

**THE OPEN UNIVERSITY OF SRI LANKA**

B. Sc. Degree Programme — Level 4

Assignment III (Test) — 2010/2011

[Part I -thermo(1-6)and Part III- Mol. Spec(1-6)]

CHU 2124/CHE 4124 — Physical Chemistry I

(1½ hours)

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03 <sup>rd</sup> November. 2010	4.00 pm. — 5.30 pm.
Gas constant (R)	= 8.314 J K <sup>-1</sup> mol <sup>-1</sup>
Avogadro constant (N <sub>A</sub> )	= 6.023 × 10 <sup>23</sup> mol <sup>-1</sup>
Faraday constant (F)	= 96,500 C mol <sup>-1</sup>
Planck constant (h)	= 6.63 × 10 <sup>-34</sup> J s
Velocity of light (c)	= 3.0 × 10 <sup>8</sup> m s <sup>-1</sup>
Standard atmospheric pressure	= 10 <sup>5</sup> Pa (N m <sup>-2</sup> )
Log <sub>e</sub> (X)	= 2.303 Log <sub>10</sub> (X)

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Registration Number: \_\_\_\_\_; Signature (Staff) \_\_\_\_\_

- This is a structured paper; there are 6 (six) questions to be **answered in the space provided**.
- Please write your **Registration number, Name, and Address** clearly in the space provided; see **last page** of this question paper.
- Mobile phones are **NOT** allowed; **switch off** and leave them outside.
- The use of a non-programmable electronic calculator is permitted.

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1. (a) Define absorbance (A) and transmittance (T) (using an equation or otherwise) of a sample of solution placed in a beam of electromagnetic radiation and **hence**, derive the relationship between T and A.

(16 marks)

(b) A chlorophyll solution at  $25^{\circ}\text{C}$  is placed in a cell having a path length 1.0 cm. The measured absorbance at a wavelength of  $580\ \mu\text{m}$  is 2.00. Calculate

(i) the transmittance of the above mentioned sample of chlorophyll solution.

(ii) the percentage absorption of radiation by the sample.

(12 marks)

2. (a) (i) The unit of intensity of a beam of electromagnetic radiation is  $\text{W m}^{-2}$ . Express this in *fundamental* SI units

(ii) Write down the equation relating the intensity of a beam of monochromatic radiation to the number of photons crossing a unit area (placed perpendicular to the beam) in unit time and identify all the parameters in it.

(23 marks)

(b) The intensity of a (parallel) beam of monochromatic radiation of wavelength 10 nm is  $2.5 \times 10^{-5} \text{ W m}^{-2}$ . Calculate the number of photons crossing an area of  $1.0 \text{ cm}^2$  (placed perpendicular to the beam) in 2 seconds.

**(10 marks)**

(c) The beam of radiation described in part (b) above was used to carry out an absorption experiment involving a 0.01 M aqueous solution of a species X placed in a cell of length 10.0 mm. It was observed that the emergent radiation beam had  $3.0 \times 10^{12}$  photons crossing an area of  $1.0 \text{ m}^2$  in 1 minute. Based on your knowledge of the definition of absorbance and Beer – Lambert law, calculate

(i) the absorbance of the sample of X described above.

(ii) the molar extinction coefficient of X in the above mentioned solution.

**(16 marks)**

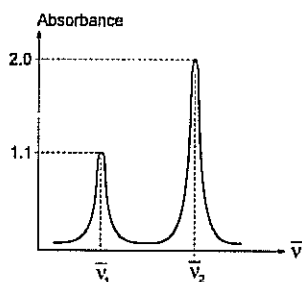
(3) (a) (i) Write down two microscopic parameters that determine the height of a peak in a spectrum.

(ii) Write down two phenomena/effects that affects the width of a peak in a spectrum.

(16 marks)

(b) A hypothetical molecule has only 3 energy levels with energy  $E_1$ ,  $E_2$  and  $E_3$ .

The absorption spectrum at low temperature has only two lines as shown in the following figure.



Here,  $\bar{\nu}_1 = 1800 \text{ cm}^{-1}$  and  $\bar{\nu}_2 = 2000 \text{ cm}^{-1}$ . Calculate  $E_2$  and  $E_3$  if  $E_1 = 1.00 \times 10^{-20} \text{ J}$ . State assumption/s, if any, you make in this calculation.

