

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 as Chromium is one of the elements that does follow the electron configurations rules

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 NH_3 has a bond angle of

True as it has 3 electron groups

False $\checkmark$ it has 4 electron groups 3 bonded 1 lone pair

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

True $\checkmark$

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 gases are discussed in terms of STP so 1 atm and 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 ✓ RDX is more stable as it has a higher activation energy

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

1p

yes cause ~~whether~~ a true ✓ as
for a Hess cycle is reversible in
any direction

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 ✓ it would multiple the react rate by a factor of 4

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

2p

~~the true as they all have negative~~
~~a H and give off energy~~
False as they have positive give
out heat when combusted

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

False ✓ ~~when a collision due to~~
the conservation laws the would repel
in the opposite direction at the same
speed

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

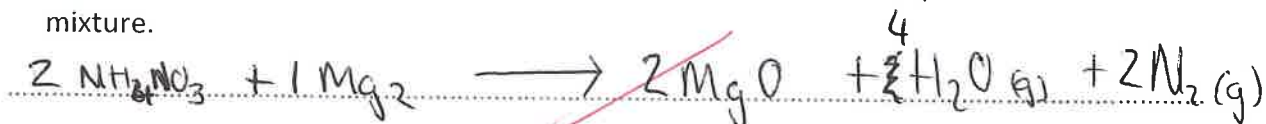
2p

False ✓ rate of decomposition would increase
with increase in heat

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

$$\Delta H_f = \sum (\text{Products}) - \sum (\text{Reactants})$$

$$= (\text{H}_2\text{O})_4 + (\text{MgO})_2 - (\text{NH}_4\text{NO}_3)_2$$

$$= (4 \times -242) + (2 \times -601) - (2 \times -365)$$

$$= (-968 + -1202) - (-730)$$

$$= (-2170) - (-730)$$

$$\Delta H_f = -1440 \text{ kJ/mol}$$

This reaction is exothermic as when calculating ΔH_f using sum of products - sum of reactants = a negative result

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

op

~~Our~~ the reaction is about half as powerful as that of 1 gram of TNT plus the reaction about is negative whereas TNT is positive meaning the reaction absorb heat rather than gives off heat.

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 ?

moles of b = $\frac{\text{coeff of B}}{\text{coeff of A}}$ moles of $\text{KNO}_3 = \frac{45}{101} = 0.446$

$$\frac{\text{CO}_2}{0.446} = \frac{3}{2}$$

$$\text{CO}_2 = \frac{3}{2} \times 0.446 \quad \text{mass of } \text{CO}_2 = 0.669 \times 44$$

$$x = 0.669 \quad = 29.436 \text{ g}$$

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

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$n = \frac{45}{101} = 0.446$$

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

$$V = \frac{0.446 \times 0.0821 \times 273}{1}$$

$$T = 273$$

$$V = 9.996 \text{ L}$$

- 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?

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

$$V_2 = \frac{760 \times 9.996 \times 373}{700 \times 273} = 14.83 \text{ L}$$

$$V_2 = 14.83 \text{ L}$$

$$P_1 = 760 \text{ mmHg}$$

$$V_1 = 9.996 \text{ L}$$

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

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

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

$$V_2 = ?$$

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.

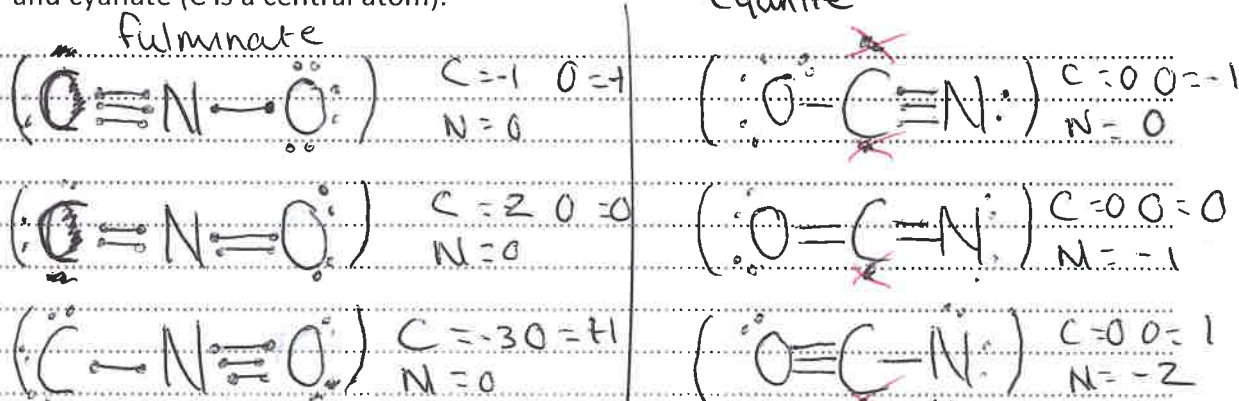
H_2O is polar compared to NH_3 which is ~~non polar~~. Both molecules include hydrogen bond which are ~~both~~ weak.

