

UNIVERSITY OF SWAZILAND
BACHELOR OF SCIENCE

EXAMINATION 2016

TITLE OF PAPER : INTRODUCTORY PHYSICAL CHEMISTRY

COURSE NUMBER : C202

TIME : 3 HOURS

INSTRUCTIONS : THERE ARE SEVEN 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) Gases behave as ideal and non-ideal gases in defined P,V and T zones. With the aid of any two of the following: [15]

Lennard-Jones potential plot;
Compressibility plots and
Isotherm plots,

Compare and contrast real and ideal gases. Your account should make mention of interactions, equations and the kinetic theory of gases to help clarify your discussion.

- b) A mixture of butane (C_4H_{10}) and propene (C_3H_6) occupied 35.5 L at 1.000 bar and 405 K. This mixture reacted completely with 220.6 g of O_2 to produce CO_2 and H_2O .

- i) What was the composition of the original mixture? Assume ideal gas behaviour.
 $MW(O_2)=32 \text{ g/mol}$ [5]
- ii) Calculate the partial pressure, mole fraction of each gas and the total pressure of the final mixture. [5]

Question 2 [25 Marks]

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

$$P = \frac{RT}{V_m - nb} - \frac{a}{V_m^2} \quad (\text{equation (1)})$$

- a) Based on van der Waals assumptions discuss the bases and significance of the main terms in equation (1) in terms of gas behaviour. [10]
- b) Derive expressions for $V_{m,c}$, T_c and P_c . [6]
- c) Find an expression for the Boyle's temperature, T_B . [5]
- d) Estimate the temperature at which oxygen behaves as an ideal gas, T_B given the constants:
 $a=6.493 \text{ L}^2 \text{atmmol}^{-2}$, $b=5.622 \times 10^{-2} \text{ Lmol}^{-1}$ [2]
- e) Estimate the radii of real gas molecules using equation (1) for real gases given a critical molar volume of $250 \text{ cm}^3 \text{mol}^{-1}$ [2]

Question 3 [25 Marks]

- a) Using examples and/or diagrams compare and contrast **Any Three** of the following terms
- reversible and irreversible expansion [5]
 - path and state functions [5]
 - change in internal energy and change in enthalpy [5]
 - Work and heat [5]
- b) the work done during the isothermal reversible expansion of a gas that satisfies the virial equation of state
Evaluate:
- $$\frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V^2_m} + \dots; B = -21.7 \text{ cm}^3 \text{ mol}^{-1} \text{ & } C = 1200 \text{ cm}^6 \text{ mol}^{-2}$$
- Derive an expression for work for a real gas that satisfies the virial equation in a reversible isothermal expansion [6]
 - Calculate work for 1.0 mol Ar at 273 K obeying the virial gas equation [4]

QUESTION 4 [25 marks]

Adiabatic expansion of an ideal gas is quite different from isothermal expansion.

- Explain what is meant by adiabatic expansion, draw an adiabat and an isotherm on a P versus V graph and compare them. [10]
- Derive the expression for the change in temperature of an adiabatic expansion of an ideal gas for a reversible process from V_i to V_f . [6]
- A sample of argon at 1.0 atm pressure and 25°C expands reversibly and adiabatically from 0.50 L to 1.00 L. calculate:
 - final temperature
 - work done
 - change in internal energy. [9]

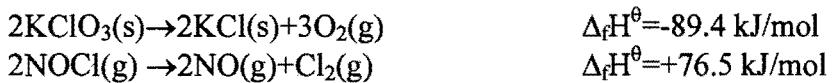
QUESTION 5 [25 MARKS]

- Write short notes on of the following
 - Hess's Law [5]
 - Kirchoff's Law [5]
- To Calibrate a calorimeter a 0.120 g naphthalene, $C_{10}H_8(s)$, was burned 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, $C_6H_5OH(s)$ or ethanol, $CH_3CH_2OH(l)$ whose enthalpies of combustion are $\Delta_C H^\theta = -3054 \text{ kJ mol}^{-1}$ and $-1368 \text{ kJ mol}^{-1}$ respectively. [4]

c) Calculate the standard enthalpies of formation of:

