University of Massachusetts Boston
Department of Chemistry
Chemistry Doctoral Program
Green Chemistry Track
Written Qualifying Exam

Physical Chemistry II

Questions are based on the following article:

"Carbide-Derived Carbons: Effect of Pore Size on Hydrogen Uptake and Heat of Adsorption", G. Yushin, R. Dash, J. Jagiello, J.E. Fisher, Y. Gogotsi, *Advanced Functional Materials* 169 (2006) 2288-2293"

1. Explain the structural difference of carbon materials (diamond, graphite and disordered carbon). Compare the conductivity of these three types of carbon and explain these differences in conductivity in terms of the structure of the material.

2. At the end of paragraph one, it says "…, and activated carbons with SSA (specific surface area) up to ca. 3000 $m^2 g^{-1}$ have been produced." Is this possible? What is the theoretical maximum SSA for carbon materials?

3. Molecules and atoms can attach to surfaces in two ways – physisorption and chemisorption.

    a. Explain the difference by discussing the types of interaction between absorbent and absorbate.
    b. The major conclusion of the paper was that hydrogen sorption in small pores is more efficient than in larger pores. Explain why small pores are more favored for hydrogen sorption. How small should the pore size be in order to have this "size-effect" and why?
    c. On page 2289, second paragraph, it says "Gas adsorption takes place when the interaction energy between an adsorbate molecule and adsorbent is equal to the ***work*** needed to bring a free molecule to the adsorbed state at a given temperature." Explain what the "work" means and why "at a given temperature" is emphasized?
    d. At 77K, can molecular hydrogen form multilayer adsorption on the carbon surface? How about nitrogen? Why? Under what conditions can molecular hydrogen form multi-layers.

4. Suppose the following assumptions are true: a) adsorption cannot proceed beyond monolayer coverage; b) all sites on the surface are equivalent; c) each adsorption is independent. The dynamic equilibrium of this system is $H_2(gas) + C(surface) \underset{k_b}{\overset{k_a}{\Leftrightarrow}} H_2 - C(surface)$, where *k* is the rate constant. Derive Langmuir isotherm $\theta = Kp / 1 + Kp$ where θ is the fractional coverage, *p* is hydrogen partial pressure and $K = k_a / k_b$.

5. The heat of adsorption was calculated using Clausius-Clapeyron equation (eqn. 3 in the paper). Derive the Clausius-Clapeyron equation from first principles. (Hint: start with $dG = -SdT + Vdp$).

6. (Green Chemistry) There are two ways of utilizing hydrogen as fuel in automobiles – as the replacement of gasoline in internal combustion engine or in a fuel cell. Can you explain why a fuel cell is more efficient using the Second Law of Thermodynamics?