(15 marks)

- (c) A hypothetical molecule has only two energy levels, one at  $2.5 \times 10^{-23} \text{ J}$  and the other at  $3.5 \times 10^{-23} \text{ J}$ . Calculate the frequency (in Hz) and wavelength of radiation (in nm) that must be absorbed for the excitation of this molecule

(10 marks)

4. (a) Write down the Boltzmann distribution function for the population of energy levels of a molecule.

(05 marks)

- (b) A hypothetical molecule has only two energy levels,  $E_1$  and  $E_2$ , where  $E_2 - E_1 = 100 \text{ cm}^{-1}$ . The degeneracies of the lower and upper energy levels are 1 and 2 respectively. The population of the lower energy level of a sample of these molecules at  $25^\circ \text{ C}$  is 1 mol. Calculate the population of the upper energy level of the same sample.

(12 marks)

5 (a) (i) Starting with the thermodynamic equation of state

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

show that  $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$

(ii) Hence, show that the pressure coefficient of isobaric thermal capacity at constant temperature is zero for an **ideal** gas.

(20 marks)

(b) The vapour pressure in the solid and liquid states of a compound, A, is given by the following expressions:

$$\log_{10} P_{solid} / Pa = 12.00 - \frac{1350}{T}(K)$$

$$\log_{10} P_{liquid} / Pa = 9.75 - \frac{875}{T}(K)$$

Calculate the temperature and pressure at the triple point of A

(10 marks)

6. (a) Derive the **integrated form** of the Gibbs-Helmholtz equation for a temperature change from  $T_1$  to  $T_2$ , starting with the expression  $\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G}{T} \right) \right]_p = -\frac{\Delta H}{T^2}$ , [Note: Given the value of  $\Delta G$  at a certain temperature, the integrated form enables you to calculate  $\Delta G$  at another temperature] when

(i)  $\Delta H$  is independent of temperature and is a constant

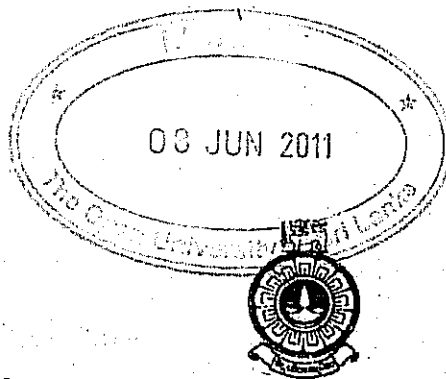
(ii)  $\Delta H = f(T) = [a - b T]$  where **a**, **b** are constants.

(23 marks)

(b) Consider the following transition  $A(s) \longrightarrow A(l)$ ;  $\Delta G = 9.0 \text{ kJ}$  at 300 K

Find  $\Delta G$  at 350 K assuming  $\Delta H = [5.5 \times 10^4 - 50.0 T] \text{ J mol}^{-1}$

(12 marks)



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1. (a)  $A = \log_{10} \frac{I_0}{I}$ ;  $T = \frac{I}{I_0}$ ;  $A = \log \frac{1}{T} = -\log_{10} T$ ;  $T = 10^{-A}$

(b) (i) the transmittance of the above mentioned sample of chlorophyll solution

$$T = 10^{-A} = 10^{-2} = \frac{1}{100}$$

(ii) the percentage absorption of radiation by the sample.

$$\% \text{absorption} = \frac{I_0 - I}{I_0} \times 100 = \left(1 - \frac{I}{I_0}\right) \times 100 = \left(1 - \frac{1}{100}\right) \times 100 = 99\%$$

2. (a) (i) *fundamental* SI units;  $\text{W m}^{-2} = \text{J s}^{-1} \text{m}^{-2} = \text{kg m s}^{-2} \text{m}^{-2} \text{s}^{-1} = \text{kg s}^{-3}$

[J = Force and distance = mass x acceleration x distance = kg x m s<sup>-2</sup> x m]

(ii)  $\eta = \frac{I}{h\nu}$

$\eta$  = number of photons crossing a unit area in unit time

I = intensity of a beam of monochromatic radiation

h = Plancks Constant;  $\nu$  = frequency of radiation

(b)  $I = 2.5 \times 10^{-5} \text{ W m}^{-2}$ ;  $\nu = \frac{C}{\lambda} = \frac{3 \times 10^8}{10 \times 10^{-9}} = 3 \times 10^{16} \text{ s}^{-1}$ ;  $1.0 \text{ cm}^2 = 1.0 \times 10^{-4} \text{ m}^2$

