University of Eswatini

Department of Chemistry

November 2018 Main Examination

TITLE OF PAPER : **Introduction to Thermodynamics**

COURSE NUMBER : **CHE 241**

TIME : **3 Hours**

Important Information : Each question is equivalent to **25%** of the entire exam.

: Answer **questions one (1)** and any other three **(3)** questions in this paper.

: Marks for **ALL** procedural calculations will be awarded.

: Start each question on a fresh page of the answer sheet.

: Diagrams must be large and clearly labelled accordingly.

: Additional material: data sheet, graph paper and the periodic table.

You are not supposed to open this paper until permission has been granted by the Chief Invigilator

Question 1: Compulsory [25 Marks]

The compressibility factor, X, for a real gas is given by

$$Z = \frac{PV}{nRT}$$

a) Use the following data to plot Z versus P for O_2 at 273 K

P (atm)	1	100	200	300	500	700	900
V_m ($L.mol^{-1}$)	22.41	0.2077	0.1024	0.0719	0.0518	0.0444	0.0403

b) Using the data in (a), compare and contrast real gases and ideal gases [10]

c) The behaviour of gaseous Naphthalene ($C_{10}H_8$) follows the Van der Waals equation of state. Given that at 100°C, $C_{10}H_8$ expands isothermally and reversibly from 20 dm^3 to 60 dm^3, calculate w, q and ΔU. [15]

Question 2 [25 Marks]

a) Write short notes on the following;

i. Enthalpy change [2]

ii. Hess's law [2]

b) Calculate the standard enthalpies of formation of:

i. $KClO_3$ from the enthalpy of formation of KCl [4]

ii. NOCl from the enthalpy of formation of NO; given the attached table and the following information; [4]

$2KClO_3 \rightarrow 2KCl(s) + 3O_2(g)$ $\Delta_f H^\theta = -89.4\ kJ/mol$

$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$ $\Delta_f H^\theta = +76.5\ kJ/mol$

c) Outline the Carnot cycle using a P-V diagram explaining all its stages and associated energy changes and conditions for each step. [6]

d) A heat engine absorbs 2500J of heat and discards 2100J. Calculate the work performed by the engine and its maximum efficiency. [7]

Question 3 [25 Marks]

a) Write short notes on the heat capacity and show how it links with ΔH as well as q_v. [10]

b) The enthalpy of vaporization of bromine is 30.9 kJ/mol and the standard entropy values of liquid and gaseous bromine are 152 J/mol and 245 J/molK. Estimate the boiling point of bromine [10]

c) Show graphically, the differences between an endothermic system and an exothermic system [5]

Question 4 [25 Marks]

a) A Carnot engine takes 4500 J of heat energy from a reservoir at 800 K.

i. How much heat will be released to a cold reservoir at 27°C? [4]

ii. Calculate the amount of work performed by this engine. [3]

iii. What is the Carnot efficiency of this engine [3]

b) Methanol boils at 64.1°C and its enthalpy of vaporization is 35.27 $kJmol^{-1}$. Calculate;

i. The entropy of vaporization at these conditions, [5]

ii. The entropy change of the surroundings. [5]

c) Write short notes on the following;

i. Nernst heat theorem [2]

ii. Standard molar entropy [3]

Question 5 [25 marks]

a) Two empirical equations of state are the Dieterici and the van der Waals equations. Derive the critical constants for both equations of state [15]

b) Write notes on surface tension, include diagrams and examples where necessary [10]

Question 6 [25 marks]

a) To calibrate a calorimeter, 0.120 g naphthalene ($C_{10}H_8$) was burnt at constant volume and it caused the temperature of the calorimeter to rise by 3.05 °C. Then 0.10g of unknown compound was burned in the same calorimeter, causing a temperature rise of 2.05 °C.

i. Calculate the heat capacity of calorimeter [5]

ii. 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 kJmol-1 and -1368 $kJmol^{-1}$, respectively [6]

b) Compare and contrast;

i. Reversible and irreversible expansion [5]

ii. Path and state functions [4]

iii. Change in internal energy and change in enthalpy [5]

