Department of Chemistry

CY101

Assignment III

November 9, 2009

Questions and answers

1. What is the kinetic energy of the photoelectron ejected from an electronic energy level whose orbital energy is -13 eV? Assume that the photoionization used HeI radiation of 21.2 eV.

IP = 13 eV
KE = 21.2 – 13 = 8.2 eV

2. Assuming that the ground state vibrational frequency of the neutral molecule is 2000 cm^{-1}, and assuming that the first ionization is from a non-bonding orbital, draw the photoelectron spectrum corresponding to the emission mentioned in problem 1. Justify your answer.

Hint: Peak at 13 eV ionization potential and the first peak will be the strongest. Adiabatic ionization potential and vertical ionization potential are the same. No vibrational progression as the ionization is from a non-bonding orbital.

3. Assuming all the molecules, O_2, N_2 and Ar adsorb on the surface at the same sites and if the adsorption enthalpy is in the order, O_2>N_2>Ar, predict the Langmuir isotherms for all these cases.

Hint: Monolayer coverage will be reached at lower pressures for gases with stronger interaction.

4. If the volume of N_2 at STP required to cover the surface of one gram of the material with a monolayer thickness is 0.1 L, calculate the surface area of the material. Assume that the van der Waals diameter of N_2 molecule is 5 Angstrom.

Hint: Calculate the number of molecules required to cover the surface from the volume at STP. Each molecule occupies πr^2 area on the surface. Add for all molecules.

5. Freundlich adsorprion isotherm is x/m = y = kP^n or ln y = ln k + ln P. Suggesting a straight line relation between ln y and ln P. When will Langmuir adsorprion become this?

Rate of desorption = $k_d\theta$
Rate of adsorption = $k_a(1-\theta)P$

At equilibrium, $k_d\theta = k_a(1-\theta)P$
$\theta = KP/[1 + KP]$
$K = k_a/k_d$

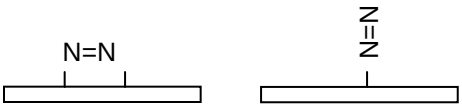
When KP<<1, or when P is small,
θ = KP or proportional to P
When KP>>1
θ = 1 or reaches a maximum value

For all pressures in between, which is the physical reality, θ is proportional to P^n, n is a value between 0 and 1. So, Langmuir adsorption isotherm will become Freundlich kind in the intermediate pressures.

6. What will be the general nature of theta vs. P graph for physical and chemical adsorption?

Hint: Only in chemisorption, one can get a monolayer coverage. Multilayers are possible in physisorption. Draw graphs in view of this.

7. Discuss all the possible adsorbate geometries of N_2 on a (111) surface.



Note: In between geometries are also possible, but difficult to evaluate.