

UNIVERSITY OF SWAZILAND

BACHELOR OF SCIENCE

EXAMINATION 2006

TITLE OF PAPER : PHYSICAL CHEMISTRY

COURSE NUMBER : C202

TIME : 3 HOURS

INSTRUCTIONS : THERE ARE SIX QUESTIONS

: ANSWER ANY FOUR QUESTIONS

: BEGIN THE ANSWER TO EACH QUESTION ON
A SEPARATE SHEET OF PAPER

: DATA SHEETS ARE PROVIDED WITH THIS
EXAMINATION PAPER

DO NOT OPEN THIS PAPER UNTIL THE INVIGILATOR INSTRUCTS YOU TO DO
SO.

Question 1 [25 Marks]

- a) With the aid of a detailed sketch of pressure-volume isotherm plots distinguish a real gas from an ideal gas. Your sketch should include the liquid/gas equilibrium zone, the supercritical fluid region, the critical point, the Boyles temperature and the liquid zone.

Your account should make mention of interactions, relevant equations and any necessary theories to help clarify your discussion. [10]

- b) A 1.00-mol. Sample of O₂ and a 3.00-mol sample of H₂ are mixed isothermally in a 125.3-L container at 125°C.
- (i) Assuming ideal gas behavior, calculate the partial pressure of each gas and the total pressure of the gaseous mixture. [6]
- (ii) After the gaseous mixture described in b(i) undergoes reaction to form water, what will be the partial pressure of each gas and the total pressure of the resulting mixture? Assume isothermal conditions and ideal gas behavior. [9]

Question 2 [25 Marks]

- a) Write short notes on any Two of the following: [10]
- Virial equation
 - Berthelot's equation
 - van der waal's equation

Use diagrams, equations or plots to clarify your notes where necessary.

- b) A real gas equation of state for a gas is given by:

$$(P+an^2/TV^2)(V-nb)=nRT \quad (1)$$

- Derive an expression for V_{m,c}, T_c and P_c. [6]
- Find an expression for the Boyle's temperature, T_B. [4]
- Estimate the temperature at which oxygen behaves as an ideal gas, T_B given the constants: a=6.493 L²atmmol⁻² and b=5.622x10⁻²Lmol⁻¹ [2]
- Estimate the radii of real gas molecules using equation (1) given that the critical molar volume is 250 cm³mol⁻¹ [3]

Question 3 [25 MARKS]

- a) Using examples and/or diagrams compare and contrast Any Two of the following terms
- reversible and irreversible expansion [5]
 - path and state functions [5]
 - work and heat [5]
 - change in internal energy and change in enthalpy [5]
 - Extensive and intensive variables [5]

- b) A 5.0 g block of solid carbon dioxide is allowed to evaporate in a vessel of volume 100 cm^3 maintained at 20°C .
- Derive an expression for reversible isothermal expansion. [5]
 - Calculate the work done when the system expands isothermally against a pressure of 1.0 atm [5]
 - Calculate the work done when the system expands isothermally and reversibly. [5]

Question 4 [25 Marks]

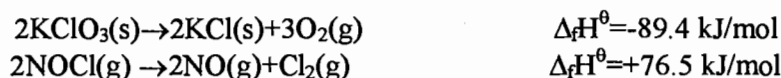
- a) Compare and contrast **Any One Pair** of the following concepts:
- Statistical view and the thermodynamic view of entropy [10]
 - Adiabatic and Isothermal expansion [10]
 - Second and Third law of thermodynamics [10]

For each concept include the origin or a short derivation showing its origin, an example where applicable and the role or implication of each of the concepts in thermodynamics.

- b) 1.00 mol of perfect gas at 27°C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm. Calculate q , w , ΔS_{sys} , ΔS_{surr} and ΔS_{tot} if the expansion is done:
- reversibly, and [5]
 - against a constant external pressure of 1.00 atm [5]
 - adiabatically against a constant pressure of 1.00 atm [5]

Question 5 [25 Marks]

- a) Write short notes on **any two** of the following
- enthalpy change [5]
 - internal energy change [5]
 - Hess's Law [5]
- b) To Calibrate a calorimeter a 0.120 g naphthalene, $\text{C}_{10}\text{H}_8(\text{s})$, was burnt at constant volume and it caused the temperature of the calorimeter to rise by 3.05 K. Then 0.10 g of an unknown compound was burned in the same calorimeter, causing a temperature rise of 2.05 K.
- Calculate the heat capacity of the calorimeter [3]
 - Is the unknown compound phenol, $\text{C}_6\text{H}_5\text{OH}(\text{s})$ or ethanol, $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$ whose enthalpies of combustion are $\Delta_c H^\ominus = -3054 \text{ kJmol}^{-1}$ and -1368 kJmol^{-1} respectively. [4]
- c) Calculate the standard enthalpies of formation of:
- $\text{KClO}_3(\text{s})$ from the enthalpy of formation of KCl [4]
 - $\text{NOCl}(\text{g})$ from the enthalpy of formation of NO [4]
- Given the attached table and the following information:



