UNIVERSITY OF SWAZILAND

EXAMINATION 2009-10

TITLE OF PAPER: INTRODUCTORY PHYSICAL CHEMISTRY

COURSE NUMBER: C202

TIME: THREE (3) HOURS

INSTRUCTIONS:

There are **six** questions. Each question is worth 25 marks. Answer **any four** questions.

A data sheet and a periodic table are attached

Non-programmable electronic calculators may be used.

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Question 1(25marks)

(a) Explain clearly what is meant by a thermodynamically reversible process. Why is the reversible work done on a system the maximum work? [5]

(b) 2 moles of oxygen gas (which can be assumed to be perfect with C_p =29.4 J $K^{-1}mol^{-1}$) are confined in a volume of 11.2 dm^3 at 273 K. The gas is then heated reversibly to 373 K at constant volume.

(i) What is the initial pressure of the gas? [4]
(ii) How much work is done on the system? [2]
(iii) What is the increase in the internal energy of the system? [5]
(iv) How much heat was added to the system? [2]
(v) What is the final pressure of the gas? [4]
(vi) What is the change in the enthalpy? [3]

Question 2 (25 marks)

Naphthalene, $C_{10}H_8$, melts at 80 °C. If the vapour pressure of the liquid is 10 Torr at 85.5 °C and 40 Torr at 119.3°C and that of the solid is 1 Torr at 52.6 °C;

(a) Calculate the $\Delta_{vap}H$ of the liquid, the boiling point temperature, T_b, and $\Delta_{vao}S$ at T_b [10]

(b) Calculate the vapour pressure at the melting point [4]

(c) Assuming the melting point and the triple temperature are the same, calculate $\Delta_{sub}H$ and $\Delta_{fus}H$ [6]

(d) What must the temperature be if the pressure of the solid is to be less than 10^{-5} Torr? [5]

Question 3(25 marks)

(a) Explain the significance of a physical observable being a state function. List at least five(5) state functions you encountered in this course. [5]

(b) Three moles of a perfect gas at 27 °C expand isothermally and reversibly from 20 dm^3 to 60 dm^3. Calculate w, q, ΔU, ΔH and ΔS. [10]

(c) Suppose the expansion in (b) was carried out isothermally but irreversibly against zero external pressure i.e. p_{ex} = 0, which of the properties calculated in (b) would have different values and what are those values. [4]

(d) Define or briefly explain the following terms

(i) Boyle temperature
(ii) Critical temperature
(iii) Principle of corresponding states [6]

Question 4(25 marks)

The water gas reaction is

$H_2(g) + CO_2 \rightarrow H_2O(g) + CO(g)$

Answer the following equations using the information given in the table below:

(a) Calculate $\Delta_r H^\theta$, $\Delta_r S^\theta$, and $\Delta_r G^\theta$ for the reaction at 298 K. Comment on the spontaneity of the reaction at this temperature. [10]

(b) Calculate $\Delta_r H^\theta$ at 1200 for the above reaction [8]

(c) Assuming, $\Delta_r S^\theta$ for this reaction is independent of temperature, calculate $\Delta_r G^\theta$ and the equilibrium constant, K_p, at 1200 K. [7]

Data for question 4. (Note $C_p = a + bT + cT^2$ in the range 273 K to 1500 K)

substance	$\Delta_f H^\theta$(298 K) kJ mol^{-1}	S^θ(298 K) J K^{-1} mol^{-1}	C_p/J K^{-1} mol^{-1}		
			a	b	c
$H_2O(g)$	-241.82	188.83	30.0	10.0×10^{-3}	12.0×10^{-7}
$CO(g)$	-110.53	197.67	26.9	7.0×10^{-3}	-8.0×10^{-7}
$CO_2(g)$	-393.51	213.74	26.0	44.0×10^{-3}	-148×10^{-7}
$H_2(g)$	0	130.68	29.0	-0.8×10^{-3}	20.0×10^{-7}

Question 5 (25 marks)

(a) Discus the physical interpretation/significance of the Maxwell relations, use the following relation to illustrate your argument; $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$. [5]

(b) A Carnot cycle uses 1.00 mol of a monatomic gas ($C_{V,m}$=3/2 R) as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.00 atm (step 1), and then adiabatically to a temperature of 300 K (step 2). This expansion is followed by an isothermal compression (step 3), and then an adiabatic compression (step 4) back to the initial state. Calculate q, w, ΔU, ΔH, ΔS, ΔS_{total}, and ΔG for each step and for the cycle as whole. [20]

Question 6 (25 marks)

(a) Measurement of the boiling point elevation can provide a determination of the molar mass of a solute.

(i) What factors guide the selection of a solvent for such measurements? [5]

(ii) Clearly describe how a value of K_b for a chosen solvent may be determined experimentally. [5]

(iii) With the value of K_b determined, show how an unknown molecular mass may be estimated. [5]

(b) The vapour pressure of chloroform, $CHCl_3$, and carbon tetrachloride, CCl_4, at 25 °C are 199.1 Torr and 114.5 Torr, respectively. Consider a liquid mixture containing 1 mol of each liquid in equilibrium with its vapour. Calculate

(i) the total vapour and [6]

(ii) the mole fraction of each component in the vapour. [4]

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = N_A e$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_A k$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		6.2364×10 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ Kg
Mass		
electron	m_e	$9.109\,39 \times 10^{-31}$ Kg
proton	m_p	$1.672\,62 \times 10^{-27}$ Kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ Kg
Vacuum permittivity	$\varepsilon_o = 1/c^2\mu_o$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_o$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	$4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^{2} J^{-1} m^{3}
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
g value	g_e	$2.002\,32$
Bohr radius	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^2$	$1.097\,37 \times 10^{7}$ m^{-1}
Standard acceleration of free fall	g	$9.806\,65$ m s^{-2}
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} Kg^{-2}

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1×10^{-7} J
1 eV	=	$1.602\,2 \times 10^{-19}$ J	1 eV/molecule	=	96 485 kJ mol^{-1}

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12					TRANSITION ELEMENTS						26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

Atomic mass → 10.811
Symbol → B
Atomic No. → 5

*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.