

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.

- 0p 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 due to tendency to have half-gull or completely gull shells. 4 is half-gull

- 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 - it has a trigonal pyramidal shape w/ bond angle of 107°

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

True $\text{NaCl} = 22.9898 + 35.453 = 58.4428 \text{ g/mol}$

$1.5 \text{ mol} = 58.4428 \times 1.5 = 87.6642 \text{ g in } 1.5 \text{ mol}$

- 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 - uses STP which is 1 atm and 273.15 K as OK the gases wouldn't have any energy and would probably be solids

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

False ✓
True - lower activation energy = easier to initiate so nitrocellulose less stable than RDX

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

True ✓ - ~~the~~ conservation of energy means that the energy gained / lost doesn't vary due to intermediate steps.

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 ✓ second order means quadruple rate if reaction is A's concentration is doubled

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

True ✓ energy is released as heat and light always

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 ✓ it assumes that all collisions are perfectly elastic

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

False ✓ explosives degrade faster at hotter temperatures

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

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

$$\Delta H_{\text{prod}} = -601 + 3(-242) = -1327 \text{ kJ/mol}$$

$$\Delta H_{\text{reacts}} = 2(-365) = -730$$

$$\Delta H_{\text{rxn}} = (-730) - (-1327) = +597 \text{ kJ/mol}$$

endothermic since positive enthalpy change so must take heat from environment

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

$$Q = \frac{\Delta H_{\text{rxn}}}{\text{MM}} = \text{kJ/g}$$

$$Q = \frac{597}{66} = 9.045 \text{ kJ/g}$$

$$\text{MM} = 14 + 16 + 3 = 33 \text{ g/mol NOH}_3$$

$$9.045 \div 2.8 = 3.231$$

but 2 moles $\therefore$ 66g
heat of reaction is 3.231 x greater than 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 ?

$$\text{MM } \text{KNO}_3 = 39 + 14 + 3(16) = 101 \text{ g/mol}$$

$$45 \div 101 = 0.4455 \text{ moles}$$

$$\text{CO}_2 = 1.5 \times \text{moles of } \text{KNO}_3$$

$$= 0.6683 \text{ moles } \text{CO}_2$$

$$\text{MM } \text{CO}_2 = 12 + 2(16) = 44 \text{ g/mol}$$

$$44 \times 0.6683 = 29.41 \text{ g } \text{CO}_2 \text{ from } 45 \text{ g } \text{KNO}_3$$

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

$$0.6683 \text{ moles } \text{CO}_2, \frac{1}{3} \text{ as many moles } \text{N}_2 = 0.2228 \text{ moles}$$

$$0.6683 \times 22.4 \text{ dm}^3 = 14.97 \text{ dm}^3$$

$$0.2228 \times 22.4 \text{ dm}^3 = 4.99 \text{ dm}^3$$

$$\text{total} = 19.96 \text{ dm}^3$$

- 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?

$$100^\circ\text{C} = 373.15 \text{ K}$$

$$700 \text{ torr} = \frac{700}{760} = 0.92 \text{ atm} = 93.219 \text{ kPa}$$

$$V = \frac{nRT}{P} = \frac{(0.891)(8.314)(373.15)}{93219}$$

$$= 0.0297 \text{ m}^3$$

$$R = 8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

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.

