UNIVERSITY OF JOHANNESBURG

FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

MODULE: **CEM2A20 / CEM 02A2** (Intermediate Physical Chemistry)

CAMPUS: **APK**

EXAM **Final Exam - 2019**

DATE: 27TH May 2019 **TIME: 8:30 – 11:30**

ASSESSOR: **Dr. S. Sitha**

MODERATOR: **Prof. R. Meijboom**

DURATION: 3 Hours **Total Marks: 100**

NUMBER OF PAGES: 5 Pages (Including this page and a periodic table)

INSTRUCTIONS: Answer all the questions. Using of a non-graphing scientific calculator is allowed.

Important Equations & Physical Constants:

Trigonometric identities:	$Sin^2\theta = \frac{1-cos2\theta}{2}$	$\sin 2\theta = 2 \sin \theta . \cos \theta$ $2Sin\theta.Sin\phi = Cos(\theta-\phi) - Cos(\theta+\phi)$

Planck's Constant	h	6.626×10^{-34} J•S, 6.626×10^{-34} kg•m^2•S^{-1}
Universal Gas Constant	R	8.314 J• K^{-1}•mol^{-1}, 1.986 cal• K^{-1}•mol^{-1}, 0.082 L•atm• K^{-1}•mol^{-1},

Question 1: (18 marks)

An ideal gas is enclosed in a container with a movable piston. Initially it occupied a volume of V_1 and after going through an isothermal reversible process at temperature of T, the final volume became V_2 (where $V_2 > V_1$).

- **(a)** For such a process, derive the mathematical expression for the work done, starting from the equation, dw = - P_{ext} . dV.
- **(b)** For such a process, derive the mathematical expression for the change in entropy, starting from differential equation of entropy, $dS = \frac{dq_{rev}}{T}$.
- **(c)** In the above isothermal reversible expansion process happening at 25 °C, the final volume becomes 3 times the initial volume (system contains 10 moles of N_2 as the ideal gas), calculate the work-done.
- **(d)** In the above isothermal reversible expansion process happening at 25 °C, if the system was initially at 15 atm pressure and after the process is done the final pressure reduced to 5 atm (system contains 10 moles of N_2 as the ideal gas), calculate the change in entropy.

Question 2: (8 marks)

Consider the combustion reaction of propane. If the combustion of propane is happening at 25 °C, using the data shown below calculate the $\Delta S°_{rxn}$. If the system contains 220.5 grams of propane at 25 °C, calculate the quantity of heat generated during this combustion process.

$S°$ of CO_2 = 213.7 J/K·mol	$S°$ of H_2O = 69.9 J/K·mol
$S°$ of C_3H_8 = 269.9 J/K·mol	$S°$ of O_2 = 205.0 J/K·mol

Question 3: (7 marks)

One of the key steps in the manufacturing of sulphuric acid is the formation of sulphur trioxide from the oxidation of sulphur dioxide. As this oxidation step is too slow at 298 K to be useful, so the reaction is usually carried out at high temperature. Calculate equilibrium constants, K for this oxidation process at 298 K and at 973 K, ($\Delta G°_{298}$ = -141.6 kJ/mol and $\Delta G°_{973}$ = -12.12 kJ/mol) to show the validity of the above observation.

Question 4: (7 marks)

According to first law of thermodynamics the enthalpy and internal energy of a system are related to each other through a mathematical equation. Write that equation for a system containing 'n' mole of an ideal gas at temperature 'T'.

For the reaction: $H_{2\,(g)} + O_{2\,(g)} \rightarrow H_2O_{2\,(g)}$, occurring at 25 °C, if the $\Delta U = -35.5$ kJ, calculate the ΔH of the reaction at the same temperature.

Question 5: (10 marks)

(a) Why is the work done equal to zero in free expansion?
(b) State the Zeroth Law of Thermodynamics.
(c) What happens to the entropy of a pure crystalline substance at absolute zero?
(d) Why is the change in entropy zero for an adiabatic expansion process?
(e) What is the value of change in free energy when the system is at equilibrium?

Question 6: (15 marks)

(a) Write the mathematical expression for the quantum mechanical operator for kinetic energy in three dimensional Cartesian space.

(b) Write the general mathematical expression for the condition of orthogonality.

(c) Write the conditions for a wave function to be considered as a well behaved wave function.

(d) Define what is meant by a commutator operator, using appropriate mathematical expression.

(e) Write the mathematical expression for the Hermitian condition.

Question 7: (10 marks)

Write the complete general mathematical expression for the Eigen value equation and identify the term which represents the Eigen value.

Is the function $e^{-\frac{x^2}{2}}$ an eigen function for the following two operators?

(a) $\frac{d^2}{dx^2} - x^2$

(b) $\frac{1}{x}\frac{d}{dx}$

If so, calculate the eigen values in respective cases.

Question 8: (25 marks)

(a) If the reaction: A + B → C is zero order, write the rate law.

(b) How will the rate of a reaction change when $[A]_0$ is doubled and tripled for:

(i) zero order reaction

(ii) second order reaction

(c) A reaction that is of first order with respect to reactant A has a rate constant 6 min^{-1}. If we start with [A] =5.0 mol L^{-1}, when would [A] reach the value of 0.05 mol L^{-1}?

