

ACDA5014 ADVANCED CHEMISTRY OME FINAL EXAM

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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.

1p

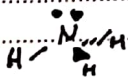
1. (2p) Chromium metal (atomic number 24) produces silver-white colour in a standard flame test as a result of the excitation of valence electrons. Chromium atom has 4 unpaired electrons in the outermost shells that can be excited in such test.

False.

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° .

False - Ammonia forms a pyramidal structure due to the presence of the electron lone pair. This causes the bond angle of $\text{H}-\text{N}-\text{H}$ to be less than 109.5° .



2p

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

True, there is 1.5 mol of NaCl present.
Corresponding mass of NaCl = $1.5 \times \text{MM NaCl}$
 $= 1.5 \times (23 + 35.5)$
 ≈ 87.75 or 87.8 g.

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 - at these ~~low~~ temperatures, the volume of gas would tend towards 0 which is impossible. Vice-versa for const T as $P \rightarrow 0$ volume would approach infinity.

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 and is therefore more difficult to initiate.

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

2p

True ✓ - A multi step reaction resulting in the same products should have the same enthalpy change as a single step reaction. This is how "Reactants $\rightarrow$ Products" can be used to calculate reaction enthalpy. $\xrightarrow{\text{elements}}$ using $\Delta H_f^\circ - \Delta H_f^\circ = \Delta H_{rxn}$.

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 ✓ - If second order then $k = [A]^2$ by doubling [A], k will increase with respect to $(2)^2 = 4$. And so will quadruple not double.

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

1p

True ✓ - all combustion reactions result in bonds forming with O_2 . Bond-forming is an exothermic process.

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 ✓ - for an ideal gas it is assumed that collisions are elastic, therefore no energy is lost in collisions.

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

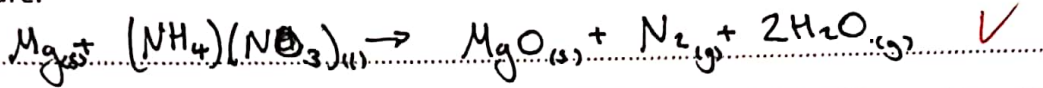
2p

False ✓ - Using $k = Ae^{-\frac{E_a}{RT}}$ as T increases, $-\frac{E_a}{RT}$ decreases. Therefore $\frac{A}{e^x}$ also increases, leading to an increase in reaction rate. Not decrease.

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.

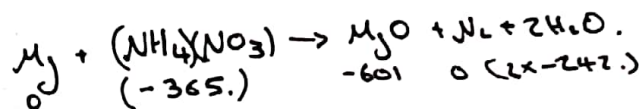


- b) (3p) Using the standard heats of formation listed below, calculate the heat of reaction for molar quantities of the reactants. Is this process exothermic or endothermic? Explain

Ammonium nitrate (solid) -365 kJ/mol

Magnesium oxide (solid) -601 kJ/mol

Water (gas) - 242 kJ/mol



$$\Delta H_{\text{rxn}} = \Delta H_{\text{f, p}} - \Delta H_{\text{f, r}}$$

$$[-601 + (2 \times -242)] - (-365)$$

$$= (-1085) - (-365)$$

$$= -720 \text{ kJ mol}^{-1} \quad 2p$$

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

Convert into kJ mol⁻¹

$$= \frac{\text{mm kJ}}{\text{g}}$$

$$\text{mm} = 275$$

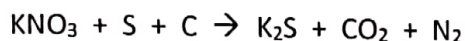
$$\text{MM TNT} = (7 \times 12) + (5 \times 1) + (14 \times 3) + (16 \times 9)$$

$$275 \times 2.8 = 770 \text{ kJ mol}^{-1} \text{ released.}$$

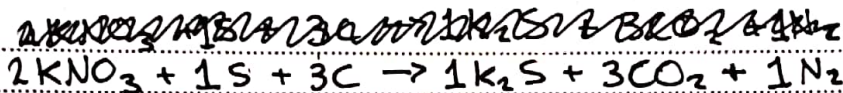
$$-770 < -720 \text{ therefore, TNT releases more energy.}$$

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 ?

$$\text{mol KNO}_3 = \frac{45}{\text{MM KNO}_3} = \frac{45}{39.1 + 14 + (3 \times 16)} = \frac{45}{101.1} = 0.4451 \text{ mol KNO}_3.$$

$$\text{Ratio of CO}_2 \text{ produced per mol KNO}_3 = \frac{3}{2} \therefore 0.4451 \times \frac{3}{2} = \text{mol CO}_2 = 0.6677 \text{ mol CO}_2.$$

$$g = n \times \text{MM} \quad 0.6677 \times 44 = 29.3768 \text{ g CO}_2.$$

$$\approx \underline{29.38 \text{ g}}$$

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

$$\text{Produce } 0.6677 \text{ mol CO}_2 + \frac{0.4451}{2} \text{ mol N}_2$$

$$= 0.6677 + 0.2226 = 0.8903 \text{ mol gasses formed.}$$

$$1 \text{ mol occupies } 22.4 \text{ L at STP.}$$

$$\text{Therefore } 0.8903 \text{ mol occupies } 0.8903 \times 22.4$$

$$= \underline{19.94 \text{ L}}$$

- 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?

