

UNIVERSITY OF FORT HARE

**PHYSICAL CHEMISTRY 1
(PAC 224)**

SUPPLEMENTARY EXAMINATIONS

JANUARY 2019

.....
Time: 3 HOURS

Subject: PAC 224

Marks: 100

This paper consists of 6 pages including the cover page

Internal Examiners

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INSTRUCTIONS

**ANSWER BOTH QUESTIONS
THE PERIODIC TABLE OF ELEMENTS, A DATA SHEET, AND A
TABLE OF CONSTANTS AND USEFUL RELATIONS ARE
ATTACHED**

Question 1

1. An aerosol can is labeled "do not incinerate the can, even when empty". Explain why we have to adhere to this instruction by using the gas laws. [3]
 2. What are the requirements for a reaction to be at equilibrium in terms of:
 - (a) the Gibbs free energy
 - (b) the entropy[4]
 3. The internal energy change in the conversion of the calcite form of CaCO_3 to the aragonite form is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 atm given that the densities of the solids are 2.71 g/mL (calcite) and 2.93 g/mL (aragonite). [6]
 4. In terms of solubility rules, salts containing the ammonium ion are always soluble. Using thermodynamic arguments and ammonium nitrate dissolving in water as an example, show that this reaction is both endothermic and spontaneous. [8]
 - 5(a) Derive expressions for w_{rev} , q_{rev} , ΔU_m and ΔH_m all in terms of R, temperature, numerical values, and the heat capacities for an ideal gas undergoing a reversible pressure change at constant volume. [8]
 - (b) Prove that isotherms in a P vs V graph cannot cross each other. [6]
 - 6(a) Two different gases, A and B, from two separate containers with volumes V_a and V_b respectively are transferred into a container of volume V. Derive the formula for the change in total entropy with mole fractions after the two gases have been mixed. [6]
 - (b) Is the mixing spontaneous or not? Explain. [3]
 - (c) What will be the total change in entropy if gases A and B are identical and have equal pressure? [3]
 7. Why is the Helmholtz function not used as frequently as the Gibbs function? [3]
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Question 2

1(a) Starting from definitions of the thermodynamic functions, derive the expression $\Delta G_{\text{rev}} = -nRT \ln (P_1/P_2)$ for an ideal gas undergoing an isothermal change. [4]

(b) Using the expression for ΔG_{rev} in 1(a) above, draw a graph showing the variation of the Gibbs free energy with the pressure change. [4]

2. Draw a fully labelled phase diagram for carbon dioxide. [9]

3. Using the liquid-vapour phase boundary, derive the Clapeyron equation. [5]

4(a) Calculate the equilibrium constant for the ammonia synthesis reaction at 298K,



(b) Is this reaction spontaneous or not. Explain. [2]

5. Derive the Maxwell relations from enthalpy. [8]

6. What will be the freezing point of a solution obtained by mixing 250 g of water and 55.0 g of glycerol, $\text{C}_3\text{H}_5(\text{OH})_3$, which is a non-volatile, non-dissociating solute? [7]

7(a) What is the difference between a galvanic cell and an electrolytic cell? [2]

(b) Calculate the standard cell potential and give the cell reaction at 25°C for the cell:



if $\text{Al}^{3+} (\text{aq}) + 3\text{e}^- \rightarrow \text{Al} (\text{s})$, $E^\circ = -1.66 \text{ V}$ and $\text{Fe}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Fe} (\text{s})$, $E^\circ = -0.40 \text{ V}$ [4]

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CONSTANTS AND USEFUL RELATIONS

Faraday constant = $9.649 \times 10^4 \text{ C.mol}^{-1}$

Avogadro's constant = $6.022 \times 10^{23} \text{ units/mol}$

Standard atmosphere (P°) = $1.013 \times 10^5 \text{ Pa}$

Standard molar volume of an ideal gas (V_m°) = $22.414 \times 10^{-3} \text{ m}^3.\text{mol}^{-1}$