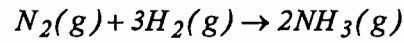
Question 6 [25 Marks]

a) Derive the integrated Gibbs-Helmholtz equation [5]

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

from the fundamental thermodynamic equation $dG = VdP - SdT$

b) Given the reaction:



Calculate the change in Gibbs free energy ΔG^θ

i) at 298K [5]

ii) at 500K [5]

iii) Comment on the significance of the values obtained in (i) and (ii). [2]

c) The Master Equation states that $dU = TdS - PdV$.

(i) Using the Master Equation above derive the Maxwell's relation

$$(\delta S / \delta V)_T = (\delta P / \delta T)_V \quad [5]$$

(ii) Using the Maxwell's relation in (i) find the expression for internal energy change with volume under isothermal conditions for real gases using Van der Waal's relation:

$$(P + an^2/TV^2)(V - nb) = nRT \quad [5]$$

PHYSICAL CHEMISTRY
GENERAL DATA SHEETS

5 PAGES

THIS LEAFLET CONSISTS OF:

- ◆ GENERAL CONSTANTS
- ◆ STANDARD MOLAR ENTHALPIES
- ◆ STANDARD MOLAR ENTROPIES
- ◆ STANDARD MOLAR GIBBS FREE ENERGIES
- ◆ HEAT CAPACITIES
- ◆ PERIODIC TABLE

Useful Relations				General Data		
$(RT)_{298.15K} = 2.4789$ kJ/mol		speed of light	c	$2.997\ 925 \times 10^8$ ms ⁻¹		
$(RT/F)_{298.15K} = 0.025\ 693$ V		charge of proton	e	$1.602\ 19 \times 10^{-19}$ C		
T/K: 100.15 298.15 500.15 1000.15		Faraday constant	$F = Le$	$9.648\ 46 \times 10^4$ C mol ⁻¹		
T/Cm ⁻¹ : 69.61 207.22 347.62 695.13		Boltzmann constant	k	$1.380\ 66 \times 10^{-23}$ J K ⁻¹		
1mmHg = 133.222 N m ⁻²		Gas constant	$R = Lk$	$8.314\ 41$ J K ⁻¹ mol ⁻¹		
hc/k = 1.438 78 x 10 ⁻² m K				$8.205\ 75 \times 10^{-2}$ dm ³ atm K ⁻¹ mol ⁻¹		
1atm	1 cal	1 eV	1cm ⁻¹			
1.01325×10^5 Nm ⁻²	4.184 J	$1.602\ 189 \times 10^{-19}$ J	Planck constant	h		
760 torr	96.485 kJ/mol	1.9864×10^{-23} J		$\hbar = \frac{h}{2\pi}$		
	8065.5 cm ⁻¹			$1.054\ 59 \times 10^{-34}$ Js		
SI-units:			Avogadro constant	$6.022\ 14 \times 10^{23}$ mol ⁻¹		
$1\ L = 1000\ ml = 1000\ cm^3 = 1\ dm^3$			Atomis mass unit	$1.660\ 54 \times 10^{-27}$ kg		
1 dm = 0.1 m			Electron mass	$9.109\ 39 \times 10^{-31}$ kg		
1 cal (thermochemical) = 4.184 J			Proton mass	$1.672\ 62 \times 10^{-27}$ kg		
dipole moment: 1 Debye = 3.335 64 x 10 ⁻³⁰ C m			Neutron mass	$1.674\ 93 \times 10^{-27}$ kg		
force: $1N = 1J\ m^{-1} = 1kg\ ms^{-2} = 10^5$ dyne			Vacuum permittivity	$8.854\ 188 \times 10^{-12}$ J ⁻¹ C ² m ⁻¹		
pressure: $1Pa = 1Nm^{-2} = 1Jm^{-3}$			Vacuum permeability	$4\pi \times 10^{-7}$ Js ² C ⁻² m ⁻¹		
$IJ = 1Nm$			Bohr magneton	$9.274\ 02 \times 10^{-24}$ JT ⁻¹		
power: 1W = 1J s ⁻¹			Nuclear magneton	5.05079×10^{-27} JT ⁻¹		
magnetic flux: 1T = 1Vsm ⁻² = 1JCsm ⁻²						
current: 1A = 1Cs ⁻¹			Gravitational constant	6.67259×10^{-11} Nm ² kg ⁻²		
Prefixes:			Gravitational acceleration	9.80665 ms ⁻²		
p nano	m micro	m milli	Bohr radius	$5.291\ 77 \times 10^{-11}$ m		
c centi	d deci	k kilo				
M mega	G giga					
10 ⁻¹²	10 ⁻⁹	10 ⁻⁶				
10 ⁻³	10 ⁻²	10 ⁻¹				
10 ³	10 ⁶	10 ⁹				