$\left(\eta = \frac{I}{h\nu}\right)$  The number of photons crossing an area of  $1.0 \text{ cm}^2$  in 2 seconds

$$= \frac{2.5 \times 10^{-5}}{6.63 \times 10^{-34} \times 3 \times 10^{16}} \times 1.0 \times 10^{-4} \times 2$$

$$= \frac{2.5 \times 2}{3 \times 6.63} \times 10^{-5+34-16-4} = 0.25 \times 10^9 = 2.5 \times 10^8$$



(c) (i) the absorbance of the sample of X described above.

$$I = \frac{3.0 \times 10^{12}}{60} \times h\nu = 5.0 \times 10^{10} \times 6.63 \times 10^{-34} \times 3 \times 10^{16} = 99.45 \times 10^{-8} \text{ W m}^{-2}$$

$$A = \log_{10} \frac{I_0}{I} = \log \frac{2.5 \times 10^{-5}}{99.45 \times 10^{-8}} = \log[0.025 \times 10^3] = 1.4$$

(ii) the molar extinction coefficient of X in the above mentioned solution.

$$A = 1.4; \quad C = 0.01 \text{ mol dm}^{-3}; \quad l = 10 \text{ mm} = 1 \text{ cm}$$

$$A = \epsilon Cl \quad ; \quad \epsilon = \frac{A}{Cl} = \frac{1.4}{0.01} = 1.4 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$$

(3) (a) (i) Path length, population difference, magnitude of Einstein Coefficient, B.

(ii) Doppler Broadening and life time or uncertainty broadening

(b) Here,  $\bar{\nu}_1 = 1800 \text{ cm}^{-1}$  and  $\bar{\nu}_2 = 2000 \text{ cm}^{-1}$ . Calculate  $E_2$  and  $E_3$  if

$$E_1 = 1.00 \times 10^{-20} \text{ J}.$$

Assumption/s: Only  $E_1$  is appreciably populated since the experiment is done at low temperatures.

$E_1$  to  $E_2$  and  $E_1$  to  $E_3$  are allowed transitions

$$E = h\nu = hc\bar{\nu}; \quad \bar{\nu} = \frac{E}{hc}$$

$$\bar{\nu}_1 = 1800 \text{ cm}^{-1} \text{ corresponds to } E_2 - E_1; \text{ thus } 1800 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} = E_2 - 10^{-20}$$

$$E_2 = 1800 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} + 10^{-20}$$

$$= 358.02 \times 10^{-22} + 10^{-20} = 4.58 \times 10^{-20} \text{ J}$$

$$\text{Similarly, } E_3 - 10^{-20} = 2000 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} = 3.98 \times 10^{-20}$$

$$E_3 = 4.98 \times 10^{-20} \text{ J}$$

$$(c) \quad \Delta E = 3.5 \times 10^{-23} \text{ J} - 2.5 \times 10^{-23} \text{ J} = 10^{-23} \text{ J} = h\nu = \frac{hc}{\lambda};$$

$$\nu = \frac{10^{-23}}{6.63 \times 10^{-34}} = 1.5 \times 10^{10} \text{ s}^{-1}; \quad \lambda = \frac{3 \times 10^8}{1.5 \times 10^{10}} \text{ m} = 2 \times 10^{-2} \times 10^9 \text{ nm} = 2 \times 10^7 \text{ nm}$$

$$4. (a) \quad \frac{N_i}{N_j} = \frac{g_i}{g_j} \exp\left[\frac{-(E_i - E_j)}{kT}\right]$$

$$(b) \quad N_1 = 1 \text{ mol}; \quad g_1 = 1; \quad g_2 = 2; \quad kT = (R/N_A)T = 1.38 \times 10^{-23} \times 298 \text{ J}$$

$$E_2 - E_1 = 100 \text{ cm}^{-1} = 100 \times hc = 100 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} = 19.89 \times 10^{-22} \text{ J}$$

$$\frac{N_1}{N_2} = \frac{1}{2} \exp\left[\frac{-(E_1 - E_2)}{kT}\right] = \frac{1}{2} \exp\left[\frac{19.89 \times 10^{-22}}{1.38 \times 10^{-23} \times 298}\right] = \frac{1}{2} [1.62]$$

$$N_2 = 2/1.62 = 1.23 \text{ mol}$$

5 (a) (i)

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P = \left(\frac{\partial V}{\partial T}\right)_P - \left[\frac{\partial}{\partial T}\left(T\left(\frac{\partial V}{\partial T}\right)_P\right)\right]$$

$$= \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P - T\left[\frac{\partial^2 V}{\partial T^2}\right]_P = -T\left[\frac{\partial^2 V}{\partial T^2}\right]_P$$

Since H is a thermodynamic function, the order of differentiation does not matter.

