

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.

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$ True as there are only 4 electrons in the outer shell and they like to be by themselves.
 $AR [4s^2 3d^4]$ $\uparrow\downarrow \uparrow \uparrow \uparrow$

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° .

$\begin{array}{c} H - \overset{\cdot\cdot}{N} - H \\ | \\ H \end{array}$ False because it is not trigonal planar. it is tetrahedral which gives a different bond angle.

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

$M = \frac{\text{moles}}{\text{litres}}$ $1.5 = \frac{\text{moles NaCl}}{1}$ $\therefore 1.5 \text{ mol NaCl}$
 $MM \text{ NaCl} = 58.5 \text{ g/mol}$ $58.5 \times 1.5 \text{ mol} = 87.75 \text{ g NaCl}$ True if you round up. false if you don't.

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.

$PV = nRT$ True. As temperature decreases so too does pressure.
 Gay-Lussac $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

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

Qp
RDX is less stable as it requires less energy to start the reaction. So True.

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

2p
True. ✓ The enthalpy will be the enthalpy, whether you get there by doing heats of formation or Calorimetry.

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 A is second order, then doubling A will quadruple the rate.

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

2p
True. ✓ Combustion gives off heat so is exothermic.

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. ✓ They wouldn't lose all of their kinetic energy. They would bounce off each other like snooker balls do.

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

2p
False. ✓ If you make a bomb hotter, the faster the fill will degrade.

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

3p

$$\Delta H_{\text{rxn}} = \sum \Delta H_f \text{ products} - \sum \Delta H_f \text{ reactants}$$

$$= (5 \times -601 + 3 \times -242) - (2 \times -365)$$

$$= (-3005 - 726) - (-730)$$

$$= -3731 + 730$$

$$\Delta H_{\text{rxn}} = -3001 \text{ kJ/mol}$$

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

1p

$$\text{Molar Mass } \text{NH}_3\text{O}_4 = 81 \text{ g/mol} \quad \text{So } 81 \text{ g } \text{NH}_3\text{O}_4 \text{ gives } 3001 \text{ kJ energy}$$

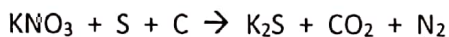
$$\therefore 1 \text{ g } \text{NH}_3\text{O}_4 \text{ gives } \frac{3001}{81}$$

$$= 37 \text{ kJ/g}$$

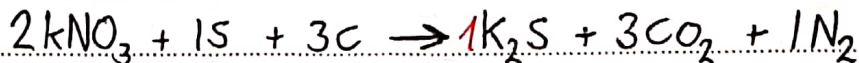
This reaction gives 13 times more heat than 1g of TNT

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 ?

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

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

$$\text{moles} = \frac{m}{\text{MM}}$$

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

$$\text{ratio KNO}_3 : \text{CO}_2$$

$$2 : 3$$

$$0.45 : 0.68$$

$$\text{MM CO}_2 = 44$$

$$\text{mass CO}_2 = 0.68 \text{ mol} \times 44 \text{ g/mol}$$

$$\text{mass CO}_2 = 29.92 \text{ g} \checkmark$$

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

$$\text{mol CO}_2 = 0.68 \checkmark$$

$$\text{mol N}_2 = 0.23 \checkmark$$

$$\text{ratio KNO}_3 : \text{N}_2$$

$$2 : 1$$

$$0.45 : 0.23$$

$$\text{total mol gas produced} = 0.91 \text{ mol} \checkmark$$

$$\text{STP } 1 \text{ atm}$$

$$273 \text{ K } 298 \text{ K}$$

$$PV = nRT$$

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

$$V = \frac{0.91 \times 0.821 \times 298}{1}$$

$$V = 222.64 \text{ Litres of gas}$$

- 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?

