University of Eswatini

Department of Chemistry

November 2018 Re-Sit 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 <u>ALL</u> 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]

a) Write Short notes on the following;

   i. Extensive property [2]

   ii. The system, surroundings and the boundary as defined in thermodynamics [5]

   iii. Adiabatic processes [3]

b) The formation of $FeCl_2$ and H_2 from the reaction of Fe and HCl takes place in an open beaker at 29°C, assuming perfect gas behaviour. Calculate the expansion work done given that you start with 39g of HCl. [8]

c) Calculate the work done when 26 g of iron reacts with HCl to produce $FeCl_2$ and H_2 in two conditions;

   i. Closed volume of fixed volume, [3]

   ii. An open beaker at 28°C [4]

Question 2 [25 Marks]

a) Write short notes on the following;

   i. Compressibility factor [3]

   ii. Entropy [2]

   iii. Helmholtz Function [3]

b) Explain what is meant by adiabatic expansion, draw an adiabat and an isotherm on a P versus V graph and compare them. [7]

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

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

   i. 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

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

Question 3

a) 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]

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

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

b) Write short notes on the heat capacity and show how it links with ΔH as well as q_v.

[10]

c) Write short notes on the following;

i. Nernst heat theorem [3]

ii. Standard molar entropy [4]

Question 4 [25 Marks]

a) 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:

i. reversibly, and [5]

ii. against a constant external pressure of 1.00 atm. [5]

iii. adiabatically against a constant pressure of 1.00 atm. [5]

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

c) If 50g water at 80°C is poured into 100g water at 10°C in an insulated vessel given that C_p,m=75.5 JK^{-1}mol : Calculate:

i. final temperature of the mixture [3]

ii. the entropy change [2]

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) Many gases show nearly ideal behaviour at room temperature and low pressures. Using a sketch of either an isotherm or the compressibility factor 'z' for a real gas and that of an ideal gas, briefly explain how they compare at high pressure, moderate pressure, and at low pressure. [15]

b) Write short notes on the following;

i. Hess's law of thermodynamics [5]

ii. Kirchoff's law of thermodynamics [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 (l)	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	$SiO_2(s)$	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
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⊥	
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)

⊥ 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	3268
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
$NH_2CO.NH$, urea(s)	60.056	-333.0	632.2
$CH_2(NH_2)CO_2H$, glycine (s)	75.068	-537.2	964.4
$C_6H_{12}O_6$, 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

THE PERIODIC TABLE OF ELEMENTS

NON-METALS

METALLOIDS

METALS

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**									

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.

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⁻
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, S_m^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 **=1 bar**		=96.485 kJ/mol = 8065.5 cm^{-1}	=1.9864x10^{-23}J

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

General Data		
speed of light	c	**2.997 925x10^8 ms^{-1}**
charge of proton	e	1.602 19x10^{-19} C
Faraday constant	F=Le	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^{2}C^{-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^{2}kg^{-2}
Gravitational acceleration	g	**9.80665 ms^{-2}**
Bohr radius	a_o	5.291 77x10^{-11} m