

University of Canterbury

End-of-year Examinations 2009

Prescription Number(s): CHEM 273

Paper Title: Physical Chemistry

Time Allowed: Two hours

Number of pages: Five

Values for constants and equations are shown on page 2.

Answer **THREE** questions out of FOUR.

TURN OVER

Constants:

$$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$$

$$h = 6.62606876 \times 10^{-34} \text{ J s}$$

$$\hbar = 1.054571596 \times 10^{-34} \text{ J s}$$

$$1 \text{ amu} = 1.66053873 \times 10^{-27} \text{ kg}$$

$$\text{electron mass} = 9.109390 \times 10^{-31} \text{ kg}$$

$$k_B = 1.3806503 \times 10^{-23} \text{ J K}^{-1}$$

$$1 \text{ cm}^{-1} = 1.98660 \times 10^{-23} \text{ J}$$

Selected Formulae

$$E_n = n^2 h^2 / (8mL^2)$$

$$E = h\nu$$

$$E_\nu = \left(\nu + \frac{1}{2}\right) \frac{h}{2\pi} \left(\frac{k}{\mu}\right)^{1/2}$$

$$\mu = m_1 m_2 / (m_1 + m_2)$$

$$I = \mu r_o^2$$

$$I = 2m_A r_o^2$$

$$E_J = J(J+1)B$$

$$B = h^2 / (8\pi^2 I)$$

1.
 - (a) Briefly describe the principal mechanism by which electromagnetic radiation interacts with matter.
 - (b) The rotational constants for $^{12}\text{C}^{32}\text{S}$ and (linear) $^{32}\text{S}^{12}\text{C}^{32}\text{S}$ are respectively $B_{\text{CS}} = 24,495.576$ MHz and $B_{\text{SCS}} = 3,245.457$ MHz. The relevant atomic masses are $^{12}\text{C} = 12.000$ amu and $^{32}\text{S} = 31.972$ amu.
 - (i) What are the C-S bond lengths within each of the two molecules?
 - (ii) *Qualitatively*, what happens to the rotational constants for each of the two molecules when ^{12}C is replaced by ^{13}C ? (^{13}C atomic mass = 13.003 amu)
 - (c) Carbon monoxide has a fundamental vibrational frequency of 2212.0 cm^{-1} . Relevant atomic masses are: ^{12}C (12.000 amu), ^{16}O (15.995 amu).
 - (i) What is the force constant, k , for the C–O bond, in N m^{-1} ?
 - (ii) Is the fundamental vibrational frequency of $^{13}\text{C}^{16}\text{O}$ greater than, less than, or equal to the $^{12}\text{C}^{18}\text{O}$ isotopomer value?
2.
 - (a) Briefly discuss why some molecules absorb microwave radiation while others don't.
 - (b) Briefly discuss why some molecules absorb infrared radiation while others don't.
 - (c) Electronic absorption spectra for molecules are typically characterized by extremely broad spectral features, with the most intense peaks often at frequencies very different from the fundamental frequency separating the pure electronic energy levels. Discuss and account for this tendency in one or two paragraphs, with diagrams as appropriate.
 - (d) The vibrational spectroscopy of two different triatomic molecules, ABC and DEF, is investigated. One molecule, ABC, is found to possess four vibrational modes in total (counting a degenerate mode as two), while DEF has only three vibrational modes. Structurally, how do these molecules differ? How many distinct rotational constants does each molecule possess?
 - (e) What are 'hot bands' in vibrational spectroscopy. Explain, briefly, how anharmonicity in the vibrational potential can give rise to these.

3. The time-dependent Schrödinger equation for a one-dimensional system involving a single particle of mass m can be written;

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} \quad (1)$$

For an unconstrained particle, the solution is

$$\Psi(x, t) = Ae^{i(px - Et)/\hbar} \quad (2)$$

- (a) Define the variables x , p , E and t .
- (b) With reference to the variables in (a), explain what is meant by the term **conjugate variables**.
- (c) If the potential energy is independent of time, show that equation (1) can be reduced to the time-independent form in (3)

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \quad (3)$$

where $\psi(x) = e^{ipx/\hbar}$

- (d) Consider a quantum mechanical particle confined to a one dimensional box of length L . The potential energy of the particle is zero inside the box and infinite everywhere else. Show that the kinetic energy of the particle inside the box is quantised by the relationship

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (4)$$

- (e) Starting with equation 4, show that the magnitude of the linear momentum of the particle is quantised according to the relationship

$$p_n = \frac{nh}{2L} \quad (5)$$

4. The non-relativistic wave function for a hydrogen atom can be written

$$\Psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m_l}(\theta, \phi)$$

- (a) Define the coordinates r , θ and ϕ , and explain why they are used in preference to Cartesian coordinates.
- (b) Explain the roles of the functions $R_{n,l}(r)$ and $Y_{l,m_l}(\theta, \phi)$.
- (c) Describe (with the help of equations and diagrams) how the quantum numbers n , l and m_l relate to the quantisation of *energy* and *angular momentum* of the atom.
- (d) The non-relativistic energy of a hydrogen atom depends only on the quantum number n , but the energies of the orbitals of a many-electron atom depend on both n and l . Explain.
- (e) Describe at least one consequence of the inclusion of relativistic effects on the wavefunction of an electron in an atom.

END OF PAPER