The End

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

	M_r	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}
$H_2O(g)$	18.015	-228.57	188.83	$O_3(g)$	47.998	163.2	238.93
$H_2O(l)$	18.015	-120.35	109.6	NO(g)	30.006	86.55	210.76
$H_2O_2(l)$	34.015	-120.35	109.6	$NO_2(g)$	46.006	51.31	240.06
$NH_3(g)$	17.031	-16.45	192.45	$N_2O_4(g)$	92.012	97.89	304.29
$N_2H_4(l)$	32.045	149.43	121.21	$SO_2(g)$	64.063	-300.19	248.22
$N_3H(l)$	43.028	327.3	140.6	$H_2S(g)$	34.080	-33.56	205.79
$N_3H(g)$	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
$NH_2OH(s)$	33.030			HCl(g)	36.461	-95.30	186.91
$NH_4Cl(s)$	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
$H_2SO_4(l)$)	98.078	-690.00	156.90	HI(g)	127.912	1.70	206.59
$H_2SO_4(aq)$	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_2O_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
$C_2H_2(g)$ ethyne	26.038	209.20	200.94
$C_2H_4(g)$ ethene	28.05	68.15	219.56
$C_2H_6(g)$ ethane	30.070	-32.82	229.60
C_3H_6 cyclopropane(g)	42.081	104.45	237.55
C_3H_6 propene(g)	42.081	62.78	267.05
C_4H_{10} n-butane (g)	58.124	-17.03	310.23
C_5H_{12} n-pentane(g)	72.151	-8.20	348.40
C_6H_{12} cyclohexane (i)	84.163	26.8	
C_6H_{14} n-hexane (l)	86.178		204.3
C_6H_6 benzene (l)	78.115	124.3	173.3
C_6H_6 benzene (g)	78.115	129.72	269.31
C_8H_{18} n-octane (l)	114.233	6.4	361.1
$C_{10}H_8$ naphthalene (l)	128.175		
CH_3OH (g)	32.042	-161.96	239.81
CH_3OH (l)	32.042	-166.27	126.8
CH_3CHO (g)	44.054	-128.86	250.3
CH_3CH_2OH (l)	46.07	-174.78	160.7
CH_3COOH (l)	60.053	-389.9	159.8
$CH_3COOC_2H_5$ (l)	88.107	-332.7	259.4
C_6H_5OH (s)	94.114	-50.9	146.0
$C_6H_5NH_2$ (l)	93.129		
$CH_2(NH_2)CO_2H$, glycine (s)	75.068	-373.4	103.5
$C_6H_{12}O_6$, □-D-glucose (s)	180.159		
$C_6H_{22}O_6$, □-D-glucose (s)	180.159	-910	212
$C_{12}H_{22}O_{11}$, sucrose (s)	342.303	-1543	360.2
$CH_3CH(OH)COOH$	90.079		
lactic acid (s)			

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

Standard molar enthalpies of formation at 298.15 K

	M_r	ΔH_f^θ/KJ/mol		M_r	ΔH_f^θ/KJ/mol
$H_2O(g)$	18.015	-241.8	$O_3(g)$	47.998	+142.7
$H_2O(l)$	18.015	-285.8	NO(g)	30.006	+90.2
$H_2O_2(l)$	34.015	-187.8	$NO_2(g)$	46.006	+33.2
$NH_3(g)$	17.031	-46.1	$N_2O_4(g)$	92.012	+9.2
$N_2H_4(l)$	32.045	+50.6	$SO_2(g)$	64.063	-296.8
$N_3H(l)$	43.028	+264.1	$H_2S(g)$	34.080	-20.6
$N_3H(g)$	43.028	+294.1	$SF_6(g)$	146.054	-1209
$HNO_3(l)$	63.013	-174.1	HF(g)	20.006	-271.1
$NH_2OH(s)$	33.030	-114.2	HCl(g)	36.461	-92.3
$NH_4Cl(s)$	53.492	-314.4	HCl(aq)	36.461	-167.2
$HgCl_2(s)$	271.50	-224.3	HBr(g)	80.917	+36.4
$H_2SO_4(l)$	98.078	-814.0	HI(g)	127.912	+26.5
$H_2SO_4(aq)$	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	$AL_2O_3(\alpha,s)$	101.945	-1675.7
KCl(s)	74.555	-435.9	SiO2(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
Diatomics(g)	—	0	AgCl(s)	143.323	-127.1

