

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:

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

For each of the following statements determine if it is true or false. Justify your answer.

- 2p 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~~ Cr has 24 electrons total. 2, 8, 8, 6. So 6
False. in outermost shell.

6 unpaired ✓

- 0p 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 of the dipole.

~~True~~
False. 180° C.

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

$$1.5 = \text{mol of salt} / \text{Kg of solvent}$$

$$1.5 \times (23 + 35.5) = 87.75 \text{ g}$$

$$1.5 = x / 1 \text{ Kg}$$

$$x = 1.5$$

TRUE.

$$g = n \times m$$

- 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.

~~True~~ But also has many assumptions. Such as collisions are perfectly elastic.

False. It is very hard to achieve OK. You need gas particles to have energy to obey gas laws.

RDX is 199.

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 contains binders and plastisers. RDX reaction is slower than nitrocellulose as it has more AE.
RDX is actually 199 kJ/mol. RDX has more AE meaning it is harder to set off so more stable.

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

1p True ✓ Reactions can be reversible.

7. (2p) For a hypothetical reaction $A^2 + B \rightarrow C$ 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 10 originally it will be 100 because $10 \times 10 = 100$.
If A is then 20. It will be 400. So 4x rate.
Also depends what order B is.

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

2p True ✓ Because you need oxygen for combustion and this means energy is given out.
Negative 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. Kinetic energy is transferred to container walls and other particles.

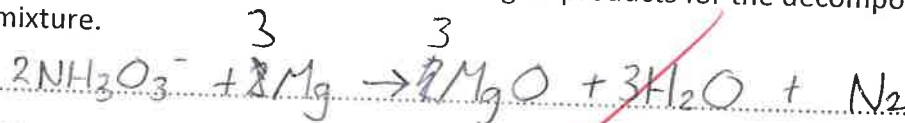
10. (2p) The rate of decomposition of the explosive material decreases when the temperature increases.

2p False ✓ True As it receives more energy from heat to do so, the decomp will increase.
Depends on type of explosive though & it's oxygen balance.

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

$$2\text{NH}_4\text{NO}_3 = (3 \times 14) + (9 \times 1) + (9 \times 16) = 195$$

h.o.f. = heat released or absorbed when 1 mole of pure substance 'X' is formed from its elements under standard conditions.

$$3\text{mol} = 195 \quad 65\text{g}$$

$$1\text{mol} = 65\text{mm}$$

Exothermic as negative energy

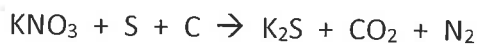
$$\Delta \text{Enthalpy} = \text{products} - \text{reactants}$$

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

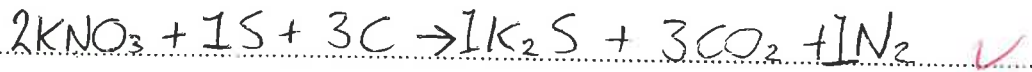
TNT produces more heat. It's more exothermic.

QUESTION 3:

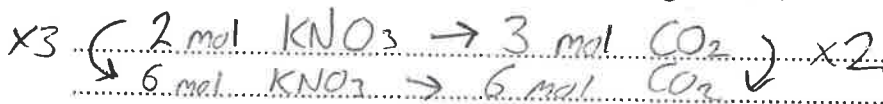
A simple chemical equation for the combustion of gun powder can be written as:



- 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 ?



$$45 \times 6 = 270\text{g}$$

$$6 \times (12 + (16 \times 2)) = 264\text{g} = 6 \text{ mol}$$

$$g = n \times \text{MM} \quad \left(\begin{array}{l} 270 \\ 45 \end{array} \right)$$

$$270 - 45 = n \times \text{MM}$$

$$44\text{g}$$

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

litres = liquid $\rightarrow$ gas?

How can you measure gas in litres... It depends how compressed it is?

$$45\text{g} \quad g = n \times \text{MM}$$

$$n = 0.44 \text{ mol}$$

$$45 = n \times 101$$

$\rightarrow 25^\circ\text{C}$?

- 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?

$$298.15 \rightarrow 373.15 \text{ K}$$

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

$$760 \text{ mmHg} \rightarrow 700 \text{ mmHg}$$

We need the original volume?

$$45 = n \times \text{MM}$$

$$PV = nRT$$

$$0.4 = \text{mol}$$

$$760 \times V = 0.4 \times 0.0821 \times 298.15$$

$$V = 0.4 \times 0.0821 \times 298.15$$

$$760$$

$$9.79 = P_2 V_2$$

$$\frac{9.79}{700} = 0.013$$

$$0.013 \text{ L}$$

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.

Op

Water is dipolar, has stronger bonds.
 ~~NH_3 has longer bonds. Longer bonds = weaker.~~

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.

