Thermodynamics, Kinetics, and Quanta

22CMB105

Semester 1 2022/23 In-Person Exam paper

This examination is to take place in-person at a central University venue under exam conditions. The standard length of time for this paper is **2 hours**.

You will not be able to leave the exam hall for the first 30 or final 15 minutes of your exam. Your invigilator will collect your exam paper when you have finished.

Help during the exam

Invigilators are not able to answer queries about the content of your exam paper. Instead, please make a note of your query in your answer script to be considered during the marking process.

If you feel unwell, please raise your hand so that an invigilator can assist you.

You may use a calculator for this exam. It must comply with the University's Calculator Policy for In-Person exams, in particular that it must not be able to transmit or receive information (e.g. mobile devices and smart watches are **not** allowed).

Planck constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^{8}$ m s^{-1}

Boltzmann constant, $k = 1.380 \times 10^{-23}$ J K^{-1}

Gas constant, $R = 8.315$ J mol^{-1} K^{-1}

Unit charge, $e = 1.602 \times 10^{-19}$ C

Mass of electron, $m_e = 9.109 \times 10^{-31}$ kg

Avogadro constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}

Faraday constant, $F = 96485$ C mol^{-1}

Answer **ALL** questions, show **ALL** your working.

A total of 100 marks are available. Breakdown of marks per question:

1.	25 marks
2.	13 marks
3.	12 marks
4.	25 marks
5.	25 marks

1. Answer **ALL** parts

   a. Describe the difference between a *galvanic cell* and an *electrolytic cell*.

   [2 marks]

   b. Consider the following cell:

   Cu (s) | Cu^{2+} (aq) (0.1 M) | | Ag^{+}(aq) (1.0 M) | Ag (s)

      i. Write the half-cell reactions for the reduction and oxidation reactions and the overall cell reaction.

      [3 marks]

      ii. Calculate E_{cell} for this cell at 298 K, if $E°_{cell}$ is + 0.46 V.

      [4 marks]

   c. Sketch an appropriately labelled graph that demonstrates the relationship between molar conductivity (Λ_m) and concentration for strong electrolyte KI and weak electrolyte NH_4OH.

   [4 marks]

   d. Using the sketch in 1c, describe the differences in molar conductivities, Λ_m between strong and weak electrolytes at different concentrations.

   [4 mark]

   e. Define the term *infinite dilution*.

   [1 marks]

   f. Calculate the *ionic strength*, *mean activity coefficient* and *activity* of 0.0018 mol kg^{-1} of magnesium sulphate, $MgSO_4$.

   [7 marks]

2. Answer **ALL** parts

   a. Explain what is meant by the term surface tension and why it arises.

   [2 marks]

   b. Triton X is a zwitterionic surfactant with a critical micelle concentration of 200 µmol dm^{-3}. The force, *F*, required to detach a 9.5 mm diameter Pt ring from the surface of Triton X solutions of different concentrations, *C*, at 298 K is shown below. Assuming a simplified geometry, such that β = 1, calculate the surface tension at 0.96 µmol dm^{-3}. Show your working.

   [2 marks]

C (μmol dm^{-3})	0.96	2.74	5.13	7.81	1.01
F (mN)	3.49	3.25	3.03	2.88	2.80

c. The surface tension values are reasonably fit by the equation

$$\gamma = 116C^2 - 2.52C + 0.061$$

where γ is in units of N m^{-1}, and C has units of mol m^{-3}. Differentiate this equation with respect to C and use it to find the surface excess of Triton X at 1.5 μmol dm^{-3}. State any assumptions made. Comment on your answer.

[7 marks]

d. Predict the trend in surface tension with concentrations at millimolar concentrations. State your reasoning.

[2 marks]

3. Answer **ALL** parts

a. Ruthenium oxide is an excellent catalyst, but only when its surface is reduced to a metallic state. Discuss how X-ray photoelectron spectroscopy (XPS) is a suitable technique to study surface oxidation state.

[3 marks]

b. A ruthenium oxide sample was exposed to hydrogen and partially reduced. An XPS measurement was performed and less than 1% oxidised Ru was observed. Given that the inelastic mean free path of the electron was 0.5 nm, calculate the thickness of the reduced Ru surface film.

[2 marks]

c. Ethanol is dosed onto the Ru surface and monitored by oxygen KL_1L_3 Auger spectroscopy.

