NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH AND APPLIED SCIENCES

DEPARTMENT OF NATURAL AND APPLIED SCIENCES

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	**LEVEL:** 6
COURSE CODE: PCH602S AND CHY620S	**COURSE NAME:** PHYSICAL CHEMISTRY AND CHEMISTRY 223
SESSION: JANUARY 2019	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

SUPPLEMENTARY/SECOND OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	**Prof Habauka M. Kwaambwa**
MODERATOR:	**Dr Rajaram Swaminathan**

INSTRUCTIONS
1. Answer ALL the questions. 2. Write clearly and neatly. 3. Number the answers clearly.

PERMISSIBLE MATERIALS

Non-programmable Calculators

ATTACHMENTS
List of Useful Constants
Standard Electrode (Reduction) Potentials Table

THIS QUESTION PAPER CONSISTS OF 7 PAGES (Including this front page and attachments)

SECTION A: MULTIPLE CHOICE QUESTIONS **[20]**

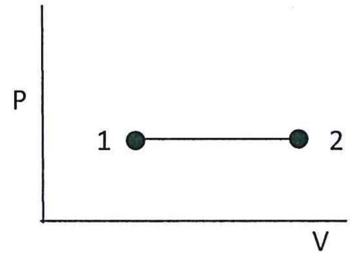
There are 10 questions in this section. Choose the correct answer. Each question carries 2 marks.

1. A container is filled with a sample of an ideal gas at the pressure of 1.5 atm. The gas is compressed isothermally to one-fourth of its original volume. What is the new pressure of the gas?
   A. 2 atm
   B. 3 atm
   C. 4 atm
   D. 5 atm
   E. 6 atm

2. Change in internal energy in a closed system is equal to heat transferred if the reversible process takes place at constant
   A. Pressure
   B. Temperature
   C. Volume
   D. Internal energy
   E. Entropy

3. For a reversible adiabatic process, change in entropy is
   A. Maximum
   B. Minimum
   C. Zero
   D. Negative
   E. Unpredictable

4. Which of the following is true about the process 1 $\rightarrow$ 2 shown in the PV diagram below?
   A. $\Delta U > 0, w > 0, q = 0$
   B. $\Delta U > 0, w = 0, q > 0$
   C. $\Delta U > 0, w > 0, q > 0$
   D. $\Delta U > 0, w < 0, q > 0$
   E. $\Delta U < 0, w < 0, q > 0$



5. One mole of an ideal gas expands isothermally until its volume is doubled. What is the change in Gibbs free energy, ΔG, for the process?
   A. $R\ln\frac{1}{2}$
   B. $R\ln 2$
   C. $RT\ln\frac{1}{2}$
   D. $RT\ln 2$
   E. $e^{-2/RT}$

6. The equilibrium constant of the reaction $COCl_2 (g) \rightleftharpoons CO(g) + Cl_2(g)$ was determined as a function of temperature. $\ln K_p$ was plotted against 1/T (van't Hoff isochore). The slope was found to be 1.408×10^4. For this reaction:
   A. $\Delta H > 0$
   B. $\Delta H < 0$
   C. $\Delta H = 0$
   D. $\Delta H = \Delta U$
   E. $\Delta H = \Delta G$

7. What mass (in grams) of nickel could be electroplated from a solution of nickel (II) chloride by a current of 0.25 amperes flowing for 10 hours? (Relative atomic mass of nickel: 58.69 amu)
   A. 12 g
   B. 5.5 g
   C. 0.046 g
   D. 2.7 g
   E. 6.0 g

8. Which pairing of quantity and unit is incorrect?
   A. Resistivity; Ω m
   B. Ionic mobility; $ms^{-1}V^{-1}$
   C. Conductance; Sm^{-1}
   D. Resistance; Ω
   E. Cell constant; cm^{-1}

9. The half-reaction that occurs at the anode during the electrolysis of molten sodium bromide is:
   A. $2Br^- \rightarrow Br_2 + 2e^-$
   B. $Br_2 + 2e^- \rightarrow 2 Br^-$
   C. $Na^+ + e^- \rightarrow Na$
   D. $Na \rightarrow Na^+ + e^-$
   E. $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

10. Consider the standard voltaic (or galvanic) cell: Fe^{2+}/Fe versus Au^{3+}/Au. Which answer identifies the cathode and gives the E° for the cell?
   A. Fe, - 0.44 V
   B. Au, 1.94 V
   C. Fe, 1.06 V
   D. Au, 1.06 V
   E. Fe, 1.94 V

SECTION B **[80]**

There are **SIX** questions in this section. Answer all Questions.

QUESTION 1 **[10]**

Show under what conditions **any two** of the following are true, i.e. derive the expressions.

(a) dH = VdP, starting with the definition of enthalpy, H = U + PV.

(b) $w = nRT\ln\frac{P_2}{P_1}$, starting with the definition of work, $w = -\int_{V_1}^{V_2} P_{ext}dV$.

QUESTION 2 **[12]**

State whether each of the following statements is **true** or **false.** If false, either correct it or state the reason for being false.

(a) $\Delta S_{system} + \Delta S_{surrounding}$ is positive for every spontaneous process

(b) The entropy of a solid substance is zero at absolute zero temperature.

(c) For the reaction, $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ $\Delta H_{reaction} > \Delta U_{reaction}$

(d) For the reaction, $2C(g) + O_2(g) \rightarrow 2CO(g)$ $\Delta H^o_{rxn} = \Delta H^o_f$ (CO(g))

(e) $C_p = \left(\frac{\partial U}{\partial T}\right)_p$

(f) ΔH, ΔS, w and V are all state functions.

QUESTION 3 **[10]**

Two moles of an ideal monatomic gas initially at 298 K and a pressure of 5 atm are heated under constant pressure conditions until the volume doubles. Deduce with reasons or calculate the following thermodynamic quantities for the expansion:

(a) Final temperature

(b) ΔU

(c) ΔH

(d) w

(e) q

Assume: $C_p = \frac{5}{2}R$

QUESTION 4 **[10]**

The enthalpy of formation of nitrous oxide (N_2O) at 298 K is 82.4 kJ mol^{-1} and the heat capacities of nitrogen, oxygen and nitrous oxide in the temperature range 298 K to 423 K are given by the following equations:

$C_p(N_2) = (27.0 + 6 \times 10^{-3}T)$ JK^{-1}mol^{-1}

$C_p(O_2) = (25.6 + 14 \times 10^{-3}T)$ JK^{-1}mol^{-1}

$C_p(N_2O) = (27.2 + 44 \times 10^{-3}T)$ JK^{-1}mol^{-1}

where T is the thermodynamic temperature

(a) Write a balanced target equation for the formation of N_2O gas. (1)

(b) Calculate the enthalpy change of formation of nitrous oxide at 423 K. (9)

QUESTION 5 **[20]**

(a) The resistance of a conductance cell containing 0.100 $moldm^{-3}$ KCl solution at 25°C is 47.85 Ω. If the same cell contains $NaNO_3$ solution of concentration 0.0200 $moldm^{-3}$, the resistance is 254 Ω. The conductivity of KCl solution is 0.0129 $\Omega^{-1}cm^{-1}$. Calculate:

(i) the cell constant. (3)

(ii) the conductivity of the $NaNO_3$ solution. (3)

(iii) the conductivity of the $NaNO_3$ at a concentration of 0.0200 $moldm^{-3}$. (3)

(b) Explain briefly why conductivity, κ, as a practical quantity has restricted use in characterising electrolyte solutions. (2)

(c) Using Kohlrausch's law, calculate Λ_o for acetic acid (HAc). The Λ_o (in $ohm^{-1}\,cm^2\,mol^{-1}$) values for NaAc, HCl, and NaCl are 91.0, 426.2 and 126.5, respectively. (2)

(d) If the conductivity of 0.010 $moldm^{-3}$ acetic acid is 1.63×10^{-4} Scm^{-1}, what is the degree of dissociation of acetic acid at this concentration? (2)

(e) Using the same schematic diagram, compare and contrast the variation of molar conductivity with concentration for (i) HCl, (ii) Acetic acid (CH_3COOH) and (iii) surfactant cetyl trimethyl ammonium bromide ($C_{16}TAB$). (5)

QUESTION 6 **[18]**

(a) Discuss briefly Faraday's contribution to electrolysis. (4)

(b) Suppose that you construct a Galvanic cell which combines the $Ce^{4+}(aq)$, $Ce^{3+}(aq)$/Pt cell having a standard reduction (E°) of 1.61 v with a Cu(s)/$Cu^{2+}(aq)$ cell having a standard reduction potential of 0.158 V at 298 K. Write balanced chemical equations for the reactions at the anode and cathode, indicating which reaction occurs at a particular electrode. Also write a balanced equation for the overall reaction. (5)

(c) Using half reactions, overall reaction and cell notation, describe the Galvanic cell resulting from a **spontaneous** overall reaction consisting of the following half reactions:

$Pb^{2+}(0.5M) + 2e \rightarrow Pb(s)$ E° = - 0.126 V

$Au^{+}(1.00M) + e \rightarrow Au\,(s)$ E° = 1.69 V

(5)

(d) Calculate the emf of the cell in (c) at 298 K (using the Nernst equation). (4)

LIST OF USEFUL EQUATION AND CONSTANTS:

Van der Waals eq$^{\underline{n}}$. $P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$

Universal Gas constant	R	=	8.314 J K^{-1} mol^{-1}
Boltzmann's constant,k	=	1.381 x 10^{-23} J K^{-1}	
Planck's constant	h	=	6.626 x 10^{-34} J s
Debye-Hückel's constant,	A	=	0.509 (mol $dm^{-3})^{1/2}$ or $mol^{-0.5}kg^{0.5}$
Faraday's constant	F	=	96485 C mol^{-1}
Mass of electron	m_e	=	9.109 x 10^{-31} kg
Velocity of light	c	=	2.998 x 10^8 m s^{-1}
Avogadro's constant	N_A	=	6.022 x 10^{23}
1 electron volt (eV)		=	1.602 x 10^{-19} J

Standard Electrode (Reduction) Potentials at 25°C

Electrode	$E^{\ominus}/V$	*Half-cell reaction*
$Li^+ \mid Li$	−3.045	$Li^+ + e \rightarrow Li$
$K^+ \mid K$	−2.925	$K^+ + e \rightarrow K$
$Rb^+ \mid Rb$	−2.925	$Rb^+ + e \rightarrow Rb$
$Na^+ \mid Na$	−2.714	$Na^+ + e \rightarrow Na$
$Mg^{2+} \mid Mg$	−2.37	$\frac{1}{2}Mg^{2+} + e \rightarrow \frac{1}{2}Mg$
$Pu^{3+} \mid Pu$	−2.07	$\frac{1}{3}Pu^{3+} + e \rightarrow \frac{1}{3}Pu$
$Th^{4+} \mid Th$	−1.90	$\frac{1}{4}Th^{4+} + e \rightarrow \frac{1}{4}Th$
$Np^{3+} \mid Np$	−1.86	$\frac{1}{3}Np^{3+} + e \rightarrow \frac{1}{3}Np$
$Al^{3+} \mid Al$	−1.66	$\frac{1}{3}Al^{3+} + e \rightarrow \frac{1}{3}Al$
$Zn^{2+} \mid Zn$	−0.763	$\frac{1}{2}Zn^{2+} + e \rightarrow \frac{1}{2}Zn$
$Fe^{2+} \mid Fe$	−0.440	$\frac{1}{2}Fe^{2+} + e \rightarrow \frac{1}{2}Fe$
$Cr^{3+}, Cr^{2+} \mid Pt^{b,c}$	−0.41	$Cr^{3+} + e \rightarrow Cr^{2+}$
$Cd^{2+} \mid Cd$	−0.403	$\frac{1}{2}Cd^{2+} + e \rightarrow \frac{1}{2}Cd$
$Tl^+ \mid Tl$	−0.3363	$Tl^+ + e \rightarrow Tl$
$Br^- \mid PbBr_2(s), Pb$	−0.280	$\frac{1}{2}PbBr_2 + e \rightarrow \frac{1}{2}Pb + Br^-$
$Co^{2+} \mid Co$	−0.277	$\frac{1}{2}Co^{2+} + e \rightarrow \frac{1}{2}Co$
$Ni^{2+} \mid Ni$	−0.250	$\frac{1}{2}Ni^{2+} + e \rightarrow \frac{1}{2}Ni$
$I^- \mid AgI(s), Ag$	−0.151	$AgI + e \rightarrow Ag + I^-$
$Sn^{2+} \mid Sn$	−0.140	$\frac{1}{2}Sn^{2+} + e \rightarrow \frac{1}{2}Sn$
$Pb^{2+} \mid Pb$	−0.126	$\frac{1}{2}Pb^{2+} + e \rightarrow \frac{1}{2}Pb$
$D^+ \mid D_2, Pt$	−0.0034	$D^+ + e \rightarrow \frac{1}{2}D_2$
$H^+ \mid H_2, Pt$	0.0000	$H^+ + e \rightarrow \frac{1}{2}H_2$
$Ti^{4+}, Ti^{3+} \mid Pt$	0.04	$Ti^{4+} + e \rightarrow Ti^{3+}$
$Br^- \mid AgBr(s), Ag$	0.095	$AgBr + e \rightarrow Ag + Br^-$
$Sn^{4+}, Sn^{2+} \mid Pt$	0.15	$\frac{1}{2}Sn^{4+} + e \rightarrow \frac{1}{2}Sn^{2+}$
$Cu^{2+}, Cu^+ \mid Pt$	0.153	$Cu^{2+} + e \rightarrow Cu^+$
$Cl^- \mid AgCl(s), Ag$	0.2224	$AgCl + e \rightarrow Ag + Cl^-$
$Cl^- \mid Hg_2Cl_2(s), Hg^d$	0.268	$\frac{1}{2}Hg_2Cl_2 + e \rightarrow Hg + Cl^-$
$Cu^{2+} \mid Cu$	0.337	$\frac{1}{2}Cu^{2+} + e \rightarrow \frac{1}{2}Cu$
$H^+ \mid C_2H_4(g), C_2H_6(g), Pt$	0.52	$H^+ + \frac{1}{2}C_2H_4(g) + e \rightarrow \frac{1}{2}C_2H_6(g)$
$Cu^+ \mid Cu$	0.521	$Cu^+ + e \rightarrow Cu$
$I^- \mid I_2(s), Pt$	0.5355	$\frac{1}{2}I_2 + e \rightarrow I^-$
H^+, quinhydrone(s) $\mid$ Pt	0.6996	$\frac{1}{2}C_6H_4O_2 + H^+ + e \rightarrow \frac{1}{2}C_6H_6O_2$
$Fe^{3+}, Fe^{2+} \mid Pt$	0.771	$Fe^{3+} + e \rightarrow Fe^{2+}$
$Hg_2^{2+} \mid Hg$	0.789	$\frac{1}{2}Hg_2^{2+} + e \rightarrow Hg$
$Ag^+ \mid Ag$	0.7991	$Ag^+ + e \rightarrow Ag$
$Hg^{2+}, Hg_2^{2+} \mid Pt$	0.920	$Hg^{2+} + e \rightarrow \frac{1}{2}Hg_2^{2+}$
$Pu^{4+}, Pu^{3+} \mid Pt$	0.97	$Pu^{4+} + e \rightarrow Pu^{3+}$
$Br^- \mid Br_2(l) \mid Pt$	1.0652	$\frac{1}{2}Br_2(l) + e \rightarrow Br^-$
$Tl^{3+}, Tl^+ \mid Pt$	1.250	$\frac{1}{2}Tl^{3+} + e \rightarrow \frac{1}{2}Tl^+$
$Cl^- \mid Cl_2(g) \mid Pt$	1.3595	$\frac{1}{2}Cl_2(g) + e \rightarrow Cl^-$
$Pb^{2+} \mid PbO_2 \mid Pb$	1.455	$\frac{1}{2}PbO_2 + 2H^+ + e \rightarrow \frac{1}{2}Pb^{2+} + H_2O$
$Au^{3+} \mid Au$	1.50	$\frac{1}{3}Au^{3+} + e \rightarrow \frac{1}{3}Au$
$Ce^{4+}, Ce^{3+} \mid Pt$	1.61	$Ce^{4+} + e \rightarrow Ce^{3+}$
$Co^{3+}, Co^{2+} \mid Pt$	1.82	$Co^{3+} + e \rightarrow Co^{2+}$
$F^- \mid F_2(g) \mid Pt$	2.87	$\frac{1}{2}F_2(g) + e \rightarrow F^-$
$HF(aq) \mid F_2(g) \mid Pt$	3.06	$H^+ + \frac{1}{2}F_2(g) + e \rightarrow HF(aq)$