

ACDA5014 ADVANCED CHEMISTRY OME FINAL EXAM

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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.

True chromium has 4 unpaired electrons in outer most shell electron configuration is ~~[Ar]~~ $4s^2 3d^4$

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° .

True because 3 H equally repelling each other meaning even angles between $360/3 = 120^\circ$

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

True ~~1.5 M/L~~ $23 + 35 = 58 \text{ g/mol NaCl}$

mass = moles $\times$ mm

$$\text{moles} = \frac{\text{mass}}{\text{mm}} = \frac{87.8}{58} = 1.5 \text{ moles} \quad \frac{1.5}{1.5} = 1$$

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 STP - standard temperature and pressure is $0^\circ\text{C} / 273\text{K}$ at 1 atm

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

False ✓ RDX more sensitive due to lower activation energy

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

True ✓ $\Delta H_d = \Delta H_2 - \Delta H_1$ meaning ΔH_d is energy from products - reactance so between not included

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.

False ✓ double the rate will give the square root of A

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

True ✓ combustion gives energy to its environment

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.

False ✓ due to the conservation of energy law the energy can't be lost only changed to another form of energy

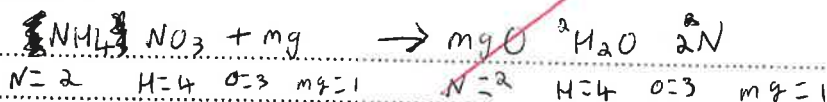
10. (2p) The rate of decomposition of the explosive material decreases when the temperature increases.

False ✓ the rate 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

Products - reactance

$-365 - (-601 + -242) = 478 \text{ kJ/mol}$

endothermic

~~endothermic~~ absorbs

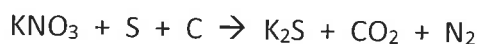
heat from environment because positive answer

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

Heat of reaction is lower with ammonium nitrate

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 ?

$$\text{STP} = T = 273 \quad P = 1 \text{ atm} \quad 12 + 32 = 44 \text{ g/mol CO}_2$$

$$C = 12$$

$$O = 16 \times 2 = 32$$

$$3 \times 44 = 132 \text{ g/mol CO}_2$$

$$K = 39$$

$$N = 14$$

$$O = 16 \times 3$$

$$101 \text{ g/mol KNO}_3$$

$$45/101 = 0.455 \text{ mole KNO}_3$$

$$0.455 \times 44 = 20.02 \text{ g CO}_2$$

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



$$\text{STP} = T = 273 \text{ K} \quad P = 1 \text{ atm}$$

$$K = 39$$

$$N = 14$$

$$O = 16 \times 3$$

$$101 \text{ g/mol KNO}_3$$

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{0.455 \times 0.0821 \times 273}{1}$$

$$V = 10.198 \text{ L KNO}_3 \text{ 3.D.P.}$$

$$45/101 = 0.455 \text{ mole KNO}_3$$

- 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?

$$T_1 = 273 \text{ K}$$

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

$$T_2 = 100^\circ\text{C} = 373 \text{ K}$$

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

$$V_1 = 10.198 \text{ L}$$

$$V_2 = ?$$

$$P_1 V_1 T_2 = P_2 V_2 T_1$$

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

$$V_2 = \frac{1 \times 10.198 \times 373}{0.92 \times 273}$$

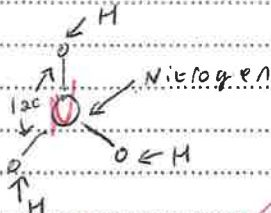
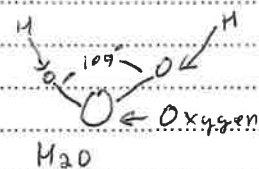
$$V_2 = 15.145 \text{ L KNO}_3 \text{ 3.D.P.}$$

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.