$$V = ?$$

$$n = 0.91 \text{ mol}$$

$$R = 0.821$$

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

$$P = 0.92$$

$$100^\circ\text{C} = 100 + 273 \text{ K}$$

$$= 373 \text{ K}$$

$$1 \text{ atm} = 760 \text{ mm Hg}$$

$$700 \text{ mm Hg} = 0.92 \text{ atm}$$

$$V = \frac{0.91 \times 0.821 \times 373}{0.92}$$

$$V = 302.9 \text{ Litres of gas}$$

QUESTION 4:

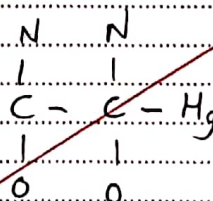
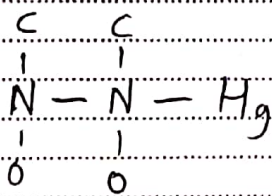
(4p) The normal boiling point is 100°C for H_2O and -33.3°C for NH_3 , even though the two molecules have almost identical atomic weights. Explain this difference in terms of intermolecular forces, using narrative or cartoons or both.

H_2O has special intermolecular forces and dipole-dipole interaction on the molecules which NH_3 doesn't have, so more energy is required to turn water from liquid to gas.

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 cyanite is not

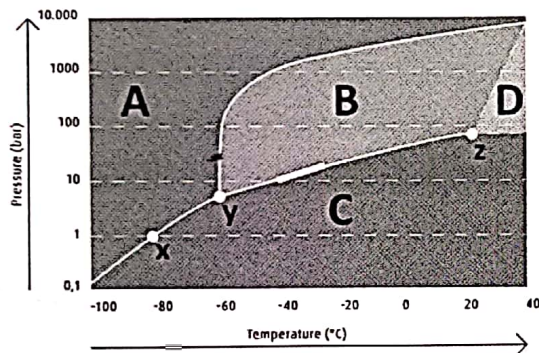
Fulminate is less formal than cyanite so tends to explode at the slightest provocation. Cyanite wears a dinner jacket and bow tie everywhere so doesn't want to explode.

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

As my apprentice mentor once told me "It is one angry little sod".

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: Where it can be both liquid & Gas at the same time.

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

point x: Here be treasure.
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?

Condensation.

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

-60°C ?

- g) (1p) Estimate the conditions of a critical point. 20°C at 95 bar.

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.

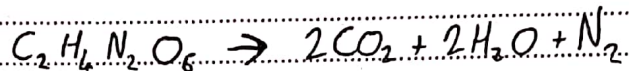
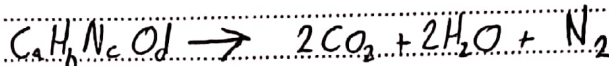
- a) (4p) For an unknown explosive of general formula $C_a H_b N_c O_d$ and a molar mass of 152 g/mol, determine the coefficients a , b , c and d if 152 g of this material decomposes to form 44.8 dm³ of CO_2 , 44.8 dm³ of H_2O , and 22.4 dm³ of N_2 .

$$4. 1 \text{ mol} = 22.4 \text{ dm}^3$$

$$\therefore 2 \text{ mol } CO_2 \text{ produced}$$

$$2 \text{ mol } H_2O$$

$$1 \text{ mol } N_2$$



$$MM \text{ } C_2 H_4 N_2 O_6 = 152 \text{ g/mol}$$

$$a = 2, b = 4, c = 2, d = 6$$

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

$$\text{Velocity of gas} = \frac{1}{\sqrt{MM}}$$

$$CO_2 = \frac{1}{\sqrt{44}}$$

$$H_2O = \frac{1}{\sqrt{18}}$$

$$N_2 = \frac{1}{\sqrt{28}}$$

$$= 0.15$$

$$= 0.24$$

$$N_2 = 0.18$$

~~H_2O~~ H_2O fastest as is lightest Molar Mass.

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

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

$$1 \text{ mol } C_2 H_4 N_2 O_6 = 152 \text{ g}$$

$$\text{Mass } O_2 = 1 \times 96$$

$$= 96 \text{ g}$$

$$\frac{96}{152} \times 100 = 63.16\% \text{ oxygen by mass}$$

- 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).

