EASETRN UNIVERSITY, SRI LANKA

THIRD EXAMINATION IN SCIENCE – PROPER

SECOND SEMESTER 2004/2005 (OCTOBER 2006)

CH 306 SURFACE CHEMISTRY AND MOLECULAR SPECTROSCOPY

Time allowed: **ONE Hour**

Candidate must NOT start writing their answers until told to do so

You may find the following data useful

Avogadro constant (N_A): 6.023×10^{23} mol^{-1}

Electron charge (e): 1.602×10^{-19} C

Faraday constant (F): 9.648×10^{4} $Cmol^{-1}$

Gas constant (R): 8.314 $JK^{-1}mol^{-1}$

Planck's constant (h): 6.626×10^{-34} Js

Rest mass of electron (m_e): 9.1×10^{-31} kg

Velocity of light (c): 3×10^{8} ms^{-1}

The use of a non –programmable calculator is permitted

1. (a) (I) Write the expression of Langmuir adsorption isotherm and identify the terms in it.

(10 marks)

(II) Write the Clasius – Clapayron equation for adsorption

(05 marks)

(III) The slope of graph between log (P /atm) and 1/T / K^{-1} under the experiment of CO adsorption on catalytic surface is -395 K. The volume required to form a monolayer is 110.0 cm^3 and volume of adsorption to be 10.0 cm^3 at each temperature. Determine the following factors at the pressure 0.08 atm and the temperature 230 K.

(i) The isoteric heat of adsorption (10 marks)

(ii) The surface coverage (θ) (10 marks)

(iii) The equilibrium constant (k) (10 marks)

(iv) The ΔG^{θ} and ΔS^{θ} of adsorption (20 marks)

(b) The Gibbs adsorption equation is given as $\Gamma = -\frac{c}{RT}\frac{d\gamma}{dc}$

(i) Identify the terms involved in the above expression (05 marks)

(ii) In an adsorption experiment, surface tension of the adsorbent follows the relation $\frac{\gamma}{\gamma_0} = 1 - b\ln\left(1+\frac{c}{a}\right)$, where '$a$' and '$b$' are constants and 'c' is the concentration of a solution. Show that

$$\Gamma = \frac{b\gamma_0}{RT}\left(\frac{c/a}{1+c/a}\right)$$ (20 marks)

(iii) If Γ is assumed to be proportional to fraction of surface coverage θ, show that the above expression may be written as

$$\theta = K_1\frac{K_2 c}{1+K_2 c}$$

where K_1 and K_2 are constants. (10 marks)

Turn over

2. (a) (I) Write the energy expression for the rotational energy level and identify the terms in it

(10 marks)

(II) Three consecutive lines in the rotational spectrum of $H^{79}Br$ are 84.543, 101.355 and 118.167 cm^{-1}.

(i) Deduce value for rotational constant 'B'

(15 marks)

(ii) Evaluate the bond length of $H^{79}Br$ [Reduced mass: $\mu_{H^{79}Br} = 1.64 \times 10^{-27} kg$]

(25 marks)

(c) (i) What are selection rules for the pure rotational Raman spectra of diatomic molecules?

(05 marks)

(ii) Show that the Raman lines appear at the wave numbers:

$$\nu = \nu_o \pm B\left(4J'' + 6\right)$$

where ν_o is the frequency of incident radiation (or Raleigh line)

(15 marks)

(d) (i) What type of molecules show vibrational spectra?

(10 marks)

(ii) The force constant of $^{79}Br^{79}Br$ is 240 Nm^{-1}. Calculate the fundamental frequency

(20 marks)

End