The H_2O has a strong dipole which attracts the Hydrogen atoms to its Oxygen, whereas NH_3 only has London forces and hydrogen bonds which are a lot weaker. Oxygen attracts the hydrogen as they are its very electronegative.

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 cyanate is not

Fulminate is explosive as the formal charge of the fulminate ion is -2 whereas the cyanate anion is negative 1.

Therefore the fulminate ion attracts more electrons therefore ~~it~~ requires more to be complete. This could have an overload of oxygens and explode.

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

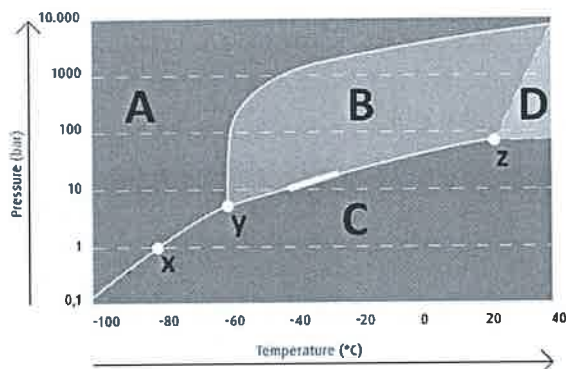
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QUESTION 6:

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



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

- A: Solid
- B: liquid
- C: gas
- D: Super-critical *what?*

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

- point x: Melting point
- 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°C to -85°C at a pressure of 100 bar, what phase change will occur? gas to liquid - ~~solid~~ deposition

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?

-90°C is freezing, boiling point is past critical temperature

g) (1p) Estimate the conditions of a critical point. 90 bar, 20°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 .

$$\text{No of moles } CO_2 = 44.8 \div 44 = 1.02 \quad \text{moles of } CO_2 = \frac{44.8}{44} = 1.02$$

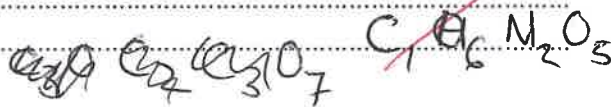
$$H_2O = 44.8 \div 18 = 2.5$$

$$N_2 = 22.4 \div 28 = 0.8$$

$$CO_2: 1.02 \times 1.4 = 1.43$$

$$H_2O: 2.5 \times 1.4 = 3.5$$

$$N_2: 0.8 \times 1.4 = 1.12$$



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

~~Oxygen H_2O as its the most electro negative so attracts the most electrons~~

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

$$16 \times 5 = \frac{80}{152} \times 100 = 52.6\%$$

- 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).

