EASTERN UNIVERSITY, SRI LANKA

SPECIAL DEGREE EXAMINATION IN CHEMISTRY

2008/2009 (NOVEMBER 2011)

CH 403 PHYSICAL CHEMISTRY

Answer all questions | Time: 02 hours

Velocity of light (c) = 2.9979×10^{8} m s^{-1} Planck's constant (h) = 6.6256×10^{-34} J s

Boltzmann's constant (k) = 1.38054×10^{-23} J K^{-1} Mass of electron (m) = 9.109×10^{-31} kg

Gas constant (R) = 8.314 J K^{-1} mol^{-1} 1 pm = 1×10^{12}m

1) (a) The energy states for a particle in a 3 – dimensional box with lengths L_1, L_2 and L_3 are given by

$$E = \frac{h^2}{8m}\left[\left(\frac{n_1}{L_1}\right)^2 + \left(\frac{n_2}{L_2}\right)^2 + \left(\frac{n_3}{L_3}\right)^2\right]$$

i) Show that that the lowest energy level is non degenerate and the second energy level is triply degenerate if the box is cubical

ii) Consider a box of volume $V = L_1L_2L_3$ with 3 electrons (2 electrons in the lowest energy level, one in the next). Show that the total energy in this case is equal to

$$E = \frac{h^2}{8m}\left(\frac{12}{L_1^2}\right)$$

iii) The lower total energy due to rectangular distortion ($L_1 = L_2 \neq L_3$) at constant volume is given by

$$E = \frac{h^2}{8m}\left(\frac{6}{L_1^2} + \frac{6}{L_3^2}\right) \quad \text{Where } L_3 > L_1.$$

A) Write down the E in terms of L_1 and V

B) Find $\frac{dE}{dL_1}$

C) Show that for minimization of the energy $\frac{L_3}{L_1} = \sqrt{2}$ (Remember $V = L_1^2 L_3$)

(b) The π - network in hexatriene can be assumed to be linear and the bond length o $C = C$ and $C - C$ are 135 and 154 pm respectively.

i) Determine the length of the box.

ii) Calculate the energies of the first four energy level of the hexatriene using the free electron molecular model.

iii) Sketch and label the energy level diagram showing HOMO and LUMO.

iv) What is the wavelength of light required to induce a transition from th ground state to first exited state.

v) How does this compare with experimentally observed value of 240 nm?

(c) Write the Slater determinant wave function for the ground state of $'Be'$ atom.

2) (a) i) Write the Gibbs – Duhem equation and explain the terms in it.

ii) The experimental value of the partial molar volume of Na_2SO_4(aq) at 298 K i given by the expression $V_B/(cm^3 mol^{-1}) = 32.280 + 18.216\left(\frac{m}{m'}\right)^{1/2}$ wher m is the molality of Na_2SO_4(aq). Show that the molar volume of water (V_A) i solution is

$$V_A = 18.079 - 0.109296\left(\frac{m}{m'}\right)^{3/2}$$

The molar volume of pure water at 298 K is 18.079 cm^3 mol^{-1} and molar mass i 18 g mol^{-1}.

(b) i) Define the term 'fugacity'.

ii) Derive an expression for the fugacity coefficient of a gas which obeys th equation of the state $P(V_m - b) = RT$.

iii) Estimate the fugacity of NH_3 (g) at 10.0 atm and 298.15 K. where the value o 'b' is 3.707×10^{-2} l mol^{-1}

(c) (i) Show that the Gibbs energy change of mixing (ΔG_{mix}) of two perfect gases A and B in the amounts of n_A and n_B at temperature T is

$$\Delta G_{mix} = nRT(x_A \ln x_A + x_B \ln x_B)$$

where x_A and x_B are mole fraction of gases A and B respectively and n is the total number of moles.

(ii) Calculate the change in entropy when two moles of N_2 (g), three moles of H_2 (g) and two moles of NH_3(g) are mixed at constant pressure assuming no chemical reaction occurs during the mixing of the gases.

3) (a) Derive the following relations using statistical thermodynamics

i) $U = U(0) - \frac{N}{q}\frac{dq}{d\beta}$

ii) $C_v = -k\beta^2 \left(\frac{\partial U}{\partial \beta}\right)_V$

iii) The ground level of Cl is ${}^2P_{3/2}$ and first excited level ${}^2P_{1/2}$ lies at 881 cm^{-1}.

A) Express the electronic partition function in terms of ε and β

B) Show that $U - U(0) = \frac{N\varepsilon e^{-\beta\varepsilon}}{2+e^{-\beta\varepsilon}}$

C) Calculate the electronic contribution to the molar heat capacity of Cl atoms at 500 K.

(b) i) Write down the expression for the canonical partition function Q .

ii) Show that the Sackur – Tetrode equation for the entropy of a ideal monatomic gas is

$$S = nR\ln\left(\frac{e^{5/2}kT}{p\Lambda^3}\right), \text{ where } \Lambda = \frac{h}{(2\pi mkT)^{1/2}}$$

iii) Calculate the standard molar ($S_m^{\emptyset}$)entropy of gaseous argon at 298 K. [$\Lambda = 16.0$ pm and $p = p^{\emptyset} = 1$ atm]

(c) i) Derive the perfect –gas law from the canonical partition function

ii) Show that the equation state of a sample for which $Q = {q^N f}/{N!}$, where f depends on the volume is

$$P = \frac{nRT}{V} + kT\left(\frac{\partial \ln f}{\partial V}\right)_T$$

[Use the relation $P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$]

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