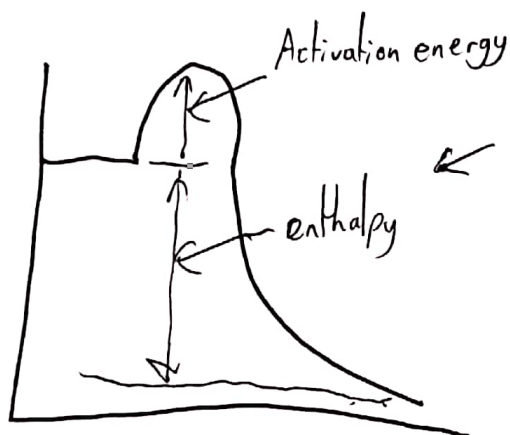
$$\Omega = \frac{[d - (2a) - (\frac{b}{2})] \times 1600}{M} = \frac{[6 - (2 \times 2) - (\frac{4}{2})] \times 1600}{152}$$

$$\Omega = 0\%$$

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



Sure it was something to do with this. Can't remember and forgot to put it on sheet!

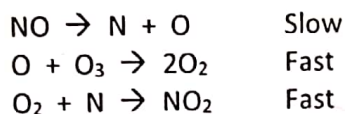
- b) (2p) The activation energy for the explosive detonation of RDX is 199 kJ mol^{-1} whereas the activation energy for the explosive detonation of mercury fulminate is 105 kJ mol^{-1} . Define the term activation energy and hence comment on the relative stability of these two explosives.

Activation energy is the energy required to be input in to a system in order for the reaction to start.

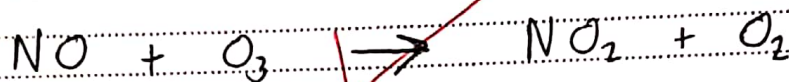
As mercury fulminate requires less energy input in order to detonate than RDX does, I would argue that mercury fulminate is the least stable of the 2 explosives.

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

①② double NO, double rate. NO is 1st order.
②③ double O_3 , no rate change. O_3 is 0th order

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

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

$$0.102 = k[0.012]^1[0.02]^0$$

$$0.102 = 0.012k$$

$$k = 8.5 \text{ s}^{-1}$$

Unit of k is per second s^{-1}

↑ note five

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

Supports: The slowest reaction $\text{NO} \rightarrow \text{N} + \text{O}$ is the rate limiting reaction and as such changing the other reactions doesn't impact the rate. As they can't happen till $\text{NO} \rightarrow \text{N} + \text{O}$ is complete.

2p

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.

$$q = mc\Delta T$$

$$c_p = \frac{q}{m\Delta T} \quad c_p = 4.184 \quad \Delta T = 3$$

$$m = 610\text{g}$$

$$\text{Water } q = 7.66\text{ J}$$

4p

3

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.

$E = mc^2$ $\lambda = \frac{c}{\nu}$ Shorter Wavelength more energy. That's why microwaves cook stuff and the radio doesn't.

$$\frac{3 \times 10^8}{554 \times 10^{-9}} = 5.42 \times 10^{14} \text{ J} \quad \frac{3 \times 10^8}{616 \times 10^{-9}} = 4.89 \times 10^{14} \text{ J}$$

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

Calcium $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Orbital diagram: $1s$ (up, down), $2s$ (up, down), $2p$ (three boxes, each up, down), $3s$ (up, down), $3p$ (three boxes, each up, down), $4s$ (up, down)

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

As the electrons drop energy levels, they emit the energy in the form of a photon which can be seen as visible light.

- 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.

56
Ba
137 56 protons ^{132}Ba $132 - 56 = 76$ neutrons.

^{138}Ba $138 - 56 = 82$ neutrons. ✓

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleev?

AH! → He element of Surprise.