

REFERENCE SHEET FOR ACDA5014 ADVANCED CHEMISTRY OME

FINAL EXAM

PERIODIC CHART OF THE ELEMENTS

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IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA					
1 H 1.00797														1 H 1.00797	2 He 4.0026				
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183		
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948		
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80		
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30		
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)								

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
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† Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)
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PHYSICAL CONSTANTS:

$c = 3.0 \times 10^8$ m/s (speed of light)

$R_H = 3.29 \times 10^{15} \text{ s}^{-1}$ (Rydberg constant)

$h = 6.6 \times 10^{-34}$ Js (Planck's constant)

1 amu = 1.66×10^{-24} kg (atomic mass unit)

$N_A = 6.02 \times 10^{23}$ Avogadro's number

$R = 0.0821 \text{ L-atm/mol-K}$ gas constant

0 degC = 273 K

1 atm = 101.3 kPa = 101,325 Pa = 760 mm Hg = 760 torr = 14.7 lb/in² (psi)

ACDA5014 ADVANCED CHEMISTRY OME FINAL EXAM

NAME _____ 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.

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.** For the outermost electrons in Cr the configuration is $4s^1 3d^5$ (exception called half-filled shell) so there are 6 unpaired electrons.*

2. (2p) In ammonia, NH_3 , which is used in the industrial production of ammonium nitrate, the bond angle between nitrogen atom and two hydrogen atoms is 120° .

***FALSE.** In ammonia, NH_3 , there are four electron groups, three bonding and one lone pair. The electron group geometry is tetrahedral, but the molecular shape is trigonal pyramidal with a bond angle less than 109.5° .*

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

***TRUE.** In 1 L of this solution, there is 1.5 mole of NaCl. 1 mole of NaCl has a mass of 58.5 g so 1.5 mole of table salt would have mass of 87.75 g.*

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 low temperatures, the ideal gas equation is less successful in describing the behaviour of a gas. At 0 K the molecular motion ceases. This is particularly true at high pressures, if the pressure is increased enough, the gas will liquefy, causing a marked decrease in volume with no change in gas pressure – non-ideal behaviour.*

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

FALSE. *NC is less stable than RDX as a greater proportion of molecules are able to achieve the activation energy and decompose faster over time.*

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

TRUE. *Enthalpy is a state function.*

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. *For the 2nd order reaction, the rate would be $k[A]^2$, so if the concentration is doubled, the rate will increase four times.*

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

TRUE. *Heat is released*

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 collisions are fully elastic and no energy is lost*

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

FALSE. *For every 10 degC increase in temperature the rate of decomposition approximately doubles.*

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

$$\Delta_{\text{rxn}}H^\circ = \Sigma\Delta_{\text{f}}H^\circ (\text{products}) - \Sigma\Delta_{\text{f}}H^\circ (\text{reactants})$$

$$\Delta_{\text{rxn}}H^\circ = [0 + (2 \times (-242)) + (-601)] - [(-365) + 0] = -720 \text{ kJ/mol}$$

$\Delta_{\text{rxn}}H^\circ$ is negative so the reaction is exothermic (heat is released to surrounding)

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

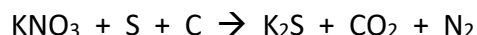
720 kJ of heat is released for the following quantities of reactants/products:

$$80 \text{ g} + 24 \text{ g} \rightleftharpoons 28 \text{ g} + 36 \text{ g} + 40 \text{ g} = 104 \text{ g}.$$

720 kJ for 104 g is 6.9 kJ/g. This is higher 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 ?

MM KNO_3 = 101 g/mol so 45 g KNO_3 is the mass of (45/101) 0.445 mol of KNO_3

MM CO_2 = 44 g/mol

According to the stoichiometry of this reaction, 2 moles of KNO_3 produce 3 moles of CO_2 , so 0.445 mol of KNO_3 produces ((0.445 mol KNO_3 x 3 mol CO_2)/2 mol KNO_3) 0.668 mol of CO_2

If 1 mol of CO_2 has a mass of 44 g, 0.668 mol of CO_2 will have a mass of (0.668 mol x 44 g/mol) 29.4 g

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

As found in part c) 45 g of KNO_3 produces 0.668 mol CO_2 .

According to the stoichiometry of this reaction, 2 moles of KNO_3 produce 1 mol of N_2 , so 0.445 mol of KNO_3 (calculated in part b)) produces ((0.445 mol KNO_3 x 1 mol N_2)/2 mol KNO_3) 0.223 mol of N_2

CO_2 and N_2 are both considered to behave like an ideal gas, so there is no difference between them and total number of moles of gas produced in this reaction is (0.668 mol CO_2 + 0.223 mol N_2) 0.891 mol of gases.

At STP 1 mole of an ideal gas occupies a volume of 22.4 L, so 0.891 mol of gas will occupy (0.891 mol gas x 22.4 L) 20.0 L.

