

UNIVERSITY OF ESWATINI

FINAL EXAMINATION 2018/2019

TITLE OF PAPER: ADVANCED PHYSICAL CHEMISTRY

COURSE NUMBER: C402

TIME: THREE (3) HOURS

INSTRUCTIONS:

There are **six (6)** questions and each question carries 25 marks. **Answer any four (4) questions**

NB: Each question should start on a new page.

A data sheet and a periodic table are attached

A non-programmable electronic calculator may be used

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QUESTION1. [25 Marks]

- a) Define the ionic strength of a solution. What is the molality of $\text{Al}_2(\text{SO}_4)_3$ that has the same ionic strength as 0.500 mol/kg $\text{Ca}(\text{NO}_3)_2$ [6]
- b) Devise cells in which the following are the reactions
- i. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{aq})$ [3]
- ii. $\text{Sn}(\text{s}) + 2\text{AgCl}(\text{s}) \rightarrow \text{SnCl}_2(\text{aq}) + 2\text{Ag}(\text{s})$ [3]
- c) Derive an expression for the potential of an electrode for which the half reaction is the reduction of MnO_4^- ions and Mn^{2+} ions in acidic solution [6]
- d) Starting with $dw = d\mu$ and that $\mu = \mu^\ominus + RT \ln a$, show that the thermodynamic force is given by

$$F = -\frac{RT}{c} \left(\frac{\partial c}{\partial x} \right)_{p,T} \quad [7]$$

- e) The standard potential of the $\text{AgCl}/\text{Ag}, \text{Cl}^-$ couple has been measured over a range of temperatures and the results were found to fit the expression
- $$E^\ominus/\text{V} = 0.23659 - 4.8564 \times 10^{-4} (\theta/^\circ\text{C}) - 3.4205 \times 10^{-6} (\theta/^\circ\text{C})^2 + 5.869 \times 10^{-9} (\theta/^\circ\text{C})^3$$
- Calculate the standard Gibbs energy of formation of $\text{Cl}^-(\text{aq})$ at 25°C
- $$[\Delta_f G^\ominus(\text{AgCl}, \text{s}) = -109.79 \text{ kJ/mol}] \quad [7]$$

Question 2. [25 Marks]

- a) The adsorption of solutes on solids from liquids often follows a Freundlich isotherm,

$\theta = k p^n$. Adapt the equation to apply to a solution and check its applicability to the following data for the adsorption of acetic acid on charcoal and determine the constants k and n .

| | | | | | |
|----------------|------|------|------|------|------|
| [acid]/mol/L | 0.05 | 0.10 | 0.50 | 1.0 | 1.5 |
| W_a/g | 0.04 | 0.06 | 0.12 | 0.16 | 0.18 |

W_a is the mass adsorbed per unit mass of charcoal. [8]

- b) In a moving boundary experiment on KCl the apparatus consisted of a tube of internal diameter of 4.146 mm and it contained an aqueous KCl at a concentration of 0.021 mol/L. A steady current of 18.2 mA was passed and the boundary advanced as follows:

| | | | | | |
|---------------------|-----|-----|-----|-----|------|
| $\Delta t/\text{s}$ | 200 | 400 | 600 | 800 | 1000 |
| x/mm | 64 | 128 | 192 | 254 | 318 |

Find the transport number of K^+ , its mobility and its ionic conductivity

$$[\Lambda_m^\circ(\text{KCl}) = 149.9 \text{ Scm}^2 \text{ mol}^{-1}] \quad [10]$$

- c) The standard potential of the AgCl/Ag, Cl⁻ couple has been measured over a range of temperatures and the results were found to fit the expression

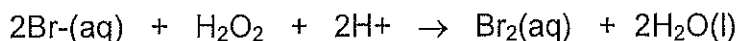
$$E^\circ/\text{V} = 0.23659 - 4.8564 \times 10^{-4} (\theta/^\circ\text{C}) - 3.4205 \times 10^{-6} (\theta/^\circ\text{C})^2 + 5.869 \times 10^{-9} (\theta/^\circ\text{C})^3$$

Calculate the standard Gibbs energy of formation of Cl⁻(aq) at 25°C

$$[\Delta_f G^\circ(\text{AgCl}, \text{s}) = -109.79 \text{ kJ/mol}] \quad [7]$$

Question 3 [25 Marks]

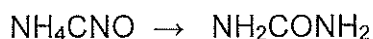
- a) Distinguish between reaction order and molecularity [5]
 b) The oxidation of bromine ions by hydrogen peroxide in acidic solution



Follows the rate law

$$v = k[\text{H}_2\text{O}_2][\text{H}^+][\text{Br}^-]$$

- i. If the concentration of hydrogen peroxide is increased by a factor of 3, by what factor is the rate of consumption of Br⁻ ions increased? [3]
 - ii. If under certain conditions, the rate of consumption of Br⁻ ions is 7.2×10^{-3} mol/Ls, what is the rate of consumption of hydrogen peroxide [2]
 - iii. What is the effect on the rate constant k of increasing the concentration of the bromine ions? [2]
 - iv. If by the addition of water to the reaction mixture the total volume was doubled, what would be the effect on the rate of change of Br⁻? What would be the effect on the rate constant k ? [3]
- c) The data below apply to the formation of urea from ammonium cyanate according to the reaction



Initially, 22.9g of ammonium cyanate was dissolved in enough water to prepare 1L of solution.

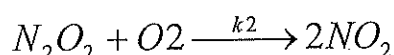
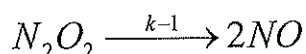
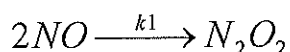
| | | | | | |
|-------------|---|----|------|------|------|
| Time/s | 0 | 20 | 50 | 65 | 150 |
| Mass urea/g | 0 | 7 | 12.1 | 13.8 | 17.7 |

- i. Show that the reaction follows second order rate law [5]

- ii. Determine the rate constant [2]
 iii. Determine the mass of ammonium cyanate left after 300 minutes [3]

Question 4 [25 Marks]

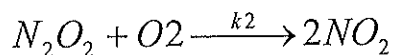
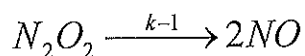
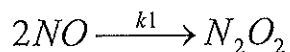
- a) Explain the essential features of a chain reaction [4]
 b) Hydrogen iodide undergoes decomposition into $H_2 + I_2$ when irradiated radiation having a wavelength of 207nm. It is found that when 1J of energy is absorbed, 440 μg of HI is decomposed. How many molecules of HI are decomposed by the photon of radiation of this wavelength [8]
 c) At 25°C. $K = 1.55 L^2 Mol^{-3} min^{-1}$ at an ionic strength of 0.0241 for a reaction in which the rate determining step involves the encounter two singly charged cations. Use the Debye-Huckel limiting law to estimate the rate constant at zero ionic strength. [5]
 d) A solid in contact with a gas at 12 kPa and 25 °C adsorbs 2.5 mg of the gas and obeys Langmuir isotherm. The enthalpy change when 1.0 mmol of the adsorbed gas is desorbed is +10.2 kJ/mol. What is the equilibrium pressure at 40°C? [8]
 e) The reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ is believed to follow the following mechanism:



- i. Assume N_2O_2 to be in a steady state and derive the rate equation. [4]
 ii. Under what conditions the rate equation does reduce to second order kinetics in NO and first order kinetics in O_2 ? [4]

Question 5 [25 Marks]

- a) Explain the origin of the London (dispersion) interaction [5]
 b) The reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ is believed to follow the following mechanism:



- iii. Assume N_2O_2 to be in a steady state and derive the rate equation. [4]
 iv. Under what conditions the rate equation does reduce to second order kinetics in NO and first order kinetics in O_2 ? [4]
 c) The relative permittivity of chlorobenzene was measured at different temperatures:

| | | | |
|-------------------------|------|-----|------|
| $\theta/^\circ\text{C}$ | -50 | -20 | 20 |
| ϵ_r | 7.28 | 6.3 | 5.71 |

- Assuming that the density, which is 1.11 g/cm^3 , does not change with temperature, estimate the dipole moment of this compound [molar mass = 112.45 g/mol] [8]
 d) The glacial angle of a Bragg reflection from a set of crystal planes separated by 99.3 pm is 20.85° . Calculate the wavelength of the x-rays. [4]

Question 6 [25 Marks]

- a) What assumptions did Langmuir make when deriving his isotherm $\theta = \frac{\alpha p}{1 + \alpha p}$ [4]
 b) For N_2 adsorbed on a certain sample of charcoal at -77°C , the volume of adsorbed N_2 (measured at 0°C and 1 atm) per gram of charcoal varied with N_2 pressure as given below:

| | | | | | | |
|------------------------------|-----|------|------|------|------|------|
| P/atm | 3.5 | 10.0 | 16.7 | 25.7 | 33.5 | 39.2 |
| V/(cm^3/g) | 101 | 136 | 153 | 162 | 165 | 166 |

- i. Show that the data fits the Langmuir isotherm.
 ii. Determine the value of α
 iii. Determine the volume of N_2 needed for monolayer coverage. [10]

c) CO adsorbs non-dissociatively on the (111) plane of Ir with $A_{\text{des}} = 2.4 \times 10^{14}/\text{s}$ and $E_{\text{a,des}} = 151\text{kJ/mol}$. Find the half life of CO chemisorbed on Ir (111) at 300K

[3]

d) A solution of potassium permanganate in water at 25 °C was prepared. A solution was in a horizontal tube of length 10 cm, and at first there was a linear gradation of intensity of purple solution from left where the concentration was 0.100mol/L to the right where the concentration was 0.050 mol/L. what is the magnitude and sign of the thermodynamic force acting on the solute

i. Close to the left face of the container

ii. In the middle

iii. Close to the right face

[8]

TOTAL

/100 Marks/

General data and fundamental constants

| Quantity | Symbol | Value |
|---------------------------------------|--|---|
| Speed of light | c | $2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$ |
| Elementary charge | e | $1.602\,177 \times 10^{-19} \text{ C}$ |
| Faraday constant | $F = N_A e$ | $9.6485 \times 10^4 \text{ C mol}^{-1}$ |
| Boltzmann constant | k | $1.380\,66 \times 10^{-23} \text{ J K}^{-1}$ |
| Gas constant | $R = N_A k$ | $8.314\,51 \text{ J K}^{-1} \text{ mol}^{-1}$ |
| | | $8.205\,78 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ |
| | | $6.2364 \times 10 \text{ L Torr K}^{-1} \text{ mol}^{-1}$ |
| Planck constant | h | $6.626\,08 \times 10^{-34} \text{ J s}$ |
| | $\hbar = h/2\pi$ | $1.054\,57 \times 10^{-34} \text{ J s}$ |
| Avogadro constant | N_A | $6.022\,14 \times 10^{23} \text{ mol}^{-1}$ |
| Atomic mass unit | u | $1.660\,54 \times 10^{-27} \text{ Kg}$ |
| Mass | | |
| electron | m_e | $9.109\,39 \times 10^{-31} \text{ Kg}$ |
| proton | m_p | $1.672\,62 \times 10^{-27} \text{ Kg}$ |
| neutron | m_n | $1.674\,93 \times 10^{-27} \text{ Kg}$ |
| Vacuum permittivity | $\epsilon_0 = 1/c^2 \mu_0$ | $8.854\,19 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ |
| | $4\pi\epsilon_0$ | $1.112\,65 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ |
| Vacuum permeability | μ_0 | $4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$ |
| | | $4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3$ |
| Magneton | | |
| Bohr | $\mu_B = e\hbar/2m_e$ | $9.274\,02 \times 10^{-24} \text{ J T}^{-1}$ |
| nuclear | $\mu_N = e\hbar/2m_p$ | $5.050\,79 \times 10^{-27} \text{ J T}^{-1}$ |
| g value | g_e | 2.002 32 |
| Bohr radius | $a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$ | $5.291\,77 \times 10^{-11} \text{ m}$ |
| Fine-structure constant | $\alpha = \mu_0 e^2 c / 2\hbar$ | $7.297\,35 \times 10^{-3}$ |
| Rydberg constant | $R_\infty = m_e e^4 / 8h^3 c \epsilon_0^2$ | $1.097\,37 \times 10^7 \text{ m}^{-1}$ |
| Standard acceleration of free fall | g | $9.806\,65 \text{ m s}^{-2}$ |
| Gravitational constant | G | $6.672\,59 \times 10^{-11} \text{ N m}^2 \text{ Kg}^{-2}$ |

Conversion factors

| | | | |
|---------|--------------------------------------|-----------------|------------------------------|
| 1 cal = | 4.184 joules (J) | 1 erg = | $1 \times 10^{-7} \text{ J}$ |
| 1 eV = | $1.602\,2 \times 10^{-19} \text{ J}$ | 1 eV/molecule = | 96 485 kJ mol ⁻¹ |

| Prefixes | f | p | n | μ | m | c | d | k | M | G |
|----------|------------|------------|-----------|-----------|-----------|-----------|-----------|--------|--------|--------|
| | femto | pico | nano | micro | milli | centi | deci | kilo | mega | giga |
| | 10^{-15} | 10^{-12} | 10^{-9} | 10^{-6} | 10^{-3} | 10^{-2} | 10^{-1} | 10^3 | 10^6 | 10^9 |

PERIODIC TABLE OF ELEMENTS

GROUPS

| PERIODS | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | | |
|---------------------|--------------|--------------|--------------|---------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--|
| | IA | IIA | IIIB | IVB | VB | VIB | VII B | VIII B | | | IB | II B | IIIA | IVA | V A | VIA | VII A | VIII A | | |
| 1 | H 1.008 | He 4.003 | | | | | | | | | | | | | | | | | | |
| 2 | Li 6.941 | Be 9.012 | | | | | | | | | | | | | | | | | | |
| 3 | Na 22.990 | Mg 24.305 | | | | | | | | | | | | | | | | | | |
| TRANSITION ELEMENTS | 4 | K 39.098 | Ca 40.078 | Sc 44.956 | Ti 47.88 | V 50.942 | Cr 51.996 | Mn 54.938 | Fe 55.847 | Co 58.933 | Ni 58.69 | Cu 63.546 | Zn 65.39 | Ga 69.723 | Ge 72.61 | As 74.922 | Se 78.96 | Br 79.904 | Kr 83.80 | |
| | 5 | Rb 85.468 | Sr 87.62 | Y 88.906 | Zr 91.224 | Nb 92.906 | Mo 95.94 | Tc 98.907 | Ru 101.07 | Rh 102.91 | Pd 106.42 | Ag 107.87 | Cd 112.41 | In 114.82 | Sn 118.71 | Sb 121.75 | Te 127.60 | I 126.90 | Xe 131.29 | |
| | 6 | Cs 132.91 | Ba 137.33 | *La 138.91 | Hf 178.49 | Ta 180.95 | W 183.85 | Rf 186.21 | Os 190.2 | Ir 192.22 | Pt 195.08 | Au 196.97 | Hg 200.59 | Tl 204.38 | Pb 207.2 | Bi 208.98 | Po (209) | At (210) | Rn (222) | |
| | 7 | Rf 223 | Ra 226.03 | **Ac (227) | Rf (261) | Ha (262) | Uuh (263) | Uus (262) | Uuo (265) | Uue (266) | Uum (267) | | | | | | | | | |

Atomic mass —
Symbol —
Atomic No. —

*Lanthanide Series

**Actinide Series

| | | | | | | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|
| 140.12 | 140.91 | 144.24 | (145) | 150.36 | 151.96 | 157.25 | 158.93 | 162.50 | 164.93 | 167.26 | 168.93 | 173.04 | 174.97 |
| Ce 58 | Pr 59 | Nd 60 | Pm 61 | Sm 62 | Eu 63 | Gd 64 | Tb 65 | Dy 66 | Ho 67 | Er 68 | Tm 69 | Yb 70 | Lu 71 |
| 232.04 | 231.04 | 238.03 | 237.05 | (244) | (243) | (247) | (247) | (251) | (252) | (257) | (258) | (259) | (260) |
| Th 90 | Pa 91 | U 92 | Np 93 | Pu 94 | Am 95 | Cm 96 | Bk 97 | Cf 98 | Es 99 | Fm 100 | Md 101 | No 102 | Lr 103 |

() indicates the mass number of the isotope with the longest half-life.