BINDURA UNIVERSITY OF SCIENCE EDUCATION

FACULTY OF SCIENCE

CHEMISTRY DEPARTMENT

BScED and CHEMICAL TECHNOLOGY

COURSE: CH 201: PHYSICAL CHEMISTRY II - JUN 2023

ANSWER **ANY FIVE (5)** QUESTIONS. EACH QUESTION CARRIES **20 MARKS**.

****

Data and formulae

$m_e = 9.11 \times 10^{-31}$ kg 1 amu = 1.66×10^{-27} kg $c = 3.0 \times 10^{8}$ ms^{-1} $h = 6.626 \times 10^{-34}$Js

1eV = 1.602×10^{-19} J

$$\int (\sin ax)\,dx = -\frac{1}{a}\cos ax + C \qquad \frac{d(ax^n)}{dx} = anx^{n-1}$$

$$\int (\cos ax)\,dx = \frac{1}{a}\sin ax + C \qquad \frac{d(ae^{bx})}{dx} = abe^{bx}$$

$$\int (\cos^2 ax)\,dx = \frac{1}{2}x + \frac{1}{4a}\sin 2ax + C \qquad \frac{d(a\sin x)}{dx} = a\cos x$$

$$\int (\sin^2 ax)\,dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax + C \qquad \frac{d(a\cos x)}{dx} = -a\sin x$$

$$\frac{A_{21}}{B_{21}} = \frac{16\pi^2 h\nu^3}{c^3}$$

****

1. (a) A molecule in an excited state can decay to the ground state either by stimulated emission or spontaneous emission. Use Einstein coefficients to predict how the relative probability of these processes changes as the frequency of transition quadruples. **[4 marks]**

   (b) Which of the following wave functions are eigen-functions of the operator d^2/dx^2 ? If they are eigen-functions, what is the eigenvalue? **[6 marks]**

   (i) ksin(6x)

(ii) $\frac{3}{4}ke^{2x}$

(c) What feature of the Morse potential makes it suitable for modeling dissociation of a diatomic molecule? **[2 marks]**

(d) Suppose the speed of a projectile of mass 2.0 g is known to be within 1 μm s^{-1}. Calculate the minimum uncertainty in its position. **[4 marks]**

(e) Write brief notes on the Born-Oppenheimer approximation. **[4 marks]**

2. (a) From the formula given for the energy levels for the particle in a box, $E_n = \frac{n^2h^2}{8ma^2}$ for n = 1, 2, 3,…., we can see that the spacing between adjacent levels increases with n. This appears to indicate that the energy spectrum does not become continuous for larger n, which must be the case for the quantum mechanical result to be identical to the classical result in the high-energy limit. A better way to look at the spacing is to form the ratio $(E_{n+1}-E_n)/E_n$. Form this ratio and show that ΔE/E becomes a smaller fraction of the energy as $n \to \infty$. **[5 marks]**

(b) Calculate the energy separations in electron volts between the levels n = 5 and n = 3 in a box of length 0.5 nm. **[5 marks]**

(c) (i) The work function of tungsten is 4.50 eV. What is the minimum frequency of light required to observe the photoelectric effect on W? **[4 marks]**

(ii) If light with a 225 nm wavelength is absorbed by the surface, what is the velocity of the emitted electrons? **[6 marks]**

3. (a) Describe the physical origins of linewidths in the absorption and emission spectra of gases, liquids, and solids. **[12 marks]**

(b) How many states does a He atom with an electronic configuration $1s^1 2s^1$ have? If more than one state arises, arrange them in terms of energy. **[8 marks]**

4. (a) Rotational absorption lines from $^1H^{35}Cl$ were found at the following wavenumbers:

83.32; 104.13; 124.73; 145.37; 165.89; 186.23; 206.60; 226.86 cm^{-1}

(i) What do you understand by the phrase 'moment of inertia'? **[2 marks]**

(ii) Calculate the moment of inertia and the bond length of the molecule. **[10 marks]**

(b) The rotational constant for CO is 1.9314 cm^{-1} and 1.6116 cm^{-1} in the ground and first excited vibrational states, respectively. By how much does the internuclear distance change as a result of this transition? **[8 marks]**

(c) Distinguish between stimulated emission and spontaneous emission. **[4 marks]**

5. (a) (i) Explain the two phrases; **allowed** and **forbidden** transitions, as used in spectroscopy? Give examples of such transitions. **[4 marks]**

(ii) Determine the number of normal modes for an ethyne (C_2H_2) molecule. **[3 marks]**

(b) Label each statement as either true or false and give a reason to answer.

(i) A forbidden transition cannot occur. **[2 marks]**

(ii) A forbidden transition always produces a weaker spectral line than every allowed transition. **[2 marks]**

(iii) All forms of spectroscopy require that the radiation is dispersed. **[2 marks]**

(iv) A molecule cannot have a permanent dipole moment if it has a center of inversion **[2 marks]**

(v) Chiral molecules lack an improper axis of rotation (S_n), a center of symmetry (i) or a mirror plane (σ). **[2 marks]**

(c) The rate of fluorescence is higher than that for phosphorescence. Can you explain this fact? **[3 marks]**

6. The ground state of O_2^+ is $X^2\Pi_g$ and the next few excited states, in order of increasing energy, are $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, $^2\Delta_g$, $^2\Sigma_g^-$, and $c^4\Sigma_u^-$. On the basis of selection rules, which of the excited states can be accessed from the ground state by absorption of UV light? **[20 marks]**

THE END