	1s	2s	$2p_{1/2}$	$2p^{3/2}$	3s
B.E. (eV)	532	24	7	7	1

From the table calculate the kinetic energy of the Auger electron.

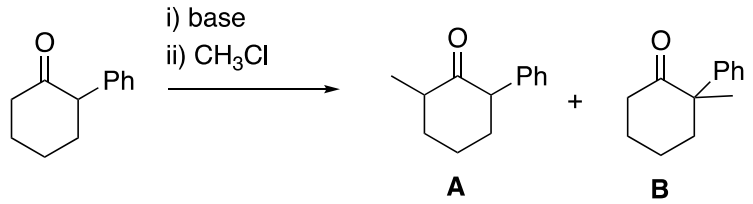
[3 marks]

d. Two molecules of adsorbed ethanol react to form butanol on the Ru surface. However, the reaction only proceeds when >25% surface is covered. Assume that there is a partial pressure of 10^{-6} Torr of ethanol within the vacuum system at 25 °C. How long would it take to see oxygen KL_1L_3 associated with butanol? 1 Torr = 1.333 x 10^{-2} N cm^{-2}.

[4 marks]

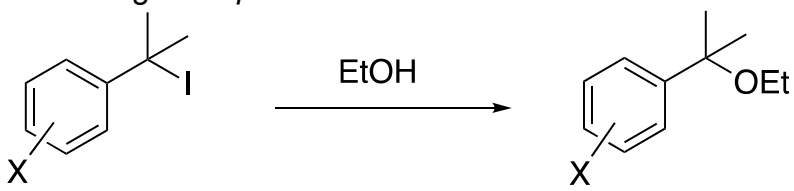
4. Answer **ALL** parts

a. Explain how the ratio of products **A** and **B** formed from the reaction below can be controlled by careful choice of the reaction conditions. Use a reaction coordinate diagram to explain your answer.



[6 marks]

b. The correlation of rate constants for the ethanolysis of dimethylbenzyl iodide with Hammett σ-values gave a ρ-value of –4.7.



i. Write a reaction mechanism that is consistent with these observations. Identify the rate determining step and draw a plausible structure of its transition state.

[4 marks]

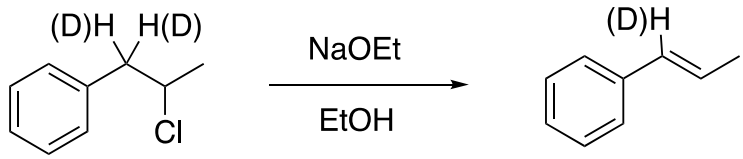
ii. Comment on the significance of the sign and magnitude of the observed ρ-value, and how this allows other mechanisms to be ruled out.

[4 marks]

iii. Comment on how substituent X can affect the rate of the reaction, including a mechanistic rationale using two different examples

[6 marks]

c. Describe how a kinetic isotope experiment could be used to elucidate the mechanism of the reaction below. State whether you would expect to observe a normal or inverse, primary or secondary kinetic isotope effect.



[5 marks]

5. Answer **ALL** parts

a. The photoelectric effect

i. Explain the photoelectric effect using a sketch and explain what it tells us about the nature of light.

[4 marks]

ii. Explain if and how the energy of the outgoing electrons depends on the frequency, wavelength and intensity of the light used.

[3 marks]

b. X-rays are generated in an X-ray tube by accelerating electrons using a high voltage and letting them collide with a target material.

i. If the X-ray tube is operated at 75 kV, what is the energy of the electrons? Give the answer in eV and J.

[3 marks]

ii. What is the wavelength of the X-rays produced for a voltage of 75 kV (assuming that the full energy of the electron is transferred to the X-ray photon)?

[2 marks]

iii. Compare the result of (ii.) with typical interatomic separations in molecules and crystals. Comment on the significance of this for X-ray diffraction experiments.

[2 marks]

c. The energy of molecules is divided into electronic excitations, rotations, vibrations, and translation. Sort these four processes according to increasing energy. Specify which type of radiation can be used to probe each of these processes.

[6 marks]

d. In quantum mechanics, the momentum operator is given as

$$\hat{p} = -i\hbar\frac{d}{dx}$$

i. Name two characteristics of a wavefunction with high momentum and kinetic energy. Explain how this relates to the above equation.

[3 marks]

ii. Apply the momentum operator to the function $\phi(x) = ax^2$. Is $\phi(x)$ an eigenfunction of the momentum operator and, if so, what is the eigenvalue?

[2 marks]

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