BINDURA UNIVERSITY OF SCIENCE EDUCATION

FACULTY OF SCIENCE

CHEMISTRY DEPARTMENT

BSc Chemical Technology and BSc Education

COURSE: CH 201: PHYSICAL CHEMISTRY II
2 HOURS

OCT 2024

Answer **ANY Five (5)** questions. Each question carries **20 MARKS.**

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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

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

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

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

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

1. (a) How did Planck conclude that the discrepancy between experiments and classical theory for blackbody radiation was at high and not low frequencies? **[3 marks]**

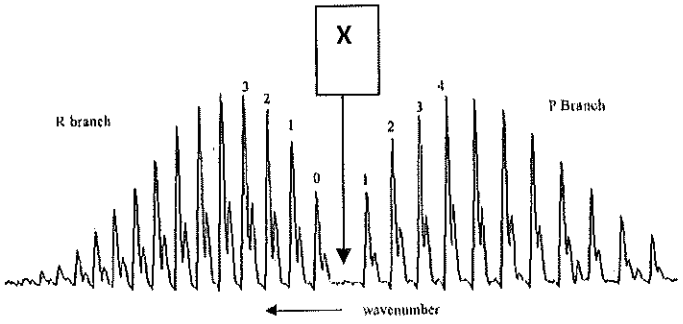
   (b) The inability of classical theory to explain the spectral density distribution of a blackbody was called the *ultraviolet catastrophe.* Why is this name appropriate? **[4 marks]**

   (c) Is the following wavefunction an eigenfunction of the operator d^2/dx^2 ? If yes what is the eigenvalue? **[4 marks]**

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

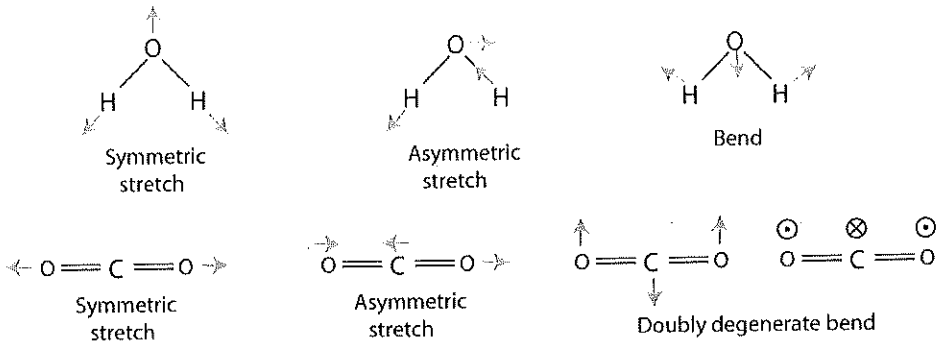
   (d) What feature of the Morse potential makes it suitable for modeling dissociation of a diatomic molecule? **[2 marks]**

   (e) What is the explanation for the absence of a peak in the rotational-vibrational spectrum near the position labeled **X**?? **[3 marks]**



(f) What information does the term symbol $^3F_4$ provide about the angular momentum of an atom? **[4 marks]**

2. (a) Calculating the motion of individual atoms in the vibrational modes of molecules (called normal modes) is an advanced topic. Given the normal modes shown in the following figure, decide which of the following modes of CO_2 and H_2O have a nonzero dynamical dipole moment and are therefore infrared active. The motion of the atoms in the second of the two doubly degenerate bend modes for CO_2 is identical to the first, but is perpendicular to the plane of the page. **[6 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) Describe the mechanism of fluorescence. **[6 marks]**

3. (a) Define, justify, and provide an example of zero-point energy. **[6 marks]**

(b) The ground-state wavefunction of a hydrogen atom is

$$\psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

where a_0 = 53 pm (the Bohr radius).

(i) Calculate the probability that the electron will be found somewhere within a small sphere of radius 1.0 pm centered on the nucleus. **[5 marks]**

(ii) Now suppose that the same sphere is located at $r = a_0$. What is the probability that the electron is inside it? **[4 marks]**

(b) Semiconductors can become conductive if their temperature is raised sufficiently to populate the (empty) conduction band from the highest filled levels in the valence band. The ratio of the populations in the highest level of the conduction band to that of the lowest level in the conduction band is

$\frac{n_{conduction}}{n_{valence}} = \frac{g_{conduction}}{g_{valence}} e^{-\Delta E/kT}$ where ΔE is the band gap, which is 1.12 eV for Si and 5.5 eV for diamond. Assume for simplicity that the ratio of the degeneracies is one and that the semiconductor becomes sufficiently conductive when

$\frac{n_{conduction}}{n_{valence}} = 5.5 \times 10^{-7}$.

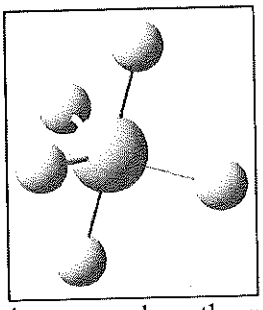
i. At what temperatures will silicon and diamond become sufficiently conductive? **[3 marks]**

ii. Given that the most stable form of carbon at normal pressures is graphite and that graphite sublimates near 3700 K, could you heat diamond enough to make it conductive and not sublimate it? **[2 marks]**

4. (a) Which of the following molecules may be polar?

(i) CH_3Cl (C_3v),
(ii) $HW_2(CO)_{10}$ (D_4h),
(iii) $SnCl_4$ (T_d). **[5 marks]**

(b) (i) What shape is the molecule below?**All the bonds in this molecule are of equal length.* **[2 marks]**



(ii) To which point group does the molecule belong? **[3 marks]**

(iii) How many vibrational modes will the molecule have? **[2 marks]**

(iv) Of these modes, which ones will be Infrared active, Raman active or both? **[4 marks]**

(c) Nitrogen and oxygen do not absorb infrared radiation and are therefore not greenhouse gases. Why is this the case? **[4 marks]**

5. (a) Describe the physical origins of linewidths in the absorption and emission spectra of gases, liquids, and solids. **[9 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. **[6 marks]**

(c) Lasers have transformed the world as they are now on the frontier of physics and chemistry. Describe the principle of a helium-neon laser. **[5 marks]**

6. (a) $^1H^{35}Cl$ has a force constant $k = 516$ N m^{-1} and a moment of inertia of 2.644×10^{-47} kg m^2. Calculate the frequency of the light corresponding to the lowest energy for pure vibrational and pure rotational transitions. **[6 marks]**

(b) In what regions of the electromagnetic spectrum do the transitions in (a) lie? **[2 marks]**

(c) It is useful to consider the result for the energy eigenvalues for the one-dimensional box $E_n = \dfrac{h^2 n^2}{8ma^2}$, $n = 1,2,3,\ldots$ as a function of n, m, and a.

(i) By what factor do you need to change the box length to decrease the zero point energy by a factor of 400 for a fixed value of m?

(ii) By what factor would you have to change n for fixed values of a and m to increase the energy by a factor of 400?

(iii) By what factor would you have to increase a at constant n to have the zero point energies of an electron be equal to the zero point energy of a proton in the box? **[2+2+4 marks]**

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

(i) A forbidden transition cannot occur. **[1 marks]**

(ii) A forbidden transition always produces a weaker spectral line than every allowed transition. **[1 marks]**

(iii) All forms of spectroscopy require that the radiation is dispersed. **[1 marks]**

(iv) Any molecule that exhibits a rotational Raman spectrum does not exhibit a microwave absorption spectrum. **[1 marks]**

END OF PAPER