$$700 \text{ mmHg} = \frac{700}{760} \text{ atm} = 0.921.$$

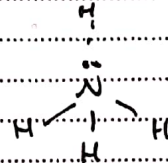
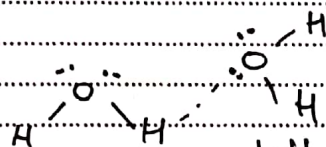
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = nR \therefore \frac{P_1 V_1 T_2}{T_1 P_2} = V_2.$$

$$\frac{1 \times 19.94 \times 373.15}{273.15 \times 0.921} = \underline{29.58 \text{ L}}$$

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.

H_2O is more polar molecule with stronger hydrogen bonding. It is easier for hydrogen bonding to occur in water due to the size and shape of the molecule.



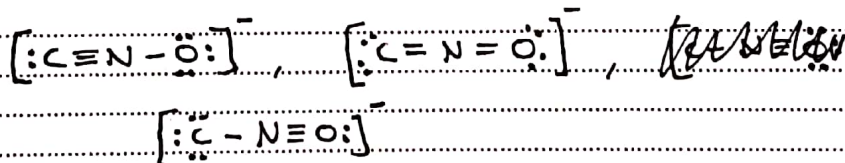
better structure for hydrogen bonding as O is more electronegative than N.

QUESTION 5:

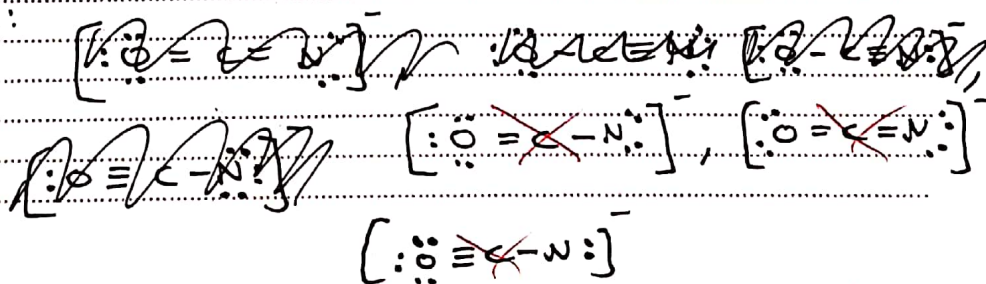
Mercury (II) fulminate $\text{Hg}(\text{CNO})_2$ is a primary explosive whereas mercury (II) cyanate $\text{Hg}(\text{OCN})_2$ is not explosive in nature.

- a) (3p) Draw all resonance structures, three for each anion, fulminate (N is a central atom) and cyanate (C is a central atom).

Fulminate:



Cyanate:



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

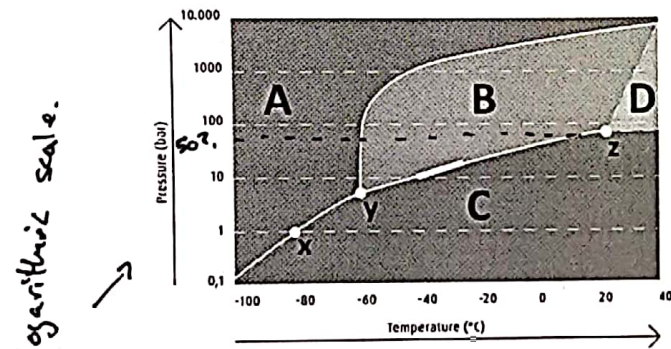
The fulminate ion has the less electronegative atom of Carbon to carry a formal charge of -1 . Whereas in the cyanate ion Carbon has a formal charge of 0 which is more stable.

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

Low activation energy for decomposition.

QUESTION 6:

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



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

A: Solid Phase ✓
 B: Liquid Phase ✓
 C: Gas Phase. ✓
 D: Supercritical fluid. ✓

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

point x: Sublimation 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? Freezing. ✓

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

Condensing. ✓

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

boil = 15°C freeze = -60°C ✓

- g) (1p) Estimate the conditions of a critical point. 31.1°C 73.8 bar? ✓

Pressure Scale is logarithmic, hard to judge pressure values from graph.

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 .