- d) (3) 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?

At STP T = 0 degC (273 K) and P = 1 atm (760 mm Hg)

100 degC = 373K

Initial volume of gases was found in c) as 20.0 L

According to Charles's law volume of gas increases with temperature.

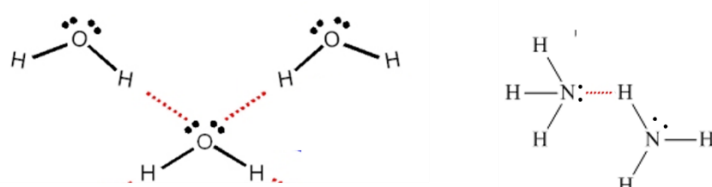
According to Boyle's law, the volume increases when the pressure decreases.

To show the above effects, the following fractions have to be used (for temperature change 373 K/273 K) and (for pressure change 700 mm Hg/760 mm Hg) and the new volume is: (20.0 L x (373 K/273 K) x (700 mm Hg/760 mm Hg)) 29.7 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 has 2 nonbonding electron pairs whereas NH_3 has only one. H_2O has more H-bonding capability resulting in a higher boiling point.

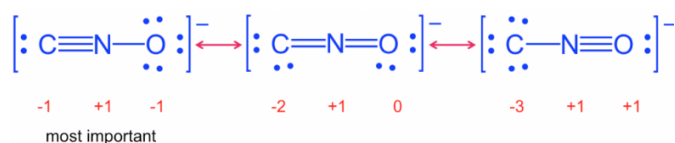


QUESTION 5:

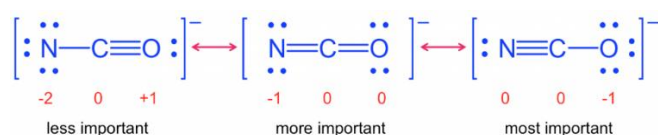
Mercury (II) fulminate $\text{Hg}(\text{CNO})_2$ is a primary explosive whereas mercury (II) cyanate $\text{Hg}(\text{OCN})_2$ is not explosive in nature.

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

fulminate ion:



cyanate ion:



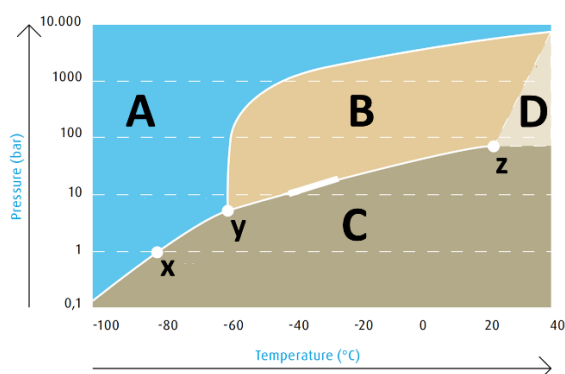
b) (3p) Explain in terms of formal charges why fulminate is explosive and cyanite is not
The structural stability of a compound depends on the formal charge. For fulminate ion and cyanate ion formal charge on oxygen, the most electronegative atom is the same (-1) but in fulminate formal charge on nitrogen is (+1). Nitrogen is also very electronegative and positive formal charge causes its lower stability when compared to cyanate ion. So the overall formal charges of fulminate ion are higher than cyanate ion for which fulminate ions are said to have less favourable molecular configurations which lead to its facile decomposition.

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

In the most stable resonance structure of fulminate ion, there is a weak single bond between the N and O atoms which makes fulminated mercury unstable and explosive.

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: supercritical phase (plasma).....

b) (1.5p) Give the names of pointsB? x, y and z:

- point x:.....(normal) 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 degC to -85 degC 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?

.....BP ~ -10 degC, FP ~ -60 degC.....

g) (1p) Estimate the conditions of a critical point~90 bar, 20 degC.....

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 .



If the molar mass of this explosive is 152 g, it corresponds to 1 mol decomposed.

22.4 L is a volume of 1 mol of a gas, so there are 2 moles of CO_2 , 2 moles of H_2O , and 1 mol of N_2 formed as the result of decomposition of 1 mol of unknown explosive.



So, $a = 2$, $b = 4$, $c = 2$ and $d = 6$. The formula of this explosive is $C_2H_4N_2O_6$

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

MM $CO_2 = 44$ g/mol, MM $H_2O = 18$ g/mol, MM $N_2 = 28$ g/mol. According to Graham's law, heavy gas molecules take longer to move because they move slower than light molecules. H_2O will move fastest because it's the lightest of the three gases produced.

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

In one mol of $C_2H_4N_2O_6$ there are 6 moles of oxygen atoms with total mass (6×16) 96 g.

