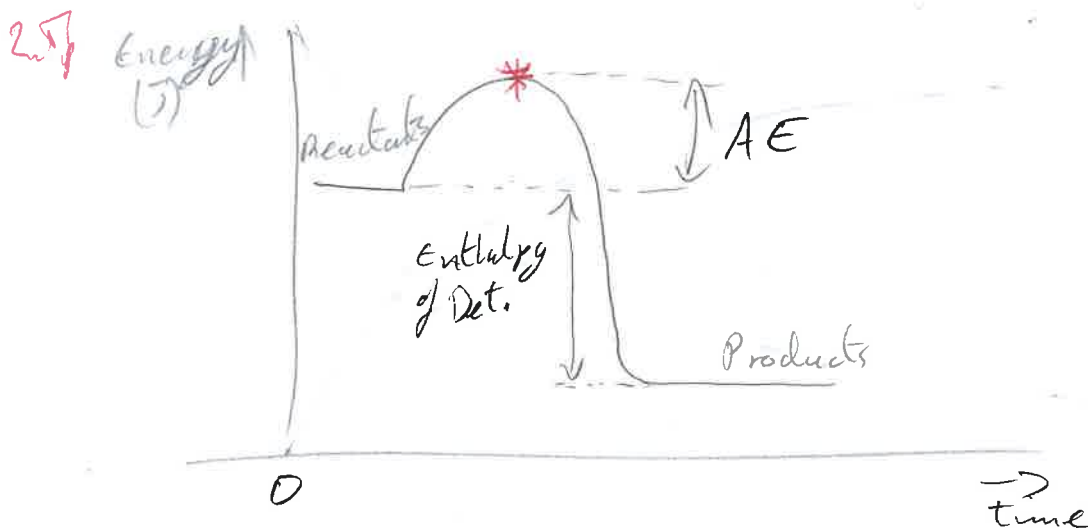
$$\frac{96}{152} = 63.1\%$$

- 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).

**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



- 2.4
- b) (2p) The activation energy for the explosive detonation of RDX is  $199 \text{ kJ mol}^{-1}$  whereas the activation energy for the explosive detonation of mercury fulminate is  $105 \text{ kJ mol}^{-1}$ . Define the term activation energy and hence comment on the relative stability of these two explosives.

Activation energy is the energy required to break the bonds between the atoms.

The less energy required the more likely the reaction is to occur and  $\therefore$  the less stable it is.

RDX requires nearly 2x the AE of mercury Fulminate.

**QUESTION 9:**

Nitrous oxide,  $\text{NO}_2$ , is a common propellant for rocket motors. The proposed mechanism for the formation of  $\text{NO}_2$  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  $\text{NO}_2$  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 | $\text{O}_3$ , 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                 |

4p  
$$\frac{1. k \times [0.012]^a \times [0.02]^b = 0.102}{2. k \times [0.024]^a \times [0.02]^b = 0.204} = \left(\frac{1}{2}\right)^a \times \left(\frac{1}{1}\right)^b = \left(\frac{1}{2}\right)$$

$\therefore a = 1$

$$\frac{k \times [0.024]^1 \times [0.02]^b = 0.204}{k \times [0.024]^1 \times [0.04]^b = 0.204} = \frac{1}{1} \times \frac{1}{2} = \frac{1}{1} \therefore b = 0$$

$k[\text{NO}]^1 \times [\text{O}_3]^0 = \text{Rate}$  ✓

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

2p  
 $k \times [0.012]^1 \times [0.020]^0 = 0.102$

$$0.012 \times 1 = 0.012k = 0.102 \quad k = \frac{0.102}{0.012} = 8.5$$

unit - 1

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

2p

$$\Delta T_{\text{water}} = 3^\circ\text{C} \quad m_{\text{water}} = 610\text{g} \quad 4.184 \times 4 \times 610 = 10.21\text{kJ}$$

$$\frac{10.21\text{kJ}}{420\text{J/}^\circ\text{C}} = 2.43^\circ\text{C} \quad \text{change in temp of calorimeter}$$

$$\text{TNT MM} = 213 \quad \therefore 2.3\text{mol} \quad \checkmark$$

$$\frac{10.21}{2.3} = 4.3\text{kJ/mol}$$

## 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.

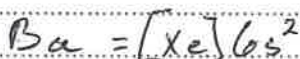
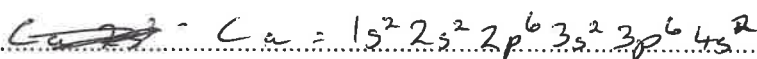
$E \propto \nu$  ~~high wavelength~~

$\nu \propto \frac{1}{\lambda}$   $\therefore$  Barium has higher frequency

and  $\therefore$  more energy

~~$E = h\nu$~~   $E = h \frac{c}{\lambda} = 6.6 \times 10^{-34} \times \frac{3 \times 10^8}{554} = 3.57 \times 10^{-28} \text{ J Barium}$   
 $= \frac{11}{616} = 3.21 \times 10^{-28} \text{ J Calcium}$

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.

Excited electrons change energy state to a lower state releasing a photon dependent on the energy state change.

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

Ba has 56 protons

$^{132}\text{Ba}$  has 76 neutrons

$^{138}\text{Ba}$  has 82 neutrons

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleev?