

ACDA5014 ADVANCED CHEMISTRY OME FINAL EXAM

73

NAME MINE PECKDATE: 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.

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 when filling its electron subshells the d subshell is only half filled meaning that each d orbital only contain 1e⁻ i.e. d $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ not $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$.

2. (2p) In ammonia, NH₃, which is used in the industrial production of ammonium nitrate, the bond angle between a nitrogen atom and two hydrogen atoms is 120°.



This is false as the bond angle is 107.5° due to repulsion of N-H bonds electrons from the lone pair (as in diagram).

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

$$MW = (22.9898 \text{ g mol}^{-1}) + (35.453 \text{ g mol}^{-1}) = 58.4428 \text{ g mol}^{-1} \quad n = \frac{m}{MW}$$

$$n = CV, \text{ where } C = 1.5 \text{ mol l}^{-1}, V = 1 \text{ L}, n = 1.5 \text{ mol}, \text{ if } m = 87.8, n = \frac{87.8}{58.4428 \text{ g mol}^{-1}} = 1.50 \text{ mol to 3 s.f.}$$

As the number of mols are equal the answer is True.

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

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

False, the lower the activation energy the less stable the compound as it requires less energy to start the reaction. RDX is more stable than nitrocellulose.

5p

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

True as you could have the following:



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 As if $Rate = k[A]^2 = [2]^2 = 4$ i.e. a quadrupling would be $[4]^2 = 16$ or 16x.

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

True as more bonds are formed, with ~~not~~ products formed than reactants
 i.e. less energy is put in to break bonds than is released when they are formed.

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 The assumption must be that for an ideal gas all collisions are elastic i.e. energy is not lost and kinetic energy is conserved.

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

False The rate of decomposition would increase, as kinetic energy increases with temperature increasing, so at successful collisions increasing rate of reaction.

QUESTION 2:

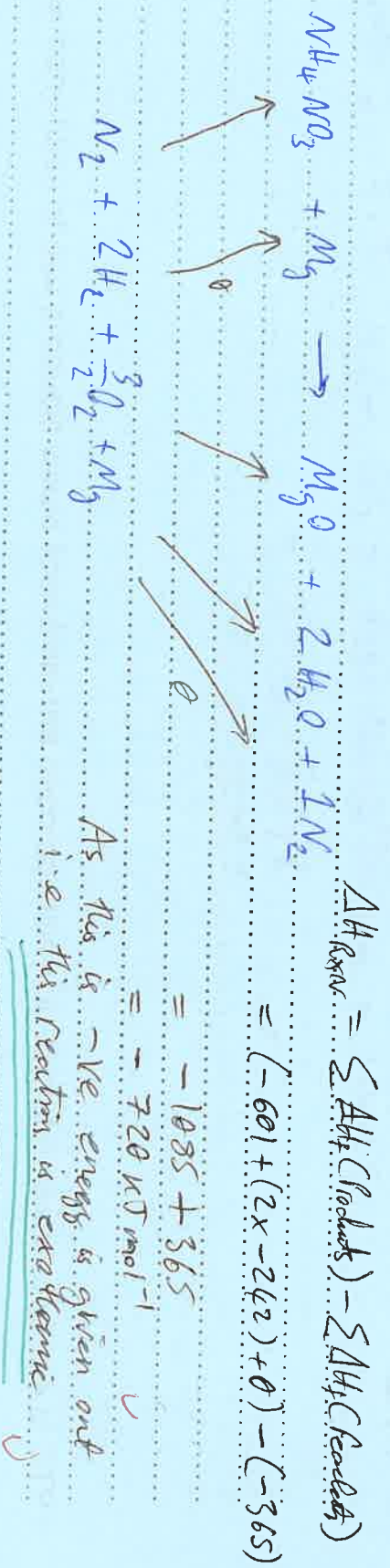
When ammonium nitrate and magnesium metal are mixed in a stoichiometric ratio, they form a pyrotechnic composition that decomposes to form magnesium oxide, water vapour and nitrogen gas.

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



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

To compare we need to convert our ΔH_{rxn} for 1 mol $\frac{\Delta H_{\text{rxn}}}{\text{mol}} = \frac{-720 \text{ kJ mol}^{-1}}{(80.04 + 12.74 \times 312)}$

MW Ammonium Nitrate (Mg)

So the reaction above produces about 3x the amount of energy per gram if Mg is included.

$$= 6.90 \text{ kJ g}^{-1}$$

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 ?

$$A + \text{STP} \quad n = \frac{m}{M_r} = \frac{45 \text{ g}}{101.103 \text{ g mol}^{-1}} = 0.445 \dots \text{ mols}$$

$$M_r(\text{KNO}_3) = 39.102 + 14.0067 + (3 \times 15.9994) = 101.1069 \text{ g mol}^{-1} \quad M_r(\text{CO}_2) = (12.011 + (2 \times 15.9994)) = 43.9992 \text{ g mol}^{-1}$$

$$\text{As the ratio is } 2:3 \quad n \text{ for } \text{CO}_2 = 0.6676102224 \text{ mols} \times M_r(\text{CO}_2)$$

$$= 29.38 \text{ g to } 2 \text{ s.f.}$$

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

Assuming only CO_2 and N_2 are gaseous products total number of moles of

$$\text{gas produced} = 0.66 \dots (\text{CO}_2) + 0.22 \dots (\text{N}_2) = 0.8901469655 \text{ moles}$$

$$\text{At STP } 1 \text{ mol of gas} = 22.4 \text{ litres} \quad 0.89 \dots \times 22.4 = 19.728 \text{ L of gas to } 2 \text{ s.f.}$$

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?

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

$$\therefore P_1 V_1 T_2 = P_2 V_2 T_1 \quad \text{and } V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$P_1 V_1 = n R T_1 \quad n R = \frac{P_1 V_1}{T_1} \quad V_2 = \frac{P_1 V_1}{P_2 T_1} \times 273 \quad \frac{101.325 \times 20 \times 273}{(13.625 \times 65789)}$$

$$= 29.7 \text{ L to } 3 \text{ s.f.}$$

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

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

$$= \frac{101.325 \times 20 \times 373 \text{ K}}{273 \times 0.821} = 29.6$$

$$0.921$$

7

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.

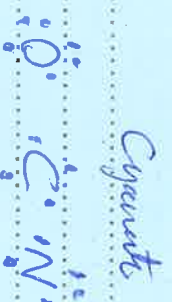
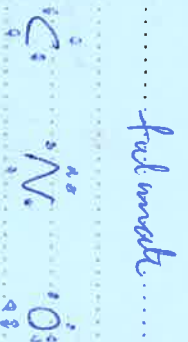
H₂O consists of a bent molecule which has 2 lone pairs and partial charges on $\text{H}^{\delta+} - \text{O}^{\delta-} - \text{H}^{\delta+}$ whereas NH_3 only contains one lone pair and is a tetrahedral shape.

Water can therefore bond with many hydrogen bonds between lone pairs and $\text{H}^{\delta+}$, given the shape it can do it more effectively, thus increasing the bond strength and no of bonds to increase the energy required to break them hence the much higher boiling point.

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).

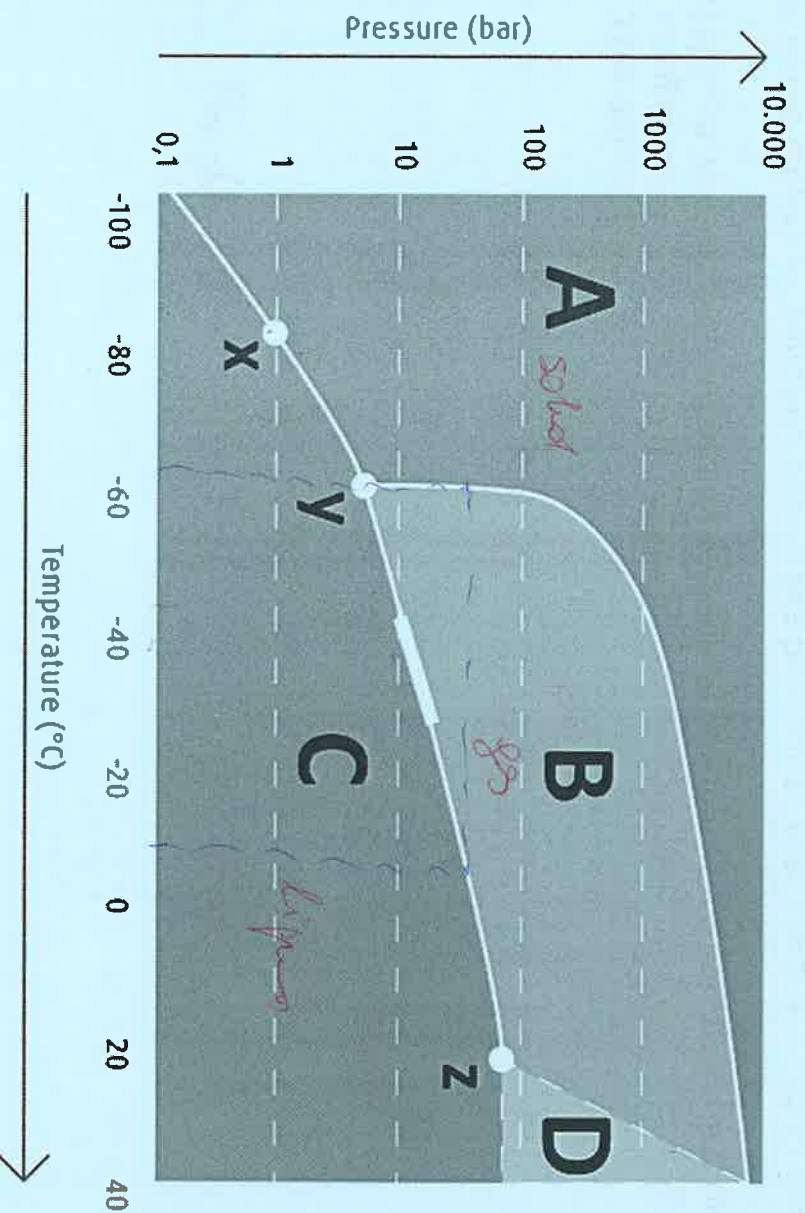


b) (3p) Explain in terms of formal charges why fulminate is explosive and cyanate is not

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

QUESTION 6:

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



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

a) (zp) identisch

Gas

C: liquid

D: Sechsmal pro Stunde

b) (1.5p) Give the names of points X, Y and Z:

point x: ~~feeding~~ ~~feeding~~ ~~point~~

point v: ~~boiling point~~

point z: ~~Sublim point~~

c) (0.5p) Which phase can exist at SATP? ... ~~Solidification~~ *Solubility*

d) (0.5p) If a sample of this substance is cooled from -45 degC to -85 degC at a pressure of 100 bar, what phase change will occur? ~~Condensation~~

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

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

$bp = -10^{\circ}C$ ~~$freezing = -65^{\circ}C$~~

g)(1p) Estimate the conditions of a critical point.

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 .



$$MW = \sim 44 \text{ g mol}^{-1} \quad \sim 18 \text{ g mol}^{-1} \quad \sim 28 \text{ g mol}^{-1}$$

i.e. 2:2:1 ratio

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

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

Water vapour will move fastest as it is the lightest

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

$$\text{Mass of oxygen present} = 6 \times 16 = 96 \text{ g}$$

$$\%O = \frac{\text{mass of oxygen}}{MW} \times 100\% = \frac{96 \text{ g}}{152 \text{ g}} \times 100\% = 63.2\% \text{ by mass to 3sf.}$$

- 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).

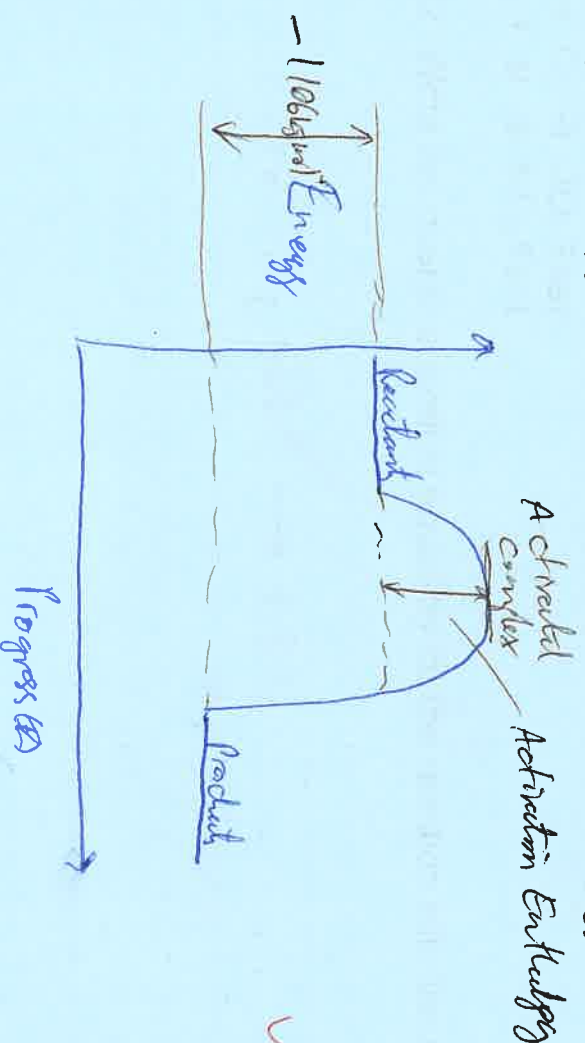
$$OB = \frac{16}{152} [6 - 4 - 2] \times 100 = \frac{16}{152} \times 0 \times 100 = 0\%$$

Just the right amount of oxygen.

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



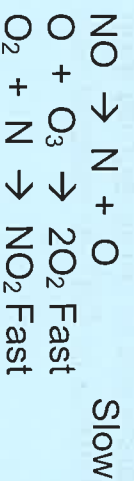
- b) (2p) The activation energy for the explosive detonation of RDX is 199 kJ mol^{-1} whereas the activation energy for the explosive detonation of mercury fulminate is 105 kJ mol^{-1} . Define the term activation energy and hence comment on the relative stability of these two explosives.

The term activation energy is the amount of energy required to start the reaction i.e. the energy needed to break products down into intermediates to their form products.

This means the higher the activation energy the more stable the reactant, as it requires more energy to initiate it. Therefore RDX is 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

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

with respect to NO the $[\text{NO}]$ double from 1 $\rightarrow$ 2 and the rate double therefore the order is 1.

with respect to O_3 the order = 0 order as the rate remains unchanged. So the $[\text{O}_3]$ does not affect the rate.

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

$$\therefore \text{Rate} = k [\text{NO}] \quad \text{So rate depends entirely on } [\text{NO}]$$

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

$$\begin{aligned} \text{If Rate} &= k [\text{NO}]^1 \text{ for experiment 1, } k = \frac{\text{Rate}}{[\text{NO}]} = \frac{0.102 \text{ mol/Ls}}{0.012 \text{ mol/L}} \\ &= \underline{8.5 \text{ s}^{-1}} \end{aligned}$$

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

1st supports the fact that $\text{NO} \rightarrow \text{N} + \text{O}$ is the rate determining step and the rate of reaction is based solely on this 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.

$$T_1 = 20.0^\circ\text{C}$$

$$T_2 = 23.0^\circ\text{C}$$

$$C_{\text{cal}} = 420 \text{ J}^\circ\text{C}^{-1}$$

$$m(\text{H}_2\text{O}) = 610 \text{ g}$$

$$h. \text{ water} = \frac{m}{M}$$

$$m_r(\text{TNT}) = (12 \times 4) + (5 \times 1) + (2 \times 14) + (6 \times 16)$$

$$= 215 \text{ g mol}^{-1}$$

$$Q = m C \Delta T$$

$$= 610 \times 4.184 \times 3$$

$$h. \text{ water TNT} = \frac{500 \text{ g}}{213.9 \text{ mol}^{-1}}$$

$$= 7656.72 \text{ J}$$

$$A_p = 7656.72 \text{ kJ mol}^{-1} = 2.34741784 \text{ kJ mol}^{-1}$$

$$\text{Heat of Combustion TNT} =$$

$$7.65672 \text{ kJ}$$

$$2.34741784 \text{ kJ mol}^{-1}$$

$$= 3.26176272 = 3.26 \text{ kJ mol}^{-1} \text{ to 3 s.f.}$$

3p

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.

$$E = hf \text{ where } f = \frac{c}{\lambda} \quad \text{and } c = 3.0 \times 10^8 \text{ m/s}, \lambda_{\text{barium}} = 554 \text{ nm}, \lambda_{\text{calcium}} = 616 \text{ nm}, h = 6.6 \times 10^{-34} \text{ Js}$$

$$\text{For Barium, } E = \frac{hc}{\lambda} = \frac{(6.6 \times 10^{-34} \text{ Js})(3.0 \times 10^8 \text{ ms}^{-1})}{(554 \times 10^{-9} \text{ m})} = 3.57 \times 10^{-19} \text{ J to 3sf}$$

$$\text{For Calcium, } E = \frac{hc}{\lambda} = \frac{(6.6 \times 10^{-34} \text{ Js})(3.0 \times 10^8 \text{ ms}^{-1})}{(616 \times 10^{-9} \text{ m})} = 3.21 \times 10^{-19} \text{ J to 3sf}$$

Given the two energies above Barium requires the most energy to produce its colour

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

$$\text{Calcium} = 1s^2 2s^2 2p^6 3s^2 3p^4 4s^2 \quad \checkmark$$

$$\text{Barium's shorthand electron structure} = [\text{Xe}] 6s^2 \quad \checkmark$$



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

Electrons within the atoms drop down from higher energy levels to lower ones, as they do this energy is emitted as photons. The photon energy is calculated by $E = hf$ where

f is the frequency of light emitted which relates to a particular wave length of light via

$$\text{the equation } f = \frac{c}{\lambda}$$

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.

Given that Barium Atomic Number = 56, this equals the number of protons in the nucleus which is also equal to the number of electrons.

The mass number is a summation of protons and neutrons, so by deducting 56 from the mass number we get the number of neutrons.

$$\text{So for } ^{132}\text{Ba} \text{ number of neutrons} = 132 - 56 = 76 \text{ neutrons} \quad \checkmark$$

$$\text{and for } ^{138}\text{Ba} \text{ number of neutrons} = 138 - 56 = 82 \text{ neutrons}$$

EXTRA CREDIT (must give all three)

What are three elements predicted by Mendeleev?

Oxygen, Nitrogen and Hydrogen