In 152 g of this explosive there are 96 g of oxygen which corresponds to $((96/152) \times 100\%)$ 63.2 % of oxygen

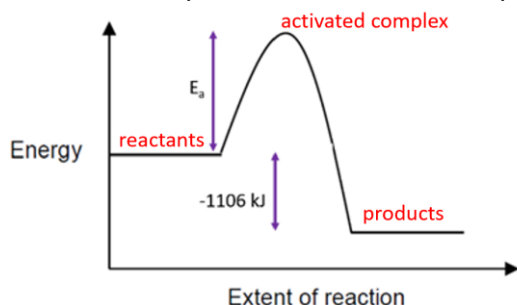
- d) (3p) The *oxygen balance* of an explosive is the mass of oxygen either in excess (the balance is positive) or in deficit (the balance is negative) of that required for complete oxidation of C and H. The *oxygen balance* is expressed as a percentage of the molar mass of the explosive. Calculate the oxygen balance for explosive with the formula determined in part a).

$$\Omega = \left(\frac{16}{MM} \right) \times \left[d - (2a) - \left(\frac{b}{2} \right) \right] \times 100\% = 0\%$$

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

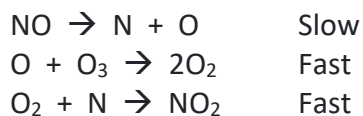


- b) (2p) The activation energy for the explosive detonation of RDX is 199 kJ mol^{-1} whereas the activation energy for the explosive detonation of mercury fulminate is 105 kJ mol^{-1} . Define the term activation energy and hence comment on the relative stability of these two explosives.

Activation energy is the minimum energy needed to “kick-start” a reaction. As mercury fulminate needs less energy to start the explosion, it must be 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.



Oxygen and nitrogen cancel out, O_2 can be moved on the product side and the overall equation is: $\text{NO} + \text{O}_3 \rightarrow 2\text{O}_2 + \text{NO}_2$

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

The general expression for the rate of this reaction is: $\text{rate} = k[\text{NO}]^a[\text{O}_3]^b$.

Comparing experiment 1 and 2, when concentration of NO is doubled, initial rate doubles as well, so this reaction is 1st order in NO ($a = 1$).

Comparing experiment 2 and 3, when concentration of O_3 is doubled, initial rate does not change, so this reaction is zero order in O_3 ($b = 0$).

The rate then is $\text{rate} = k[\text{NO}]$

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

Using the expression for rate constant from b) and values from any experiment, k is found to be $(0.102/0.012) \text{ s}^{-1}$ 8.5 ((mol/L)/(mol/L-s)) 1/s.

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

The first reaction of this mechanism is slow so it is the rate determining step. The rate law for this step is $\text{rate} = k[\text{NO}]$ which is the same as the rate law derived experimentally.

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.

$$q_{\text{rxn}} = q_{\text{H}_2\text{O}} + q_{\text{calorimeter}}$$

$$q_{\text{rxn}} = (m_{\text{H}_2\text{O}} \times c_{\text{p H}_2\text{O}} \times \Delta T) + HC_{\text{calorimeter}} \times \Delta T$$

$$q_{\text{rxn}} = (610 \text{ g} \times 4.184 \text{ J/g-degC} \times 3 \text{ degC}) + 420 \text{ J/degC} \times 3 \text{ degC} = 8917 \text{ J}$$

Molar mass of TNT is 213 g so 500g of TNT is $(500 \text{ g}/213\text{g/mol})$ 2.35 mol of TNT.

Heat of combustion per mol of TNT is $(8917 \text{ J}/2.35 \text{ mol})$ 3.79 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.

$$E = h\nu \text{ and } \nu = c/\lambda.$$

For Ba, ν is $(3 \times 10^8 \text{ m/s} / 554 \times 10^{-9} \text{ m}) 5.41 \times 10^{14} \text{ 1/s}$ and E is $(6.63 \times 10^{-34} \text{ J-s} \times 5.41 \times 10^{14} \text{ 1/s}) 3.59 \times 10^{-19} \text{ J}$

For Ca, ν is $(3 \times 10^8 \text{ m/s} / 616 \times 10^{-9} \text{ m}) 4.87 \times 10^{14} \text{ 1/s}$ and E is $(6.63 \times 10^{-34} \text{ J-s} \times 4.87 \times 10^{14} \text{ 1/s}) 3.23 \times 10^{-19} \text{ J}$

Barium emits light of 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.

Ca (20 electrons) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$



Ba (56 electrons) $[\text{Xe}]6s^2$

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

Electrons are excited and absorb energy as they move to a higher energy level. When they relax/return to a lower level this energy is given out as energy in the visible part of the electromagnetic spectrum.

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 has the atomic number 56; there are 56 protons in each barium atom. For ^{132}Ba , number of neutrons is $(132 - 56)$ 76 and for ^{138}Ba number of neutrons is $(138 - 56)$ 82.

EXTRA CREDID (must give all three)

What are three elements predicted by Mendeleev?

Gallium, scandium and germanium