Oxygen central atom with 2 Hydrogen in H_2O

Nitrogen central atom with 3 Hydrogen in NH_3



NH_3 120 between bonds with weaker bond forces meaning
break easier giving lower boiling point

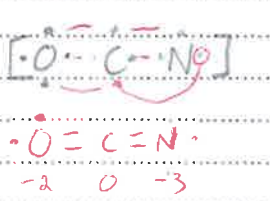
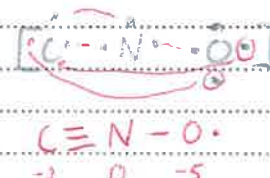
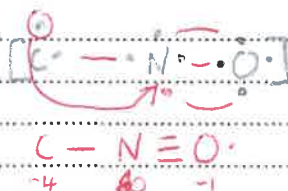
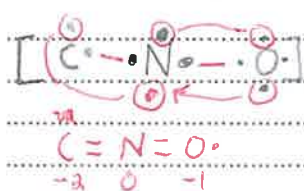
Oxygen more electro negative than N so bond to H stronger than N

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).

$1 \times 15 = 3 \text{ve}$
 $3 \times 16 = 48 \text{ve}$
 $1 \times 14 = 2 \text{ve}$



have pairs!!

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

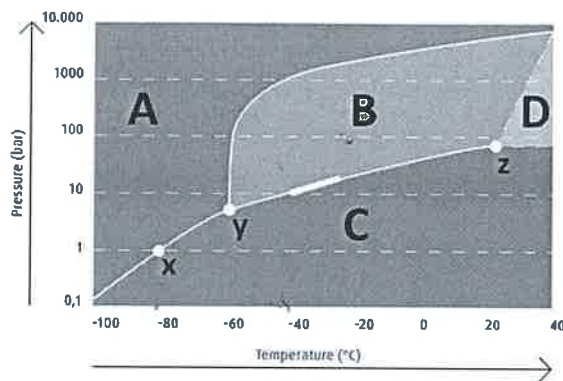
Fulminate bonds valence electrons are more energetic because
its easier to break bonds closer to all being balanced
so higher electro negativity

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

bonds can be broken and energy released relatively easily
low activation energy with good output energy

QUESTION 6:

The phase diagram of carbon dioxide, 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: ~~solidification~~ standard pressure

point y: ~~no condensation~~ critical point

point z: ~~vaporization~~ fusion

- 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? ... ~~no~~ 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?

~~0°C and 60°C~~

- g) (1p) Estimate the conditions of a critical point... All three states possible (gas)

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 .

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

$$m = 152 \text{ g}$$

$$\text{mass} = \text{moles} \times MM$$

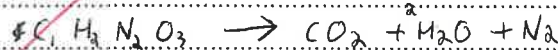
$$\text{moles} = \text{mass} / MM$$

$$\text{moles} = 152 / 152 = 1 \text{ mole}$$

$$CO_2 = 44.8 \text{ dm}^3$$

$$H_2O = 44.8 \text{ dm}^3$$

$$N_2 = 22.4 \text{ dm}^3$$



mm

$$CO_2 = 44 \text{ g/mol}$$

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

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

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

H_2O will move the fastest due to its molar mass being the lowest and Graham's law stating average velocity $\propto 1/\sqrt{MM}$

$$H_2O: 1 \times 2 + 16 = 18 \text{ g/mol}$$

$$CO_2: 12 + 16 \times 2 = 44 \text{ g/mol}$$

$$N_2: 14 \times 2 = 28 \text{ g/mol}$$

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

~~Kristian Kofsky - vision care~~

oxygen % gained by

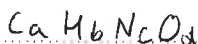


$$\% = \frac{[d - (2a) - (b/2)] \times 1600}{MM}$$

$$\% = \frac{\text{number moles oxygen}}{\text{Total moles}}$$

28

- 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).