M_r	$\Delta H_f^\ominus/\text{kJ mol}^{-1}$	M_r	$\Delta H_f^\ominus/\text{kJ mol}^{-1}$	Gases (298-2000K)		
				$a/\text{J K}^{-1}\text{mol}^{-1}$	$b/10^{-3}\text{J K}^{-2}\text{mol}^{-1}$	$c/10^5\text{J Kmol}^{-1}$
H ₂ O(g)	18.015	-241.8	O ₃ (g)	47.998	+142.7	
H ₂ O(l)	18.015	-285.8	NO(g)	30.006	+90.2	
H ₂ O ₂ (l)	34.015	-187.8	NO ₂ (g)	46.006	+33.2	
NH ₃ (g)	17.031	-46.1	N ₂ O ₄ (g)	92.012	+9.2	
NH ₄ (l)	32.045	+50.6	SO ₂ (g)	64.063	-296.8	
N ₂ H ₄ (l)	43.028	+264.1	H ₂ S(g)	34.080	-20.6	
N ₂ H ₄ (g)	43.028	+294.1	SF ₆ (g)	146.054	-1209	
HNO ₃ (l)	63.013	-174.1	HF(g)	20.006	-271.1	
NH ₄ OH(s)	33.030	-114.2	HCl(g)	36.461	-92.3	
NH ₄ Cl(s)	53.492	-314.4	HCl(aq)	36.461	-110.5	
HgCl ₂ (s)	271.50	-224.3	HBr(g)	80.917	-167.2	
H ₂ SO ₄ (l)	98.078	-814.0	HI(g)	127.912	+26.5	
H ₂ SO ₄ (aq)	98.078	-909.3	CO ₂ (g)	44.010	-393.5	
NaCl(s)	58.443	-411.0	CO(g)	28.011	-110.5	
NaOH(s)	39.997	-426.7	Al ₂ O ₃ (s)	101.945	-1675.7	
KCl(s)	74.555	-435.9	SiO ₂ (s)	60.085	-910.9	
KBr(s)	119.011	-392.2	FeS(s)	87.91	-100.0	
KI(s)	166.006	-327.6	FeS ₂ (s)	119.975	-178.2	
Diatomic(s)	—	0	AgCl(s)	143.323	-127.1	
Enthalpies of fusion and evaporation $\Delta H_m/\text{kJ mol}^{-1}$ at the transition temperature						
	T/K	Fusion ^a	T/K	Evaporation ^b		
He	3.5	0.021	4.22	0.084		
Ar	83.81	1.188	87.29	6.506		
H ₂	13.96	0.117	20.38	0.9163		
N ₂	63.15	0.719	77.35	5.586		
O ₂	54.36	0.444	90.18	6.820		
Cl ₂	172.12	6.406	239.05	20.410		
Br ₂	265.90	10.573	332.35	29.445		
I ₂	386.75	15.52	458.39	41.80		
Hg	234.29	2.292	629.73	59.296		
Ag	1234	11.30	2436	250.63		
Na	370.95	2.601	1156	98.01		
CO ₂	217.0	8.33	194.64	25.23 ^L		
H ₂ O	273.15	6.008	373.15	40.856 (44.016 at 298.15 K)		
NH ₃	195.40	5.652	239.73	23.351		
H ₂ S	187.61	2.377	212.80	16.673		
CH ₄	90.68	0.941	111.66	8.18		
C ₂ H ₆	89.85	2.86	184.55	14.7		
C ₆ H ₆	278.65	10.59	353.25	30.8		
CH ₃ OH	175.25	3.159	337.22	35.27 (37.99 at 298.15 K)		
Standard molar enthalpies of formation and combustion at 298.15 K						
				M_r	$\Delta H_f^\ominus/\text{kJ mol}^{-1}$	$\Delta H_c^\ominus/\text{kJ mol}^{-1}$
CH ₄ (g)				16.043	-74.81	1300
C ₂ H ₂ (g)				26.038	+226.8	1411
C ₂ H ₄ (g)				28.054	+52.30	1560
C ₂ H ₆ (g)				30.070	-84.64	2091
C ₃ H ₆ (propene)(g)				42.081	53.35	2058
C ₄ H ₁₀ (n-butane)(g)				58.124	-126.11	2877
C ₅ H ₁₂ (n-pentane)(g)				72.151	-146.4	3536
C ₆ H ₁₂ (cyclohexane)(l)				84.163	-156.2	4163
C ₆ H ₁₄ (n-hexane)(l)				86.178	-198.7	3268
C ₆ H ₆ (benzene)(l)				78.115	+48.99	5471
C ₁₀ H ₈ (n-octane)(l)				114.233	-249.8	726.1
C ₁₀ H ₈ (naphthalene)(l)				128.175	+78.53	1193
CH ₃ OH(l)				32.042	-239.0	1368
CH ₃ CHO(l)				44.054	-166.0	1368
CH ₃ COOH(l)				46.070	-277.0	874.5
CH ₃ COOH(l)				60.053	-484.2	2231
CH ₃ COOC ₂ H ₅ (l)				88.107	-486.6	3054
C ₆ H ₅ OH(s)				94.114	-165.0	3393
C ₆ H ₅ NH ₂ (l)				93.129	-31.1	632.2
NH ₂ CO.NH ₂ (urea)(s)				60.056	-333.0	964.4
CH ₂ (NH ₂)CO ₂ H, glycine(s)				75.068	-537.2	2802
C ₆ H ₁₂ O ₆ , α-D-glucose(s)				180.159	-1274	2808
C ₆ H ₁₂ O ₆ , β-D-glucose(s)				180.159	-1268	2808
C ₁₂ H ₂₂ O ₁₁ , sucrose(s)				342.303	-2222	5645
CH ₃ CH(OH)COOH, lactic acid(s)				90.079	-694.0	1344