Op

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

Op

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

More electronegative. Higher oxygen balance.
~~Stronger London bonds.~~

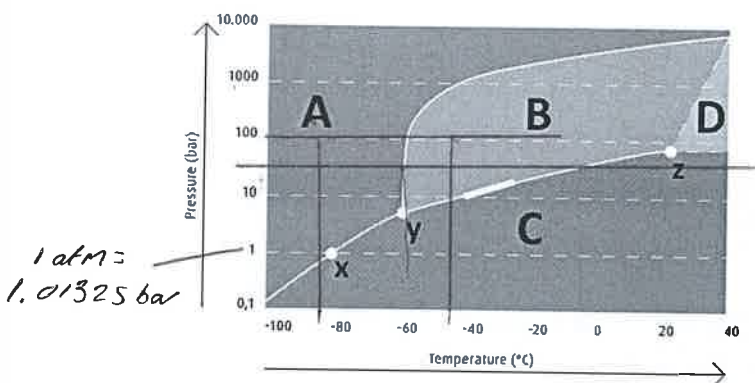
- c) (2p) What would be the other reason to explain explosive character of mercury fulminate?

ap

Unstable

QUESTION 6:

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



2p

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

A: SolidB: LiquidC: GasD: Plasma. Not really gas. Not really liquid. ✓

0.5

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

point x:

point y: Critical point

point z:

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

- 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. ✓

0.5

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

Condensation ✓

1p

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

 -5°C = boiling -60°C = freeze ✓

- g) (1p) Estimate the conditions of a critical point. -60.5°C

31.1 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 .

$$44.8 / 2 = 22.4$$

$$44.8$$

$$44.8$$

$$16$$

$$O_2 = 32$$

$$C = 12$$

$$H = 2$$

$$N = 14$$

$$36$$

$$96$$

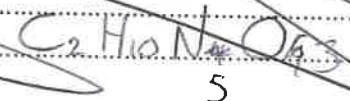
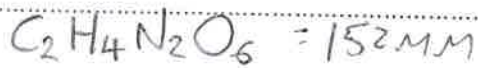
$$28$$

$$C = 4$$

$$O = 8$$

$$H = 4$$

$$N = 2$$



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

~~He as it is~~

H_2O as it has smallest Molar Mass and is lightest
So has highest speed velocity.

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

$$39.8 \text{ dm}^3$$

- 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).

$$\Omega = \frac{16}{152} \times [d - (2a) - (\frac{b}{2})] \times 100\%$$

$$\Omega = \frac{16}{152} \times 8 - (2 \times 2) - (\frac{4}{2})$$

$$0\%$$

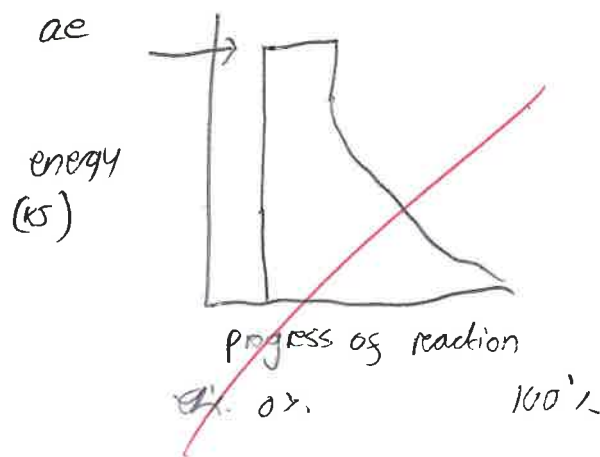
$$0 \times 16$$

$$152$$

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



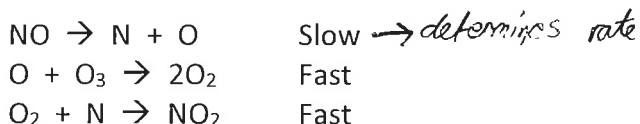
- b) (2p) The activation energy for the explosive detonation of RDX is 199 kJ mol^{-1} whereas the activation energy for the explosive detonation of mercury fulminate is 105 kJ mol^{-1} . Define the term activation energy and hence comment on the relative stability of these two explosives.

The more activation energy, the slower the reaction. The higher the stability.

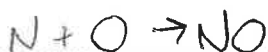
RDX is more stable than Mercury Fulminate.

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

Doubling NO = doubles rate of reaction

1 & 2 = double NO so double rate

Doubling O_3 has no effect on rate

Rate of reaction = change in conc / change in time

0.12 rate

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

$$k = A e^{-E_a/RT}$$

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

Slowest reaction is the determining
factor. Doubling O_3 had no
effect on rate.

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.

$$Q = mc\Delta T$$

$$Q = 0.61 \text{ kg} \times 4.184 \times 3$$

$$Q_{\text{water}} = 7.66 \text{ J}$$

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.

$$E = h \times \nu$$

$$c = \nu \times \lambda$$

Barium has a lower wavelength which effects the energy.

$$\nu = \frac{c}{\lambda} \rightarrow \text{You want bigger } \nu \text{ because } E = h \times \nu$$

$$\nu \downarrow = \lambda \uparrow$$

$$\nu \uparrow = E \uparrow$$

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

Ca = 20 electrons

1s² 2s² 2p⁶ 3s² 3p⁶ 4s² 3d⁰

5d¹⁰ 4s² 4p⁶ 5s² 4p¹⁰
5p⁶

Ba = 56 electrons

Cs 5p⁶

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

Electrons are excited by absorbing energy. They move up energy shells/levels. Moving further away from the nucleus. The spectra produced depends on the wavelength.

- 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.

$$^{137}\text{Ba} = 56 \text{ protons}$$

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

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

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleev?

Rb, Cs, Fr