Forms 2 mol CO_2 2 mol H_2O 1 mol N_2 .

C H N O

$C_2 H_4 N_2 O_6$

✓

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

$H_2O(g)$ - Graham's law states $u \propto \frac{1}{\sqrt{M}}$

H_2O has smallest M .

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

$$\frac{96}{152} \times 100 = 63.15\%$$

- 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).

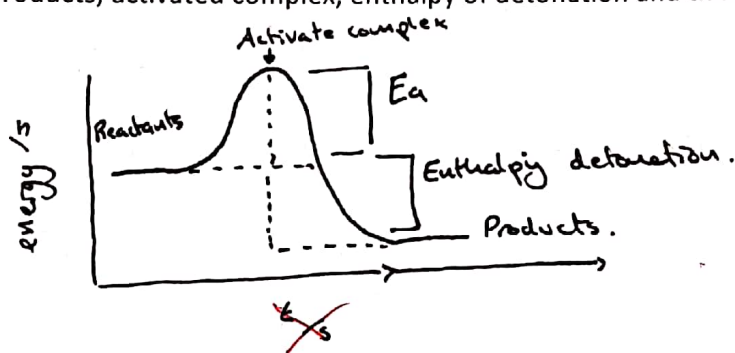
$$\frac{16}{152} \times [6 - (2 \times 2) - (\frac{4}{2})] = 0$$

$$\therefore = 0$$

QUESTION 8:

An explosive, RDX has an enthalpy of detonation of $-1106 \text{ kJ mol}^{-1}$.

- 3p a) (3p) Sketch the reaction profile ("energy" vs. "progress of reaction") showing the reactants, products, activated complex, enthalpy of detonation and the activation energy

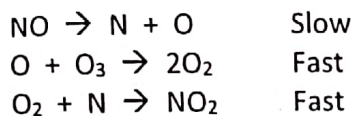


- 2p b) (2p) The activation energy for the explosive detonation of RDX is 199 kJ mol^{-1} whereas the activation energy for the explosive detonation of mercury fulminate is 105 kJ mol^{-1} . Define the term activation energy and hence comment on the relative stability of these two explosives.

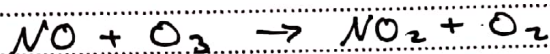
Activation energy is the energy barrier that needs to be overcome for a reaction to take place. RDX has a higher activation energy and therefore requires more energy input to initiate than mercury fulminate. Therefore, RDX can be considered more stable.

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

4p

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

Order $\text{NO} = 1$ Order $\text{O}_3 = 0$

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

$$\text{or Rate} = k[\text{NO}]$$

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

3p

$$\frac{0.102}{0.012} = 8.5 \text{ s}^{-1}$$

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

In the mechanism $\text{NO} \rightarrow \text{N} + \text{O}$ was stated to be the slowest step and therefore determines the rate. Additionally it has 1 as the coefficient for NO in the mechanism which should be the same for the rate order. ✓

QUESTION 10:

(4p) A 500 g sample of TNT ($\text{C}_7\text{H}_5\text{N}_2\text{O}_6$) 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.

$$q_{\text{system}} = -(q_{\text{water}} + q_{\text{calorimeter}})$$

$$q_{\text{water}} = mc\Delta T \quad q_{\text{cal}} = HC\Delta T$$

$$(4.184 \times 610 \times 3) + (420 \times 3)$$

$$q_{\text{sys.}} = + (8916.72) \text{ J}$$

$$\frac{500}{138} = 1.81 \text{ mol} = -8916.72 \text{ J}$$

$$1 \text{ mol} = -4904.1965$$

$$\therefore \Delta H_{\text{comb TNT}} = -4.9 \text{ kJ mol}^{-1}$$

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.

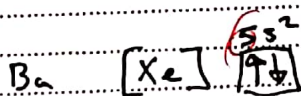
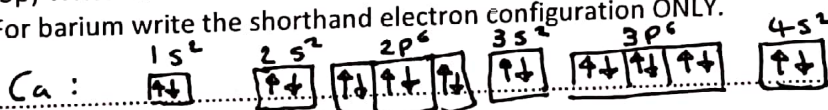
$$c = \lambda \nu \quad \nu = \frac{c}{\lambda} \quad E = h\nu$$

Ba $\frac{3 \times 10^8}{554 \times 10^{-9}} = \nu = 5.415 \times 10^{14} \times 6.63 \times 10^{-34} = 3.57 \times 10^{-19} \text{ J}$

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

Therefore Green has 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.

Electrons gain energy which elevates them to an excited state. These electrons then de-excite whilst releasing a photon with energy equal to the electron state change.

- 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}Ba has 76 neutrons.

^{138}Ba has 82 neutrons. ✓

2p

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleeev?

12