^L Sublimation; ^a Various pressures; ^b at 1 atm

Source: American Institute of Physics handbook, McGraw-Hill.

Heat capacities at 25°C

	$C_{v,m}$	$C_{p,m}$
	$\text{JK}^{-1} \text{mol}^{-1}$	$\text{JK}^{-1} \text{mol}^{-1}$
He, Ne, Ar, Kr, Xe	12.47	20.78
H_2	20.50	28.81
O_2	21.01	29.33
N_2	20.83	29.14
CO_2	28.83	37.14
NH_3	27.17	35.48
CH_4	27.43	35.74

F.P. Depression, B.P. Elevation

Solvent	F.P. °C	K_f °C kg mol ⁻¹	B.P. (°C, 101kNm ⁻²)	K_b °C kg mol ⁻¹
Water	0	1.86	100.0	0.52
Benzene	5.51	5.10	80.1	2.60
Acetic Acid	16.6	3.90	118.1	3.10
Cyclohexane	6.5	20.2	81.4	2.79
Camphor	177.7	40.0	205	-
Nitrobenzene	5.7	6.9	210.9	5.24
Ethanol	-177		78.5	1.22
Chloroform	-64		61.3	3.63

Third Law entropies at 25°C, $\text{Sm}^{\circ}/\text{JK}^{-1} \text{mol}^{-1}$

Solids		Liquids		Gases	
Ag	42.68	Hg	76.02	H_2	130.6
C(gf)	5.77	Br_2	152.3	N_2	192.1
C(d)	2.44			O_2	205.1
Cu	33.4			Cl_2	223.0
Zn	41.6	H_2O	70.0		
I_2	116.7			CO_2	213.7
S(Rh)	31.9	HNO_3	155.6	HCl	186.8
AgCl	96.2	$\text{C}_2\text{H}_5\text{OH}$	161.0	H_2S	205.6
AgBr	104.6	CH_3OH	126.7	NH_3	192.5
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	305.4	C_6H_6	49.03	CH_4	186.1
HgCl_2	144	CH_3COOH	159.8	C_2H_6	229.4
Sucrose	360.2	C_6H_{12}	298.2	CH_3CHO	265.7

THE PERIODIC TABLE OF ELEMENTS

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII B	VIII B	IB	IIB	IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
Period 1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.9	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.01	25 Mn 54.9	26 Fe 55.85	27 Co 58.71	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.7	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 91.22	42 Mo 95.94	43 Tc 98.9	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	56 Cs 132.9	56 Ba 137.3	71 Lu 174.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 196.9	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po 210	85 At 210	86 Rn 222
7	87 Fr 223	88 Ra 226.0	103 Lr 257	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.9	63 Eu 151.3	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
Actinides	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.1	94 Pu 239.1	95 Am 241.1	96 Cm 247.1	97 Bk 249.1	98 Cf 251.1	99 Es 254.1	100 Fm 257.1	101 Md 258.1	102 No 255

Numbers below the symbol indicates the atomic masses; and the numbers above the symbol indicates the atomic numbers.

SOURCE: International Union of Pure and Applied Chemistry, *I mills, ed., Quantities, Units, and symbols in Physical Chemistry*, Blackwell Scientific publications, Boston.