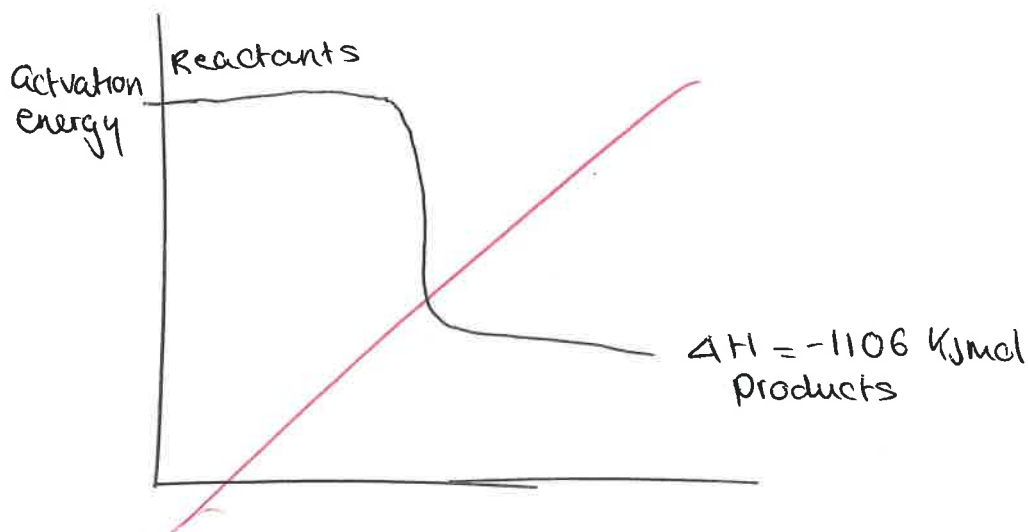
$$OB = \frac{16}{152} \times \left[5 - 2(1) - \frac{6}{2} \right] \times 100$$

$$= 0\%$$

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



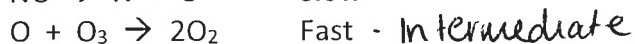
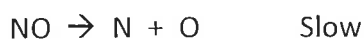
- b) (2p) The activation energy for the explosive detonation of RDX is 199 kJ mol^{-1} whereas the activation energy for the explosive detonation of mercury fulminate is 105 kJ mol^{-1} . Define the term activation energy and hence comment on the relative stability of these two explosives.

2p

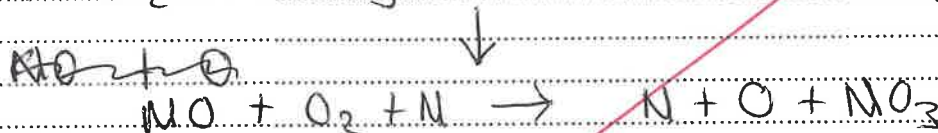
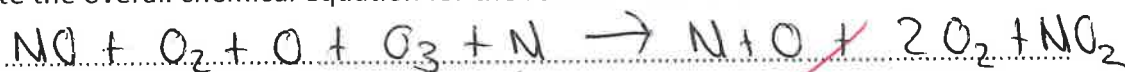
RDX would be more stable as it requires a bigger stimulus to reach the activation energy.

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

$$[\text{NO}]^1, [\text{O}_3]^0 \quad \text{rate law} = k[\text{NO}]^1 \quad \checkmark$$

the NO reaction would take

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

$$k = \frac{\text{initial rate}}{[\text{NO}]^1} = \frac{0.204}{0.024} = k = 0.85$$

unit -1

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

The rate law supports the mechanism as it doesn't include the intermediate step of $O + O_3 \rightarrow 2O_2$ as it doesn't affect the rate of the 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.

$$q = mc\Delta T$$

$$= 1100 \times 4.184 \times 3$$

$$q = 1380.72$$

$$H_c = \frac{q}{\Delta T} = 460 \text{ kJ/mol}$$

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.

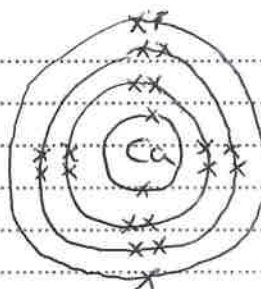
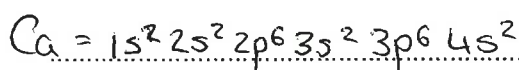
Equations
 $E = \frac{hc}{\lambda}$
 $E = h \times \nu$

Ca energy = $\nu = \frac{3 \times 10^8}{616 \times 10^{-9}}$
 $E = 4.87 \times 10^{14} \times 6.6 \times 10^{-34}$
 $E = 3.21 \times 10^{-19} \text{ J}$

Ba energy = $\nu = \frac{3 \times 10^8}{554 \times 10^{-9}}$
 $E = 5.42 \times 10^{14} \times 6.6 \times 10^{-34}$
 $E = 3.58 \times 10^{-19} \text{ J}$

therefore 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.



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

These Colours are produced by the outer shell electrons of the two atoms getting energised and excited, then jump to a higher energy level emitting light in their respective 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.

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

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

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleev?

Carbon, nitrogen, oxygen