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T = \left(\frac{\partial C_P}{\partial P}\right)_T$$

$$\text{Hence, } \left(\frac{\partial C_P}{\partial P}\right)_T = -T\left[\frac{\partial^2 V}{\partial T^2}\right]_P$$

$$(ii) \quad PV = nRT \text{ for an ideal gas; } V = \frac{nRT}{P}; \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\text{Hence, } \left[\frac{\partial^2 V}{\partial T^2}\right]_P = 0 \text{ since } \left(\frac{\partial V}{\partial T}\right)_P \text{ is independent of } T$$

$$\text{Pressure coefficient of isobaric thermal capacity} = \left(\frac{\partial C_P}{\partial P}\right)_T = -T\left[\frac{\partial^2 V}{\partial T^2}\right]_P = 0 \text{ for an ideal gas}$$

$$(b) \quad \log_{10} P_{\text{solid}} / Pa = 12.00 - \frac{1350}{T} (K)$$

$$\log_{10} P_{\text{liquid}} / Pa = 9.75 - \frac{875}{T} (K)$$

$$\text{At the triple point, } P_{\text{solid}} = P_{\text{liquid}}; \quad 12.00 - \frac{1350}{T} (K) = 9.75 - \frac{875}{T} (K)$$

$$\text{Thus, we have } \frac{1350}{T} - \frac{875}{T} = 12 - 9.75 = 2.25$$

$$475 = 2.25 T; \quad T = 211 \text{ K}$$

The corresponding pressure value can be obtained by substituting  $T = 211.11$  in any one of the above equations.

$$\log_{10} P_{\text{liquid}} / \text{Pa} = 9.75 - \frac{875}{211} (K) = 9.75 - 4.15 = 5.6 \text{ Pa}$$

$$\text{Pressure at the triple point} = 10^{5.6} = 3.98 \times 10^5 \text{ Pa}$$

6. (a) (i)  $\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G}{T} \right) \right]_P = -\frac{\Delta H}{T^2}$  ( $\Delta H$  is a constant)

$$\int \left[ d \left( \frac{\Delta G}{T} \right) \right]_P = - \int \frac{\Delta H}{T^2} dT = -\Delta H \int T^{-2} dT =$$

$$\left( \frac{\Delta G_{T_2}}{T_2} \right) - \left( \frac{\Delta G_{T_1}}{T_1} \right) = -\Delta H \frac{T^{-2+1}}{-2+1} = \Delta H \left( \frac{1}{T} \right)_{T_1}^{T_2}$$

$$= \Delta H \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

(ii)  $\Delta H = f(T) = [a - bT]$  where  $a, b$  are constants.

$$\int \left[ d \left( \frac{\Delta G}{T} \right) \right]_P = - \int \frac{\Delta H}{T^2} dT = - \int \frac{(a - bT)}{T^2} dT$$

$$\left( \frac{\Delta G_{T_2}}{T_2} \right) - \left( \frac{\Delta G_{T_1}}{T_1} \right) = - \int aT^{-2} dT + \int \frac{b}{T} dT = \left( \ln T - a \frac{T^{-1}}{-2+1} \right)_{T_1}^{T_2}$$

$$= \left( \ln \frac{T_2}{T_1} + a \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right) \text{-----(1)}$$

Do you see the difference between (i) and (ii)?

(b) Consider the following transition  $A(s) \longrightarrow A(l)$ ;  $\Delta G = 9.0 \text{ kJ}$  at  $300 \text{ K}$

Find  $\Delta G$  at  $350 \text{ K}$  assuming  $\Delta H = [5.5 \times 10^4 - 50.0 T] \text{ J mol}^{-1}$

Substituting in (1) above, where  $a = 5.5 \times 10^4$  and  $b = 50.0$ ,

$$\text{We have, } \left( \frac{\Delta G_{T_2}}{350} \right) - \left( \frac{9000}{300} \right) = \left( 50 \ln \frac{350}{300} + 5.5 \times 10^4 \left( \frac{1}{350} - \frac{1}{300} \right) \right)$$

$$= 7.7 + 5.5 \times 10^4 (2.86 \times 10^{-3} - 3.33 \times 10^{-3})$$

$$\left( \frac{\Delta G_{T_2}}{350} \right) = 7.7 + 5.5 \times 10^4 \times 10^{-3} \times (-0.47) + 30 \text{ J K}^{-1} = 7.7 - 25.85 + 30$$

$$\Delta G_{T_2} = 11.85 \times 350 = 4.15 \text{ kJ mol}^{-1}$$