oxygen % calculation

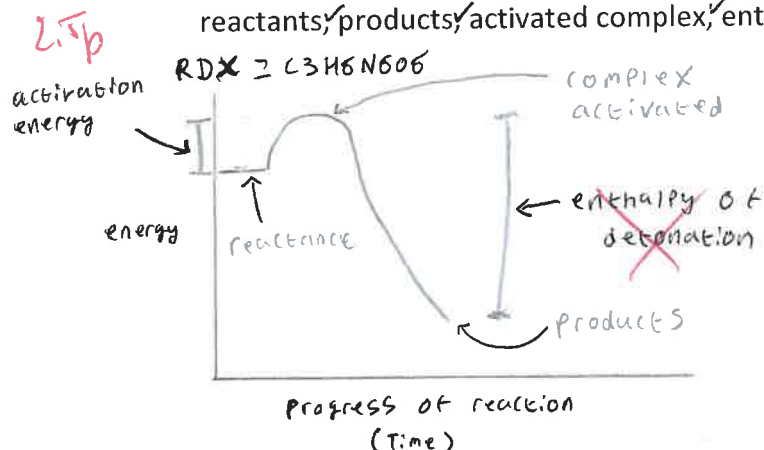
$$\% = \frac{[d - (2a) - (b/2)] \times 1600}{M}$$

$$\% = ?$$

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



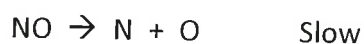
- 2p
- b) (2p) The activation energy for the explosive detonation of RDX is 199 kJ mol^{-1} whereas the activation energy for the explosive detonation of mercury fulminate is 105 kJ mol^{-1} . Define the term activation energy and hence comment on the relative stability of these two explosives.

mercury fulminate has a lower activation energy than RDX meaning its more sensitive hence its use as a primary explosive.

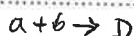
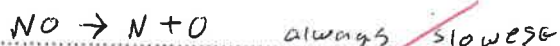
activation energy is the amount of energy required to make the product react.

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

experiment 1 and 2 O_3 same and NO doubles

In experiment 2 and 3 NO same O_3 doubles and initial rate

$$\text{Assume } \Delta H_1 = \Delta H_2 = \Delta H_3$$

$$v = k [\text{N}]^x [\text{O}_3]^y$$

$$8.29 \times 10^{-3} \left(\frac{1}{0.024} \right)^x = \frac{1}{0.020}$$

$$\text{rate} = \frac{\Delta x}{\Delta t}$$

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

$$k = \frac{\text{rate}}{(\text{A})^x (\text{B})^y}$$

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

2p The rate law is important to know so that theoretical values can be worked out and used for example to know the performance of petrol in a car

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

$$T_1 = 20.0^\circ\text{C} + 273 = 293\text{ K} \quad \Delta T = 3\text{ K}$$

$$T_2 = 23.0^\circ\text{C} + 273 = 296\text{ K} \quad 3^\circ\text{C}$$

$$\Delta H = S M \Delta T$$

$$\Delta H = 4.184 \times 500 \times 3$$

$$= 6276\text{ J}$$

500g

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

barium due to shorter wavelength

barium	calcium
$v = c/\lambda$	$v = c/\lambda$
$v = 3.0 \times 10^8 / 554 \times 10^{-9} \text{ m}$	$v = 3.08 \times 10^8 / 616 \times 10^{-9} \text{ m}$
$v = 5.415 \times 10^{14} \text{ hertz barium}$	$v = 5 \times 10^{14} \text{ hertz calcium}$
$E = h v$	$E = 6.6 \times 10^{-34} \times 5.415 \times 10^{14}$
$E = 3.5739 \times 10^{-19} \text{ J}$	$E = 6.6 \times 10^{-34} \times 5 \times 10^{14}$
	$E = 3.3 \times 10^{-19} \text{ J}$

calcium less energy

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

Op



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

Op

colours are produced by the frequency and wavelength of the molecules

- 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.

Op

~~56 $\times$ 211a~~

~~132ba $\times$ 20~~

~~138ba $\times$ 26~~

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleev?

~~Lithium~~

~~Sodium~~

~~Potassium~~