University of Canterbury

End-of-year Examinations 2009

Prescription Number(s):	CHEM 243
Paper Title:	Physical Chemistry

Time Allowed: Two hours

Number of pages: Six

Each question is worth 50% of the total marks.

Answer **BOTH** questions.

1. Complete **FIVE** of the following tasks (a) – (g):

   (a) Sketch graphs showing the typical forms of Langmuir and BET isotherms, and explain the origin of the differences between the two types of isotherm.

   (b) Describe and compare the Langmuir-Hinshelwood and Eley-Rideal mechanisms of catalysis by a surface.

   (c) Describe the properties of zeolites that make them useful as support mediums for catalysts and give one example of their use in this way.

   (d) Derive the Langmuir isotherm as it might apply to the adsorption of phosphine on tungsten, and explain why the dissociation of phosphine on tungsten obeys first-order kinetics at low phosphine pressure, but changes to zero-order kinetics at high phosphine pressure.

   (e) Outline the Michaelis-Menten mechanism of enzyme catalysis, derive the Michaelis-Menten equation, and explain how it would be used in practice to obtain the Michaelis constant of the enzyme.

   (f) Describe, with examples of their application, **ONE** of the following three methods of studying the structure of surfaces: (i) Low-Energy Electron Diffraction; (ii) Scanning-Tunnelling Microscopy; (iii) Atomic Force Microscopy.

   (g) Outline the structural properties of metal surfaces that can cause them to be effective catalysts of reaction, and briefly explain the origin of the 'volcano plot' of catalytic activity versus atomic number.

2. **Useful information** for this question:

$c = 2.998 \times 10^{10}$ cm s^{-1} $R = 8.314$ J mol^{-1} K^{-1}

$m_e = 9.109 \times 10^{-31}$ kg $e = 1.602 \times 10^{-19}$ C

$N_A = 6.022 \times 10^{+23}$ mol^{-1} amu $= 1.661 \times 10^{-27}$ kg

$h = 6.626 \times 10^{-34}$ J s $\hbar = 1.055 \times 10^{-34}$ J s

$\varepsilon_o = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1} 0 K = –273.15 °C

$E = h\nu$ $c = \nu\lambda$

(1) $E = \dfrac{n^2h^2}{8mL^2}$ $A = -\log_{10}\left(\dfrac{I}{I_0}\right)$

(2) $E = \dfrac{(m_l)^2 h^2}{8\pi^2 m r^2}$ $A = \varepsilon c l$

(3) $E = h\dfrac{\hbar}{4\pi I}J(J+1)$ $I = \mu R^2$

(4) $E = h(v + \frac{1}{2})\dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$ $\dfrac{1}{\mu} = \dfrac{1}{m_A} + \dfrac{1}{m_B}$

$E = \dfrac{-m_e e^4 Z^2}{n^2 32(\pi\varepsilon_o)^2\hbar^2}$ $\lambda = h/p$

(a) (12 marks)

For **EACH** of the equations (1)–(4) in the useful information (on the previous page):

(i) Describe the quantum mechanical system for which the equation holds;

(ii) Indicate which variable in the equation is the quantum number and what values it is permitted to take; and

(iii) State the type (or types) of electromagnetic radiation that is (are) most commonly associated with atoms or molecules that undergo transitions between such energy levels.

(b) (12 marks)

The following sentence is from your textbook for this course:

"The phenomena of chemistry cannot be understood thoroughly without a firm understanding of the principal concepts of quantum mechanics."

(i) Briefly give your understanding of the principal concepts of quantum mechanics.

(ii) Briefly outline how quantum mechanics enables a thorough understanding of the phenomena of chemistry.

(c) (12 marks)

From what you have learned about spectroscopy in this course, give brief explanations for the following well-known phenomena:

(i) That microwave ovens heat food.

(ii) That CO_2 is a 'greenhouse gas' in the atmosphere.

(iii) That the 'ozone hole' is harmful to humans.

Question 2 continued on following page

Question 2 continued

(d) (12 marks)

(i) In how many different ways does H_2O vibrate? (Be sure to explain how you arrive at your answer.)

(ii) Describe each of these vibrations.

(iii) Which of these vibrations are infrared active? Explain your answer.

(iv) How will the vibrations of D_2O (where D signifies deuterium) be different to those of H_2O? Explain your answer.

(e) (12 marks)

(i) Show that the value of the Rydberg constant for He^+ is 438 400 cm^{-1}.
(Hint: Use physical constants and an equation from the "useful information" on page 4.)

(ii) Calculate the ionisation energy of He^+ in kJ mol^{-1}.

(iii) The electron in an excited He^+ atom has $n = 4$, $l = 0$, $m_l = 0$ and $m_s = + ½$. Calculate the photon energies (in cm^{-1}) that the atom may *emit* as a result of the electron changing state.

END OF PAPER