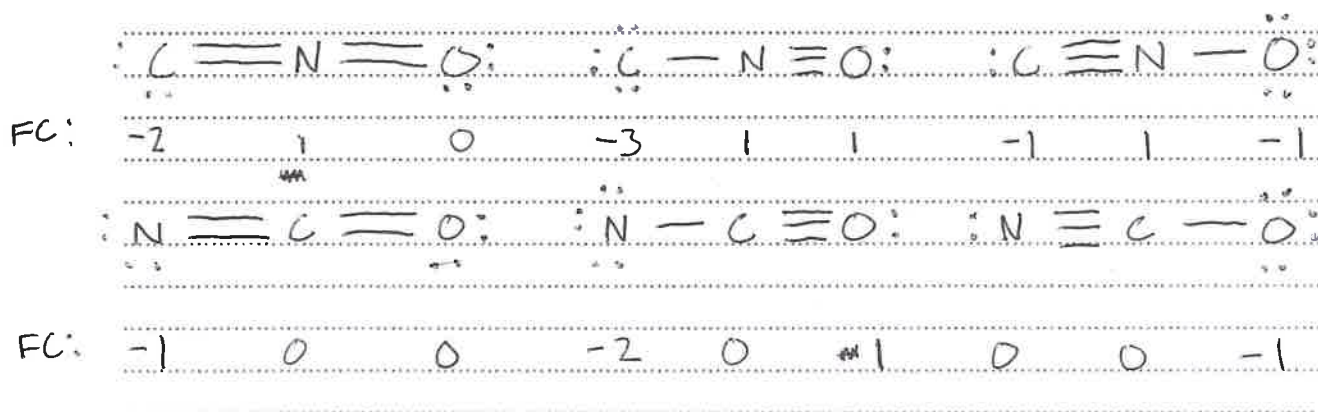
H_2O has very strong IMF due to hydrogen bonds: Oxygen much more electronegative than hydrogen so draws e^- away from hydrogen atom giving it a positive charge, which is then attracted to more negative charge of oxygen atom in another molecule. Polar molecules = strong intermolecular bonds. NH_3 has ~~not~~ such strong intermolecular forces so requires less energy to break intermolecular bonds, hence the lower boiling point.

↓
(to turn it 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 cyanate is not

formal charge = valence electrons - formal electrons

fulminate has overall formal charges -1, -1, and -1

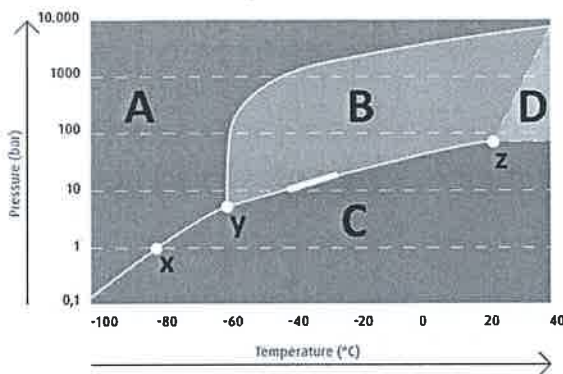
cyanate has overall formal charges -1, -1, and -1 but has a stronger resonance structure as the most electronegative atom (oxygen) has the most negative formal charge, but in fulminate oxygen never has the most negative charge so is therefore weaker + more unstable (explosive!)

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

2p It has a lower activation energy and creates stable products so can react very quickly given not much 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 (Liquid and gas) ✓

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

point x: boiling / 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? liquid $\rightarrow$ solid = freezing ✓

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

condensation = gas $\rightarrow$ liquid ✓

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

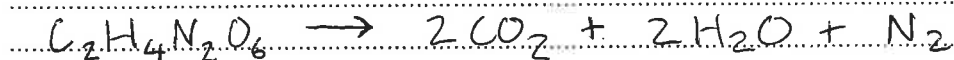
freezing $\approx -60^\circ\text{C}$, boiling $\approx 0^\circ\text{C}$ ✓

- g) (1p) Estimate the conditions of a critical point high temperature + pressure

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 .



$$2(12) + 4(1) + 2(14) + 6(16) = 152 \text{ g/mol}$$

(assuming S.T.P.)

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

$$MM \text{ } CO_2 = 44 ; MM \text{ } H_2O = 18 ; MM \text{ } N_2 = 28$$

water vapour will move fastest due to the law that states that the average velocity of a gas is inversely proportional to the root of its molar mass: $v \propto \frac{1}{\sqrt{MM}}$ ∴ smallest molar mass = fastest

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

$$6 \times 16 = 96$$

$$\frac{96}{152} = 63.2\% \text{ by mass is oxygen}$$

- 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).

$$\Omega = \frac{16}{152} \times (6 - 2(2) - \frac{4}{2})$$

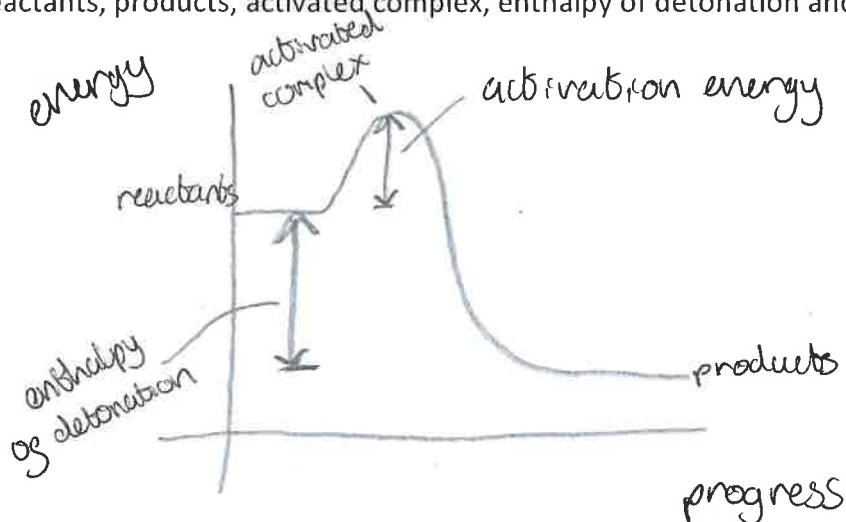
$$= 0$$

$$\Omega = 0$$

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



- 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 = amount of energy required to ~~initiate~~ cross the reaction threshold + begin the explosive reaction

$\therefore$ lower activation energy = easier to start explosive reaction = less stable

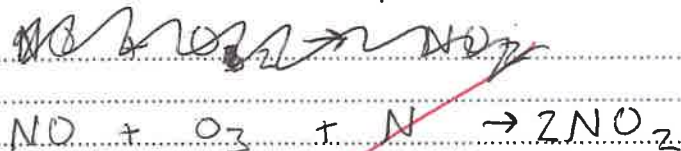
hence mercury fulminate less stable than RDX

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

conc. of O_3 doubles, rate is same i.e. order 0

conc. of NO doubles, rate doubles i.e. order 1

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

✓

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

Op

~~$$k = 1 \times \text{MM of NO} + 0 \times \text{MM of O}_3$$~~

~~$$= 14 + 16 = 20$$~~

~~$$k = 20$$~~

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

rate of reaction only dependent on concentration of NO, as shown by rate constant only affected by NO, not O₃.

decomposition of NO is slow step so is the limiting reagent / step.

QUESTION 10:

(4p) A 500 g sample of TNT (C₇H₅N₂O₆) 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.

heat of combustion = energy gained by water + energy gained by calorimeter

$$Q_{\text{water}} = mc \Delta T = (610)(4.184)(3) = 7656.72 \text{ J}$$

$$Q_{\text{calorimeter}} = HC \Delta T = (420)(3) = 1260 \text{ J}$$

$$7656.72 + 1260 = 8.91672 \text{ kJ}$$

500g TNT

$$MM = 7(12) + 5(1) + 2(14) + 6(16) = 213 \text{ g/mol}$$

$$500 \div 213 = 2.35 \text{ moles}$$

$$\frac{8.91672}{2.34741784} = 3.80 \text{ kJ/mol}$$

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.

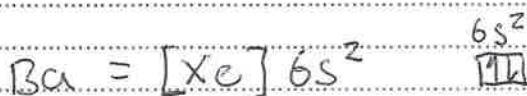
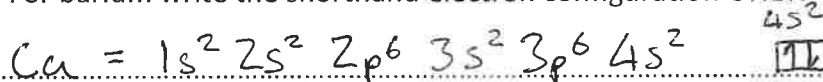
3p $E = \frac{hc}{\lambda}$; $E = \frac{hc}{\lambda}$ Green = higher energy

$E_{\text{barium}} = \frac{(6.6 \times 10^{-34}) (3 \times 10^8)}{554 \times 10^{-9}} = 3.57 \times 10^{-19} \text{ J}$ ✓

$E_{\text{calcium}} = \frac{(6.6 \times 10^{-34}) (3 \times 10^8)}{616 \times 10^{-9}} = 3.21 \times 10^{-19} \text{ J}$

b) (3p) Write the full electron configuration for calcium and show the electrons in orbitals.

For barium write the shorthand electron configuration ONLY.



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

2p When the atoms ^{release} ~~lose~~ energy (burned) the electrons in their shells move to lower energy levels closer to the nucleus as the atom has lost its energy. The electrons, as they descend the energy levels, lose their energy in the form of 'packets' (photons) of certain wavelengths 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.

Barium = 56 protons

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

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

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleeev?