

**CORK INSTITUTE OF TECHNOLOGY
INSTITIÚID TEICNEOLAÍOCHTA CHORCAÍ**

Autumn Examinations 2012/13

Module Title: Fundamental Physical Chemistry

Module Code: CHEM 6004

School : Science

Programme Title: BSc in Analytical & Pharmaceutical Chemistry – Stage 1
BSc in Analytical Chemistry with Quality Assurance – Stage 1

Programme Code: SCHEM_7_Y1
SCHQA_8_Y1

External Examiner(s): Dr. C. Roche

Internal Examiner(s): Dr. M. Sheahan

Instructions: Answer any **FOUR** questions. *All questions carry equal marks*

Duration: 2 Hours

Sitting: Autumn 2013

Requirements for this examination: Periodic Table

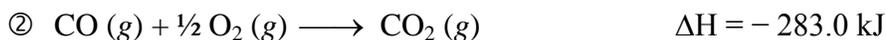
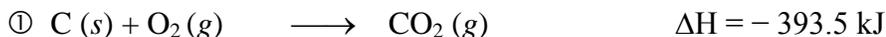
Note to Candidates: Please check the Programme Title and the Module Title to ensure that you have received the correct examination paper.
If in doubt please contact an Invigilator.

Q1.

- (a) Give the standard conditions for temperature, pressure and concentration? (3 marks)
- (b) The reaction $2\text{NO}_2(g) + \text{F}_2(g) \rightarrow 2\text{NO}_2\text{F}(g)$ is 1st order in both reactants.
- (i) Write the rate law for the reaction (2 marks)
- (ii) What is the effect on rate if the concentration of NO_2 is halved (3 marks)
- (iii) If the rate of formation of the product is $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$, what are the respective rates of disappearance of NO_2 and F_2 (3 marks)
- (iv) Outline how reaction order may be determined experimentally (5 marks)
- (c) Name two types of electrochemical cells; state the main difference between them (3 marks)
- (d) Write a brief note on buffers. State their purpose, outline their composition and explain how they work. Include a specific example of a buffer (6 marks)

Q2.

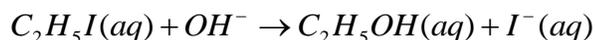
- (a) State the first law of thermodynamics. (3 marks)
- (b) What do you understand by the terms *system* and *surroundings* in the context of a chemical reaction? Give an example of both (5 marks)
- (c) If, in the course of an endothermic reaction, the volume contracts, does the energy of the system increase or decrease? Explain your answer (4 marks)
- (d) Using the thermochemical equations provided, determine the enthalpy for the combustion of carbon, $\text{C}(s)$: $\text{C}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g)$



What would be the enthalpy of combustion for 10 moles of carbon? (6 marks)

- (e) Other than thermochemical equations, write a note on three other methods which could be used to determine the enthalpy change for a chemical reaction (7 marks)

Q3. The tabulated data has been determined for the hydrolysis of ethyl iodide (C₂H₅I).

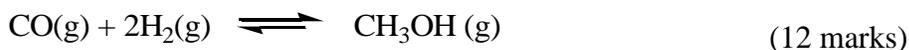


<i>k</i> (M⁻¹s⁻¹)	8.21 x 10 ⁻⁷	5.03 x 10 ⁻⁵	3.68 x 10 ⁻⁴	6.71 x 10 ⁻³	0.119
T (K)	260.50	288.83	305.02	332.75	363.61

- (a) Name each parameter in the Arrhenius equation ($k = Ae^{-E_a/RT}$) (4 marks)
- (b) Use the Arrhenius equation to derive an expression which may be used to determine the activation energy (E_a). Hence determine the activation energy for the hydrolysis of ethyl iodide (C₂H₅I). $R = 8.314J\ mol^{-1}\ K^{-1}$ (8 marks)
- (c) Use the data provided to construct a plot of $\ln k$ as a function of $1/T$. Determine the slope and hence obtain a value for the activation energy. (9 marks)
- (d) Would you expect the equation method or the graphical method to give a more accurate value for E_a ; hence account for any differences between the values obtained in (b) and (c) (4 marks)

Q4.

- (a) Discuss the parameters which can be used to change the composition of an equilibrium mixture; hence or otherwise explain how the yield from the following exothermic reaction may be maximized

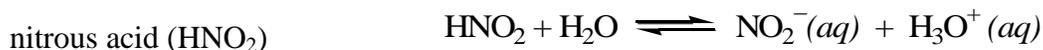


- (b) Write an equation which shows the equilibrium between the sparingly soluble salt Pb(NO₃)₂ and its ions in a saturated solution (3 marks)
- (c) Calculate the molar solubility of Ag₂SO₄ @ 25°C in water given the K_{sp} for Ag₂SO₄ @ 25°C is 1.4×10^{-5} (show all calculations); hence distinguish the solubility product (K_{sp}) for a salt and its molar solubility. (8 marks)
- (d) In general, what does the magnitude of either parameter (K_{sp} or molar solubility) indicate about the solubility (2 marks)

Q5.

- (a) Give the Arrhenius definition of acids and bases. How do these definitions differ from the Brønsted – Lowry definition? (4 marks)
- (b) What is a *conjugate acid-base pair*? Give an example (2 marks)
- (c) Give the equation showing the equilibrium established between each of the following acidic species and water: HSO_3^- , NH_4^+ , HCOOH and HClO_4 (4 marks)
- (d) Calculate the pH values of the following solutions:
- (i) 0.05M hydrochloric acid, HCl
 - (ii) 0.5M hydrocyanic acid, HCN ($K_a = 4.9 \times 10^{-10}$ at ambient temperature)
 - (iii) A buffer solution prepared from 0.12M lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$, $K_a = 1.4 \times 10^{-4}$) and 0.1M sodium lactate ($\text{NaC}_3\text{H}_5\text{O}_3$)
- (6 marks)
- (e) What do you understand by the *common-ion effect* in ionic equilibria? (3 marks)

- (f) Explain the effect, if any, of the underwritten changes on the pH of a solution of



- (i) Dilution of the solution
- (ii) Addition of sodium nitrite (NaNO_2)
- (iii) Addition of HCl

(6 marks)

Q6.

- (a) For the redox reaction between Cr/Cr^{3+} and Ag/Ag^+ ,
- (i) Give an equation for each half-cell reaction (note: Cr is higher in the activity series than Ag) and give the overall cell reaction (6 marks)
 - (ii) Construct a fully labelled sketch of a galvanic cell; show the direction of electron flow, the salt bridge, the anode and the cathode (6 marks)
 - (iii) Identify the oxidizing and reducing agents respectively (2 marks)
- (b) What is a *salt bridge*? Describe their purpose in galvanic cells (6 marks)
- (c) How many grams of Na metal are deposited in a cell if a current of 10A is passed through molten NaCl for 30 mins? Faraday constant 96 500 (5 marks)