Enthalpies of fusion and evaporation ΔH_m/KJ/mol at the transition temperature

	T_f/K	Fusion[a]	T_b/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	29.45	
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	194.84	25.23[1]	
H_2O	273.15	6.008	373.15	40.656	(44.016 at 298.15 K)
NH_3	195.40	5.652	239.73	23.351	
H_2S	187.61	2.377	212.80	18.673	
CH_4	90.68	0.941	111.66	8.18	
C_2H_6	89.85	2.86	184.55	14.7	
C_6H_6	278.65	10.59	353.25	30.8	
CH_3OH	175.25	3.159	337.22	35.27	(37.99 at 298.15K)

[1] Sublimation: [a]various pressures: [b]at 1atm

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

	a/J $K^{-1}mol^{-1}$	b/10^{-3}J $K^{-2}mol^{-1}$	c/10^5J $Kmol^{-1}$
Gases (298-2000K)			
He, Ne, Ar, Kr, Xe	20.78	0	0
H_2	27.28	3.26	0.50
O_2	29.96	4.18	-1.67
N_2	28.58	3.77	-0.50
Cl_2	37.03	0.67	-2.85
CO_2	44.23	8.79	-8.62
H_2O	30.54	10.29	0
NH_3	29.75	25.10	-1.55
CH_4	23.64	47.86	-1.92

Standard molar enthalpies of formation and combustion at 298.15 K.

	M_r	ΔH_f^θ/KJ/mol	ΔH_c^θ/KJ/mol
$CH_4(g)$	16.043	-74.81	
$C_2H_2(g)$	26.038	+226.8	1300
$C_2H_4(g)$	28.054	+52.30	1411
$C_2H_6(g)$	30.070	-84.64	1560
C_3H_6 cyclopropane(g)	42.081	53.35	2091
C_3H_6 (propene(g)	42.081	20.5	2058
C_4H_{10} n-butane (g)	58.124	-126.11	2877
C_5H_{12} n-pentane(g)	72.151	-146.4	3536
C_6H_{12} cyclohexane (l)	84.163	-156.2	3920
C_6H_{14} n-hexane (l)	86.178	-198.7	4163
C_6H_6 benzene (l)	78.115	+48.99	3288
C_8H_{18} n-octane (l)	114.233	-249.8	5471
$C_{10}H_8$ naphthalene (l)	128.175	+78.53	5157
CH_3OH (l)	32.042	-239.0	726.1
CH_3CHO (g)	44.054	-166.0	1193
CH_3CH_2OH (l)	46.070	-277.0	1368
CH_3COOH (l)	60.053	-484.2	874.5
$CH_3COOC_2H_5$ (l)	88.107	-486.6	2231
C_6H_5OH (s)	94.114	-165.0	3054
$C_6H_5NH_2$ (l)	93.129	-31.1	3393
$NH_2CO.NH_2$ urea(s)	60.056	-333.0	632.2
$CH_2(NH_2)CO_2H$, glycine (s)	75.068	-537.2	984.4
$C_6H_{12}O_6$, α-D-glucose (s)	180.159	-1274	2802
$C_6H_{22}O_6$, β-D-glucose (s)	180.159	-1268	2808
$C_{12}H_{22}O_{11}$, sucrose (s)	342.303	-2222	5645
$CH_3CH(OH)COOH$ lactic acid (s)	90.079	-694.0	1344

Source: American Institute of Physics handbook, McGraw-Hill

Heat capacities at 25°C

	$C_{v,m}$ / JK^{-1} mol^{-1}	$C_{p,m}$ / JK^{-1} 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_2O_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	H_2	130.6
C(gr)	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	CO	197.67
I_2	116.7			CO_2	213.7
S(Rh)	31.9	HNO_3	155.6	HCl	186.8
				H_2S	205.6
AgCl	96.2	C_2H_5OH	161.0	NH_3	192.5
AgBr	104.6	CH_3OH	126.7	CH_4	186.1
$CuSO_45H_2O$	305.4	C_6H_6	49.03	C_2H_6	229.4
$HgCl_2$	144	CH_3COOH	159.8	CH_3CHO	265.7
Sucrose	360.2	C_6H_{12}	298.2		

Useful Relations

$(RT)_{298.15K}$=2.4789 kJ/mol

$(RT/F)_{298.15K}$=0.025 693 V

T/K: 100.15 298.15 500.15 1000.15

T/Cm^{-1}: 69.61 207.22 347.62 695.13

1mmHg=133.222 N m^{-2}

hc/k=1.438 78x10^{-2} m K

1atm	1 cal	1 eV	1cm^{-1}
=1.01325x10^{5} Nm^{-2}	=4.184 J	=1.602 189x10^{-19} J	=0.124x10^{-3} eV
=760torr		=96.485 kJ/mol	=1.9864x10^{-23}J
=1 bar		= 8065.5 cm^{-1}	

SI-units:

1 L = 1000 ml = 1000cm^3 = 1 dm^3

1 dm = 0.1 m

1 cal (thermochemical) = 4.184 J

dipole moment: 1 Debye = 3.335 64x10^{-30} C m

force: ***1N=1J m^{-1}= 1kgms^{-2}***=10^5 dyne pressure: ***1Pa=1Nm^{-2}***=1Jm^{-3}

1J = 1 Nm

power: 1W = 1J s^{-1} potential: 1V =1 J C^{-1}

magnetic flux: 1T=1Vsm^{-2}=1JCsm^{-2} current: 1A=1Cs^{-1}

Prefixes:

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

General Data

speed of light	**c**	**2.997 925x10^{8} ms^{-1}**
charge of proton	*e*	1.602 19x10^{-19} C
Faraday constant	F=L*e*	9.648 46x10^{4} C mol^{-1}
Boltzmann constant	**k**	**1.380 66x10^{-23} J K^{-1}**
Gas constant	**R=Lk**	**8.314 41 J K^{-1} mol^{-1}**
		8.205 75x10^{-2} dm^3 atm K^{-1} mol^{-1}
Planck constant	**h**	**6.626 18x10^{-34} Js**
	$\hbar = \frac{h}{2\pi}$	1.054 59x10^{-34} Js
Avogadro constant	**L or N_{av}**	**6.022 14x10^{23} mol^{-1}**
Atomis mass unit	u	1.660 54x10^{-27} kg
Electron mass	**m_e**	**9.109 39x10^{-31} kg**
Proton mass	m_p	1.672 62x10^{-27} kg
Neutron mass	m_n	1.674 93x10^{-27} kg
Vacuum permittivity	$\varepsilon_o = \mu_o^{-1} c^{-2}$	8.854 188x10^{-12} J^{-1} C^2 m^{-1}
Vacuum permeability	μ_o	4πx10^{-7} Js^2C^{-2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 02x10^{-24} JT^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.05079x10^{-27} JT^{-1}
Gravitational constant	G	6.67259x10^{-11} Nm^2kg^{-2}
Gravitational acceleration	**g**	**9.80665 ms^{-2}**
Bohr radius	a_o	5.291 77x10^{-11} m

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	VIIB	VIIIB			IB	IIB	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	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									

NON-METALS

METALLOIDS

METALS

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.