(d) The specific rate constant for the combination of H_2 and I_2 to form HI is 2.34×10^{-3} mol/lit/sec at 673 K, and 7.50×10^{-2} mol/lit/sec at 773K. Calculate the activation energy for the reaction.

(e) The reaction: 2A + B + C → Product, is found to be first order with respect to A, second order with respect to B and zeroth order with respect to C.

(i) Write the rate law for above reaction.

(ii) What will happen to the rate of reaction when concentration of A, B and C are doubled.

Element — Hydrogen
Atomic number — 1
Symbol — H
Atomic mass — 1.008
State of matter

Gas
Liquid
Solid
Synthetic

Metal
Metalloid
Nonmetal
Recently discovered

	1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	9	10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1	Hydrogen 1 H 1.008																	Helium 2 He 4.003
2	Lithium 3 Li 6.941	Beryllium 4 Be 9.012											Boron 5 B 10.811	Carbon 6 C 12.011	Nitrogen 7 N 14.007	Oxygen 8 O 15.999	Fluorine 9 F 18.998	Neon 10 Ne 20.180
3	Sodium 11 Na 22.990	Magnesium 12 Mg 24.305											Aluminum 13 Al 26.982	Silicon 14 Si 28.086	Phosphorus 15 P 30.974	Sulfur 16 S 32.065	Chlorine 17 Cl 35.453	Argon 18 Ar 39.948
4	Potassium 19 K 39.098	Calcium 20 Ca 40.078	Scandium 21 Sc 44.956	Titanium 22 Ti 47.867	Vanadium 23 V 50.942	Chromium 24 Cr 51.996	Manganese 25 Mn 54.938	Iron 26 Fe 55.845	Cobalt 27 Co 58.933	Nickel 28 Ni 58.693	Copper 29 Cu 63.546	Zinc 30 Zn 65.39	Gallium 31 Ga 69.723	Germanium 32 Ge 72.64	Arsenic 33 As 74.922	Selenium 34 Se 78.96	Bromine 35 Br 79.904	Krypton 36 Kr 83.80
5	Rubidium 37 Rb 85.468	Strontium 38 Sr 87.62	Yttrium 39 Y 88.906	Zirconium 40 Zr 91.224	Niobium 41 Nb 92.906	Molybdenum 42 Mo 95.94	Technetium 43 Tc (98)	Ruthenium 44 Ru 101.07	Rhodium 45 Rh 102.906	Palladium 46 Pd 106.42	Silver 47 Ag 107.868	Cadmium 48 Cd 112.411	Indium 49 In 114.818	Tin 50 Sn 118.710	Antimony 51 Sb 121.760	Tellurium 52 Te 127.60	Iodine 53 I 126.904	Xenon 54 Xe 131.293
6	Cesium 55 Cs 132.905	Barium 56 Ba 137.327	Lanthanum 57 La 138.906	Hafnium 72 Hf 178.49	Tantalum 73 Ta 180.948	Tungsten 74 W 183.84	Rhenium 75 Re 186.207	Osmium 76 Os 190.23	Iridium 77 Ir 192.217	Platinum 78 Pt 195.078	Gold 79 Au 196.967	Mercury 80 Hg 200.59	Thallium 81 Tl 204.383	Lead 82 Pb 207.2	Bismuth 83 Bi 208.980	Polonium 84 Po (209)	Astatine 85 At (210)	Radon 86 Rn (222)
7	Francium 87 Fr (223)	Radium 88 Ra (226)	Actinium 89 Ac (227)	Rutherfordium 104 Rf (261)	Dubnium 105 Db (262)	Seaborgium 106 Sg (266)	Bohrium 107 Bh (264)	Hassium 108 Hs (277)	Meitnerium 109 Mt (268)	Darmstadtium 110 Ds (281)	Unununium * 111 Uuu (272)	Ununbium * 112 Uub (285)		Ununquadium * 114 Uuq (289)				

The number in parentheses is the mass number of the longest lived isotope for that element. * Names not officially assigned. Discovery of element 114 recently reported. Further information not yet available.

Lanthanide series	Cerium 58 Ce 140.116	Praseodymium 59 Pr 140.908	Neodymium 60 Nd 144.24	Promethium 61 Pm (145)	Samarium 62 Sm 150.36	Europium 63 Eu 151.964	Gadolinium 64 Gd 157.25	Terbium 65 Tb 158.925	Dysprosium 66 Dy 162.50	Holmium 67 Ho 164.930	Erbium 68 Er 167.259	Thulium 69 Tm 168.934	Ytterbium 70 Yb 173.04	Lutetium 71 Lu 174.967
Actinide series	Thorium 90 Th 232.038	Protactinium 91 Pa 231.036	Uranium 92 U 238.029	Neptunium 93 Np (237)	Plutonium 94 Pu (244)	Americium 95 Am (243)	Curium 96 Cm (247)	Berkelium 97 Bk (247)	Californium 98 Cf (251)	Einsteinium 99 Es (252)	Fermium 100 Fm (257)	Mendelevium 101 Md (258)	Nobelium 102 No (259)	Lawrencium 103 Lr (262)