1 atm = 101.325 kPa = 760 mmHg = 760 Torr

Gas constant = $8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$

$$= 8.314 \text{ kPa}.\text{dm}^3.\text{mol}^{-1}.\text{K}^{-1}$$

$$= 8.206 \times 10^{-2} \text{ atm}.\text{dm}^3.\text{mol}^{-1}.\text{K}^{-1}$$

Planck's constant (h) = $6.626 \times 10^{-34} \text{ J.s}$

Gravitational acceleration (g) = 9.807 ms^{-2}

$$(P + an^2/V^2).(V-nb) = nRT$$

$$dU = dq + dw$$

$$dU = dq_v = C_v dT$$

$$w_{\text{rev}} = -nRT \ln(V_f/V_i), \text{ ideal gas}$$

$$\Delta_r H = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

$$\Delta S = \Delta H/T$$

$$A = U - TS$$

$$dU = TdS - PdV$$

$$dA = -SdT - PdV$$

$$\Delta G^\circ = -RT \ln K_p^\circ$$

$$\Delta G = nRT \ln [P/P^\circ]$$

$$P_i = \chi_i P_{\text{total}}$$

$$\Delta T_f = \left[\frac{RT_f^2}{\Delta H_{fus}} \right] \cdot \chi_A$$

$$\Delta T_b = \left[\frac{RT_b^2}{\Delta H_{vap}} \right] \cdot \chi_A$$

$$dP/dT = \frac{\Delta H_m}{T \Delta V_m}$$

Normal boiling point (H_2O) = 100°C

Normal melting point (H_2O) = 0°C

$$1 \text{ L.atm} = 101.316 \text{ J}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$1 \text{ N} = 1 \text{ J.m}^{-1}$$

$$1 \text{ atm} = 101.316 \text{ J}$$

$$T(\text{K}) = t(^{\circ}\text{C}) + 273.15$$

$$P_i V_i = P_f V_f$$

$$P_i/T_i = P_f/T_f$$

$$P_i V_i/T_i = P_f V_f/T_f$$

$$V_i/n_i = V_f/n_f$$

$$dw = -Fdx = -P_{\text{ext}}dV$$

$$PV = nRT$$

$$dH = dq_p = C_p dT$$

$$H = U + PV$$

$$C_p - C_v = nR; \text{ ideal gas}$$

$$dS \geq dq/T$$

$$G = H - TS$$

$$dG = VdP - SdT,$$

$$dH = TdS + VdP$$

$$\left[\frac{\partial G/T}{\partial T} \right]_P = -\frac{\Delta H}{T^2}$$

$$\Delta G = \int_{P_1}^{P_2} VdP; \text{ const } T$$

$$\chi_A = \frac{n_A}{n_{\text{total}}}$$

$$\Delta_{\text{mix}} S = -R \sum n_i \ln \chi_i$$

$$= -n_{\text{tot}} R \sum \chi_i \ln \chi_i$$

$$K_p^\circ = K_\chi P^{\Delta v} = K_c (RT)^{\Delta v}$$

$$\Delta H_{\text{vap}} = 40.67 \text{ kJ/mol}; \text{ H}_2\text{O}$$

$$\Delta H_{\text{fus}} = 6.02 \text{ kJ/mol}; \text{ H}_2\text{O}$$

PAC 224

EXAM DATA SHEET

Substance	$\Delta_f H^\circ$ (kJ/mol)	S_f° (J.K-1.mol-1)	$\Delta_f G^\circ$ (kJ/mol)
H ⁺	0	0	0
NH ₄ NO ₃ (s)	-363.56	151.08	-183.87
NH ₄ ⁺ (aq)	-132.51	113.4	-79.37
NO ₃ ⁻ (aq)	-205.0	146.4	-108.74
CaCO ₃ (s)	-1206.9	92.9	-1128.8
Ca ²⁺ (aq)	-542.83	-53.1	-553.58
CO ₂ (aq)	-413.80	117.6	-385.98
H ₂ O (l)	-285.83	69.81	-237.13
N ₂ (g)	0	191.61	0
H ₂ (g)	0	130.684	0
NH ₃ (g)	-46.11	192.45	-16.45
O ₂ (g)	0	205.0	0
H ₂ O (l)	-285.8	69.95	-237.1
H ₂ O (g)	-241.8	188.7	-228.6