- i) $\text{KClO}_3(\text{s})$ from the enthalpy of formation of KCl [4]
- ii) $\text{NOCl}(\text{g})$ from the enthalpy of formation of NO [4]

Given the attached table and the following information:



Question 6 [25 Marks]

- a) Briefly discuss **Any Two** of the following:
- (i) Statistical view of entropy [5]
(ii) Second Laws of Thermodynamics [5]
(iii) Third Law of Thermodynamics [5]
- 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 ΔS_{sys} , ΔS_{surr} and ΔS_{tot} if the expansion is done:
- (1) reversibly. [3]
(2) against a constant external pressure of 1.00 atm. [2]
(3) adiabatically against a constant pressure of 1.00 atm. [5]
- c) If 50g water at 80°C is poured into 100g water at 10°C in an insulated vessel given that $C_{\text{p,m}} = 75.5 \text{ JK}^{-1}\text{mol}^{-1}$: Calculate:
- i) final temperature of the mixture [3]
ii) the entropy change [2]

QUESTION 7[25 MARKS]

- a) Draw a sketch of the phase diagram of carbon dioxide and explain briefly the slopes and curvature of the liquid-solid and the liquid-gas boundaries, respectively. [5]
- b) i) Derive the Clausius-Clapeyron equation for evaporation. [5]
- ii) The triple point of benzene is at 5.30°C and 35 mm Hg. Predict the boiling point of benzene at 0.15 atm pressure. [5]
- c) Write short notes on **Any Two** of the following terms:
- i) Zeotrope [5]
ii) Azeotrope [5]
iii) Eutectic point [5]
iv) Congruent melting point [5]
-

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
N ₂ O ₄		77.28
NO ₂		37.20

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, Sm^θ/J K⁻¹ mol⁻¹

	Solids	Liquids	Gases
Ag	42.68	Hg	76.02
C(gr)	5.77	Br ₂	152.3
C(d)	2.44		
Cu	33.4	H ₂ O	70.0
Zn	41.6		CO
I ₂	116.7		CO ₂
S(Rh)	31.9	HNO ₃	155.6
			HCl
			H ₂ S
AgCl	96.2	C ₂ H ₅ OH	161.0
AgBr	104.6	CH ₃ OH	126.7
CuSO ₄ ·5H ₂ O	305.4	C ₆ H ₆	49.03
HgCl ₂	144	CH ₃ COOH	159.8
Sucrose	360.2	C ₆ H ₁₂	298.2

