Physical Chemistry II - Homework 11

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1. 1. The adsorption of ammonia on charcoal is studied at 30 and $80°$C. It is found that the pressure required to adsorb a certain amount of NH3 per gram of charcoal is 14.1 kPa at $30°C$ and 74.6 kPa at $80°C$. Calculate the enthalpy of adsorption.

$$T_1 = 303.15K,\ P_1 = 14100Pa,\ T_2 = 353.15K,\ P_2 = 74600Pa$$

Isosteric enthalpy of adsorption: $\frac{\partial ln(\frac{CP^\theta}{P}}{\partial(1/T)} = \frac{-\Delta_{ad}H^\theta}{R}$

Therefore: $\Delta_{ad}H^\theta = -R(\frac{1}{T_1} - \frac{1}{T_2})^{-1}\ln(\frac{P_2}{P_1}) = \boxed{-29658Jmol^{-1}}$

2.Hydrogen is dissociatively adsorbed on a metal, and the pressure required to obtain half of the saturation coverage is 10 Pa.
(a) What pressure will be required to reach $\theta = 0.75$?
(b) What pressure would have been required if the adsorption were not dissociative?

Langmuir isotherm for adsorption with dissociation:

$$\theta = \frac{(\alpha P)^{1/2}}{1 + (\alpha P)^{1/2}}$$

$$0.5 = \frac{(\alpha \times 10Pa)^{1/2}}{1 + (\alpha \times 10Pa)^{1/2}} \rightarrow \alpha = 0.1$$

To get $\theta = 0.75$:

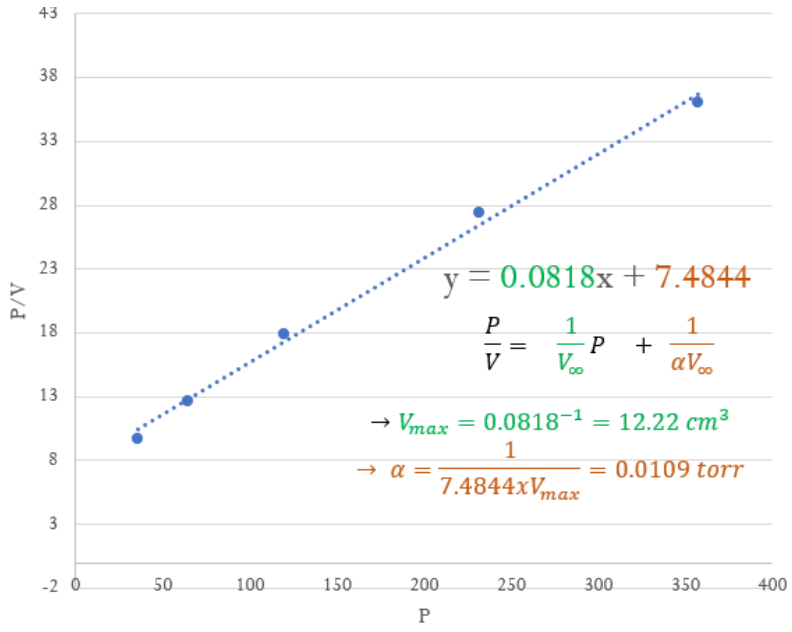
$$0.75 = \frac{(0.1 \times P)^{1/2}}{1 + (0.1 \times P)^{1/2}} \rightarrow \boxed{P = 90Pa}$$

For non-dissociative: $\theta = \frac{\alpha P}{1+\alpha P}$

$$0.75 = \frac{0.1 \times P}{1 + 0.1 \times P} \rightarrow P = \boxed{30Pa}$$

3. Use a graph of P/V vs. P to determine the Langmuir parameters for the adsorption of nitrous oxide on barium fluoride using the data below (taken at $40°$C).

P (torr)	V (cm^3	p/V
35.9	3.7	9.7027
64.5	5.09	12.672
120	6.7	17.91
232	8.48	27.358
357	9.92	35.988



4. The volume of nitrogen gas (measured at 1.013 bar and 273.15K) required to form a complete monolayer on a sample silica gel is $129cm^3g^{-1}$ of gel. Calculate the surface area per gram of the gel if each nitrogen molecule occupies $16.2 \times 10^{-20}m^2$.

$$P = 1.013atm = 101300Pa,\ T = 273.15K,\ V = 129 \times 10^{-6}m^3$$

Number of Nitrogen molecules:

$$N = \frac{PV}{RT} \times N_A = 3.465 \times 10^{21} molecules$$

Surface area per gram of the gel: $3.465 \times 10^{21} \times 16.2 \times 10^{-20} = \boxed{561m^2/g}$

5. Hydrogen iodide is strongly adsorbed on gold surfaces, but only weakly adsorbed on platinum. For all but the very lowest pressures, the rate of decomposition of HI on gold is found to be independent of the pressure of the HI. For the same process on Pt, the rate is found to be proportional to the pressure of HI. Explain these observations using Langmuir isotherms.

Rate of decomposition: $rate = k\theta$ and $\theta = \frac{\alpha P}{1+\alpha P}$ **(1)**
For gold, at low pressure, $\alpha P \lll 1$, the $1 + \theta P \approx 1$, therefore $rate \approx k\alpha P$ the decomposition of HI on gold surface is independent of the pressure of the HI because the rate of decomposition is in zero-order $(R \approx k)$
For Pt, the rate of decomposition is in first-order. Therefore, the decomposition is proportional to the pressure due to equation **(1)**