Density of mercury = 13.6 g/mL

Density of water = 0.9970 g/mL

ΔH_{fus} = 9.83 kJ/mol Benzene

ΔH_{vap} = 30.8 kJ/mol Benzene

Melting point benzene = 5.5 °C

Boiling point benzene = 80.1 °C

IUPAC Periodic Table of the Elements

Key:																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
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1	H	Hydrogen	2	He	Helium	3	Li	Lithium	4	Be	Beryllium	5	B	Boron	6	C	Carbon	7	N	Nitrogen	8	O	Oxygen	9	F	Fluorine	10	Ne	Neon	11	Na	Sodium	12	Mg	Magnesium	13	Al	Aluminum	14	Si	Silicon	15	P	Phosphorus	16	S	Sulfur	17	Cl	Chlorine	18	Ar	Argon	19	K	Potassium	20	Ca	Calcium	21	Sc	Scandium	22	Ti	Titanium	23	V	Vanadium	24	Cr	Chromium	25	Mn	Manganese	26	Fe	Iron	27	Co	Cobalt	28	Ni	Nickel	29	Cu	Copper	30	Zn	Zinc	31	Ga	Gallium	32	Ge	Germanium	33	As	Arsenic	34	Se	Selenium	35	Br	Bromine	36	Kr	Krypton	37	Rb	Rubidium	38	Sr	Strontium	39	Y	Yttrium	40	Zr	Zirconium	41	Nb	Niobium	42	Mo	Molybdenum	43	Tc	Technetium	44	Ru	Ruthenium	45	Rh	Rhodium	46	Pd	Palladium	47	Ag	Silver	48	Cd	Cadmium	49	In	Indium	50	Sn	Tin	51	Sb	Antimony	52	Te	Tellurium	53	I	Iodine	54	Xe	Xenon	55	Cs	Cesium	56	Ba	Barium	57-71	Lanthanoids	72	Hf	Hafnium	73	Ta	Tantalum	74	W	Tungsten	75	Re	Rhenium	76	Os	Osmium	77	Ir	Iridium	78	Pt	Platinum	79	Au	Gold	80	Hg	Mercury	81	Tl	Thallium	82	Pb	Lead	83	Bi	Bismuth	84	Po	Polonium	85	At	Astatine	86	Rn	Radon	87	Fr	Francium	88	Ra	Radium	89-103	Actinoids	104	Rf	Rutherfordium	105	Db	Dubnium	106	Sg	Seaborgium	107	Bh	Bhassium	108	Hs	Hassium	109	Mt	Mendelevium	110	Ds	Darmstadtium	111	Rg	Roentgenium	112	Cn	Copernicium	113	B	Boron	114	Al	Aluminum	115	Sb	Antimony	116	Te	Tellurium	117	At	Astatine	118	Xe	Xenon	119	Fr	Francium	120	Ra	Radium	121	Ac	Actinium	122	Th	Thorium	123	Pa	Protactinium	124	U	Uranium	125	Np	Neptunium	126	Pu	Plutonium	127	Am	Americium	128	Cm	Curium	129	Bk	Berkelium	130	Cf	Californium	131	Es	Einsteinium	132	Fm	Fermium	133	Md	Mendelevium	134	No	Nobelium	135	Lr	Lanthanum	136	Lu	Lutetium	137	Hf	Hafnium	138	Ta	Tantalum	139	W	Tungsten	140	Re	Rhenium	141	Os	Osmium	142	Pt	Platinum	143	Au	Gold	144	Hg	Mercury	145	Tl	Thallium	146	Pb	Lead	147	Bi	Bismuth	148	Po	Polonium	149	At	Astatine	150	Rn	Radon	151	Fr	Francium	152	Ra	Radium	153	Ac	Actinium	154	Th	Thorium	155	Pa	Protactinium	156	U	Uranium	157	Np	Neptunium	158	Pu	Plutonium	159	Am	Americium	160	Cm	Curium	161	Bk	Berkelium	162	Cf	Californium	163	Es	Einsteinium	164	Fm	Fermium	165	Md	Mendelevium	166	No	Nobelium	167	Lr	Lanthanum	168	Lu	Lutetium	169	Hf	Hafnium	170	Ta	Tantalum	171	W	Tungsten	172	Re	Rhenium	173	Os	Osmium	174	Pt	Platinum	175	Au	Gold	176	Hg	Mercury	177	Tl	Thallium	178	Pb	Lead	179	Bi	Bismuth	180	Po	Polonium	181	At	Astatine	182	Rn	Radon	183	Fr	Francium	184	Ra	Radium	185	Ac	Actinium	186	Th	Thorium	187	Pa	Protactinium	188	U	Uranium	189	Np	Neptunium	190	Pu	Plutonium	191	Am	Americium	192	Cm	Curium	193	Bk	Berkelium	194	Cf	Californium	195	Es	Einsteinium	196	Fm	Fermium	197	Md	Mendelevium	198	No	Nobelium	199	Lr	Lanthanum	200	Lu	Lutetium	201	Hf	Hafnium	202	Ta	Tantalum	203	W	Tungsten	204	Re	Rhenium	205	Os	Osmium	206	Pt	Platinum	207	Au	Gold	208	Hg	Mercury	209	Tl	Thallium	210	Pb	Lead	211	Bi	Bismuth	212	Po	Polonium	213	At	Astatine	214	Rn	Radon	215	Fr	Francium	216	Ra	Radium	217	Ac	Actinium	218	Th	Thorium	219	Pa	Protactinium	220	U	Uranium	221	Np	Neptunium	222	Pu	Plutonium	223	Am	Americium	224	Cm	Curium	225	Bk	Berkelium	226	Cf	Californium	227	Es	Einsteinium	228	Fm	Fermium	229	Md	Mendelevium	230	No	Nobelium	231	Lr	Lanthanum	232	Lu	Lutetium	233	Hf	Hafnium	234	Ta	Tantalum	235	W	Tungsten	236	Re	Rhenium	237	Os	Osmium	238	Pt	Platinum	239	Au	Gold	240	Hg	Mercury	241	Tl	Thallium	242	Pb	Lead	243	Bi	Bismuth	244	Po	Polonium	245	At	Astatine	246	Rn	Radon	247	Fr	Francium	248	Ra	Radium	249	Ac	Actinium	250	Th	Thorium	251	Pa	Protactinium	252	U	Uranium	253	Np	Neptunium	254	Pu	Plutonium	255	Am	Americium	256	Cm	Curium	257	Bk	Berkelium	258	Cf	Californium	259	Es	Einsteinium	260	Fm	Fermium	261	Md	Mendelevium	262	No	Nobelium	263	Lr	Lanthanum	264	Lu	Lutetium	265	Hf	Hafnium	266	Ta	Tantalum	267	W	Tungsten	268	Re	Rhenium	269	Os	Osmium	270	Pt	Platinum	271	Au	Gold	272	Hg	Mercury	273	Tl	Thallium	274	Pb	Lead	275	Bi	Bismuth	276	Po	Polonium	277	At	Astatine	278	Rn	Radon	279	Fr	Francium	280	Ra	Radium	281	Ac	Actinium	282	Th	Thorium	283	Pa	Protactinium	284	U	Uranium	285	Np	Neptunium	286	Pu	Plutonium	287	Am	Americium	288	Cm	Curium	289	Bk	Berkelium	290	Cf	Californium	291	Es	Einsteinium	292	Fm	Fermium	293	Md	Mendelevium	294	No	Nobelium	295	Lr	Lanthanum	296	Lu	Lutetium	297	Hf	Hafnium	298	Ta	Tantalum	299	W	Tungsten	300	Re	Rhenium	301	Os	Osmium	302	Pt	Platinum	303	Au	Gold	304	Hg	Mercury	305	Tl	Thallium	306	Pb	Lead	307	Bi	Bismuth	308	Po	Polonium	309	At	Astatine	310	Rn	Radon	311	Fr	Francium	312	Ra	Radium	313	Ac	Actinium	314	Th	Thorium	315	Pa	Protactinium	316	U	Uranium	317	Np	Neptunium	318	Pu	Plutonium	319	Am	Americium	320	Cm	Curium	321	Bk	Berkelium	322	Cf	Californium	323	Es	Einsteinium	324	Fm	Fermium	325	Md	Mendelevium	326	No	Nobelium	327	Lr	Lanthanum	328	Lu	Lutetium	329	Hf	Hafnium	330	Ta	Tantalum	331	W	Tungsten	332	Re	Rhenium	333	Os	Osmium	334	Pt	Platinum	335	Au	Gold	336	Hg	Mercury	337	Tl	Thallium	338	Pb	Lead	339	Bi	Bismuth	340	Po	Polonium	341	At	Astatine	342	Rn	Radon	343	Fr	Francium	344	Ra	Radium	345	Ac	Actinium	346	Th	Thorium	347	Pa	Protactinium	348	U	Uranium	349	Np	Neptunium	350	Pu	Plutonium	351	Am	Americium	352	Cm	Curium	353	Bk	Berkelium	35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