Standard molar enthalpies of formation at 298.15 K

Temperature dependence of heat capacities, $C_{p,m} = a+bT+cT^{-2}$

\perp Sublimation: ^avarious pressures; ^bat 1 atm

Source: American Institute of Physics handbook, McGraw-Hill

Useful Relations				General Data			
(RT) _{298.15K} =2.4789 kJ/mol				speed of light	c	2.997 925x10 ⁸ ms ⁻¹	
(RT/F) _{298.15K} =0.025 693 V				charge of proton	e	1.602 19x10 ⁻¹⁹ C	
T/K: 100.15 298.15 500.15 1000.15				Faraday constant	F=Le	9.648 46x10 ⁴ C mol ⁻¹	
T/Cm ⁻¹ : 69.61 207.22 347.62 695.13				Boltzmann constant	k	1.380 66x10 ⁻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 78x10 ⁻² m K						8.205 75x10 ⁻² dm ³ atm K ⁻¹ mol ⁻¹	
1atm	1 cal	1 eV	1cm ⁻¹				
-1.01325x10 ⁵ Nm ⁻²	-4.184 J	=1.602 189x10 ⁻¹⁹ J	=0.124x10 ⁻³ eV	Planck constant	h	6.626 18x10 ⁻³⁴ Js	
-760torr		=96.485 kJ/mol	=1.9864x10 ⁻²³ J		$\hbar = \frac{h}{2\pi}$	1.054 59x10 ⁻³⁴ Js	
-1 bar		= 8065.5 cm ⁻¹					
SI-units:				Avogadro constant	L or N _{av}	6.022 14x10 ²³ mol ⁻¹	
1 L = 1000 ml = 1000cm ³ = 1 dm ³				Atomis mass unit	u	1.660 54x10 ⁻²⁷ kg	
1 dm = 0.1 m				Electron mass	m _e	9.109 39x10 ⁻³¹ kg	
1 cal (thermochemical) = 4.184 J				Proton mass	m _p	1.672 62x10 ⁻²⁷ kg	
dipole moment: 1 Debye = 3.335 64x10 ⁻³⁰ C m				Neutron mass	m _n	1.674 93x10 ⁻²⁷ kg	
force: 1N=1J m ⁻¹ =1kgms ⁻² =10 ⁵ dyne pressure: 1Pa=1Nm ⁻² =1Jm ⁻³				Vacuum permittivity	$\epsilon_0 = \mu_0^{-1} c^{-2}$	8.854 188x10 ⁻¹² J ⁻¹ C ² m ⁻¹	
1J=1Nm				Vacuum permeability	μ_0	4πx10 ⁻⁷ Js ² C ⁻² m ⁻¹	
power: 1W = 1J s ⁻¹			potential: 1V =1 J C ⁻¹	Bohr magneton	$\mu_B = \frac{e\hbar}{2m_e}$	9.274 02x10 ⁻²⁴ JT ⁻¹	
magnetic flux: 1T=1Vsm ⁻² =1JCsm ⁻²			current: 1A=1Cs ⁻¹	Nuclear magneton	$\mu_N = \frac{e\hbar}{2m_p}$	5.05079x10 ⁻²⁷ JT ⁻¹	
Prefxes:				Gravitational constant	G	6.67259x10 ⁻¹¹ Nm ² kg ⁻²	
p n m m c d k M G				Gravitational acceleration	g	9.80665 ms ⁻²	
pico nano micro milli centi deci kilo mega giga				Bohr radius	a ₀	5.291 77x10 ⁻¹¹ m	
10 ⁻¹² 10 ⁻⁹ 10 ⁻⁶ 10 ⁻³ 10 ⁻² 10 ⁻¹ 10 ³ 10 ⁶ 10 ⁹							

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	V _B	VIB	VIIB	VIIIB			IB	IIB	III _A	IV _A	VA	VIA	VIIA	VIIIA
Period 1	1 H 1.008							NON-METALS										He 4.003
2	3 Li 6.94	4 Be 9.01						METALLOIDS			5 B 10.81	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.0		
3	11 Na 22.99	12 Mg 24.31						METALS			13 Al 26.9	14 Si 28.09	15 P 30.97	16 S 32.0	17 Cl 35.45	18 Ar 39.91		
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 136.9	54 Xe 131.3
6	55 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, 1988, pp 86-98.

Standard molar Gibbs free energy and molar entropy of formation at 298.15 K

	M _T	ΔG _f ^θ /KJ/mol	S ^θ /J K ⁻¹ mol ⁻¹		M _r	ΔG _f ^θ /KJ/mol	S ^θ /J K ⁻¹ mol ⁻¹
H ₂ O(g)	18.015	-228.57	188.83	O ₂ (g)	47.998	163.2	238.93
H ₂ O(l)	18.015	-120.35	109.6	NO(g)	30.006	86.55	210.76
H ₂ O ₂ (l)	34.015	-120.35	109.6	NO ₂ (g)	46.006	51.31	240.06
NH ₃ (g)	17.031	-16.45	192.45	N ₂ O ₄ (g)	92.012	97.89	304.29
N ₂ H ₄ (l)	32.045	149.43	121.21	SO ₂ (g)	64.063	-300.19	248.22
N ₂ H(l)	43.028	327.3	140.6	H ₂ S(g)	34.080	-33.56	205.79
N ₂ H(g)	43.028	328.1	238.97	SF ₆ (g)	146.054	-1105.3	291.82
HNO ₃ (l)	63.013	-80.71	155.60	HF(g)	20.006	-273.2	173.78
NH ₂ OH(s)	33.030			HCl(g)	36.461	-95.30	186.91
NH ₄ Cl(s)	53.492	-202.87	94.6	HCl(aq)	36.461	-131.23	56.5
HgCl ₂ (s)	271.50	-178.6	146.0	HBr(g)	80.917	-53.45	198.70
H ₂ SO ₄ (l)	98.078	-690.00	156.90	HI(g)	127.912	1.70	206.59
H ₂ SO ₄ (aq)	98.078	-744.53	20.1	CO ₂ (g)	44.010	-394.36	213.74
NaCl(s)	58.443	-384.14	72.13	CO(g)	28.011	-137.17	197.67
NaOH(s)	39.997	-379.49	64.46	Al ₂ O ₃ (s)	101.945	-1582.3	50.92
KCl(s)	74.555	-409.14	82.59	SiO ₂	60.09	-856.64	41.84
KBr(s)	119.011	-380.66	95.90	FeS(s)	87.91	-100.4	60.29
KI(s)	166.006	-324.89	106.32	FeS ₂ (s)	119.975	-166.9	52.93
				AgCl(s)	143.323	-109.79	96.2
He(g)	4.003	0	126.15	Hg(g)	200.59	31.82	174.96
Ar(g)	39.95	0	154.84	Hg(l)	200.59	0	76.02
H ₂ (g)	2.016	0	130.684	Ag(g)	107.87	245.65	173.00
N ₂ (g)	28.013	0	191.61	Ag(s)	107.87	0	42.55
O ₂ (g)	31.999	0	205.138	Na(g)	370.95	76.76	153.71
O ₃ (g)	47.998	163.2	238.93	Na(s)	22.99	0	51.21
Cl ₂ (g)	70.91	0	223.07				
Br ₂ (g)	159.82	3.110	245.46				
Br ₂ (l)	159.82	0	152.23				
I ₂ (g)	253.81	19.33	260.69				
I ₂ (s)	253.81	0	116.135				

	M _r	ΔG _f ^θ /KJ/mol	S ^θ /J K ⁻¹ mol ⁻¹
organic compounds			
CH ₄ (g) methane	16.043	-50.72	186.26
C ₂ H ₂ (g) ethyne	26.038	209.20	200.94
C ₂ H ₄ (g) ethene	28.05	68.15	219.56
C ₂ H ₆ (g) ethane	30.070	-32.82	229.60
C ₃ H ₆ cyclopropane(g)	42.081	104.45	237.55
C ₃ H ₆ propene(g)	42.081	62.78	267.05
C ₄ H ₁₀ n-butane (g)	58.124	-17.03	310.23
C ₅ H ₁₂ n-pentane(g)	72.151	-8.20	348.40
C ₆ H ₁₂ cyclohexane (l)	84.163	26.8	
C ₆ H ₁₄ n-hexane (l)	86.178		204.3
C ₆ H ₆ benzene (l)	78.115	124.3	173.3
C ₆ H ₆ benzene (g)	78.115	129.72	269.31
C ₈ H ₁₈ n-octane (l)	114.233	6.4	361.1
C ₁₀ H ₈ naphthalene (l)	128.175		
CH ₃ OH (g)	32.042	-161.96	239.81
CH ₃ OH (l)	32.042	-166.27	126.8
CH ₃ CHO (g)	44.054	-128.86	250.3
CH ₃ CH ₂ OH (l)	46.07	-174.78	160.7
CH ₃ COOH (l)	60.053	-389.9	159.8
CH ₃ COOC ₂ H ₅ (l)	88.107	-332.7	259.4
C ₆ H ₅ OH (s)	94.114	-50.9	146.0
C ₆ H ₅ NH ₂ (l)	93.129		
CH ₂ (NH ₂)CO ₂ H, glycine (s)	75.068	-373.4	103.5
C ₆ H ₁₂ O ₆ , D-glucose (s)	180.159		
C ₆ H ₂₂ O ₆ , D-glucose (s)	180.159	-910	212
C ₁₂ H ₂₂ O ₁₁ , sucrose (s)	342.303	-1543	360.2
CH ₃ CH(OH)COOH	90.079		
lactic acid (s)			

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