University of Washington
Department of Chemistry
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Lecture 25 8/18/10

A. Langmuir Equation and its Alternatives

- As covered in the last lecture the Langmuir equation quantifies f, the fraction of the surface occupied by adsorbed molecules from the gas phase…

$$f=\frac{k_aP}{k_d+k_aP}=\frac{\left({k_a}/{k_d}\right)P}{1+\left({k_a}/{k_d}\right)P}=\frac{bP}{1+bP}$$

where $b=\frac{k_a}{k_d}$, ka,d, are the kinetic constants for adsorption (a) and desorption (d), and P is the pressure exerted by the gas on the surface S.

- There are alternative forms for the Langmuir equation. Assume N enumerates the surface binding sites that must be occupied to achieve coverage by a single monolayer of molecules. If we define the volume of adsorbed gas at pressure P and temperature T as V, and the volume of adsorbed gas required to achieve monolayer coverage at the same temperature as V_m. the fractional saturation in terms of these two volumes is:

$$f=\frac{V}{V_m}$$

The Langmuir equation is now

- $$V=\frac{bV_mP}{1+bP}$$
- A plot of f or V versus P at constant T will result in a hyperbolic binding curve, as shown for ligand binding inLectures 21 and 22. At very low pressures where bP<<1, the isotherm is linear:

$$V\approx bV_mP$$

- At very high pressures where bP>>1 the isotherm displays saturation behavior and V approaches a limiting values of V_m.
- As with ligand binding, a simple rearrangement of the Langmuir equation results in a linearized form:

$$\frac{V}{P}=bV_m-bV$$

- So if adsorption of a gas onto a surface is accurately described by the Langmuir model, a plot of V/P as a function of P yields a straight line with a slope –b and intercept bV_m. The liearized Langmuir equation is analogous to the Scatchard Equation in Lecture 21 , where V corresponds to $\overline{\nu}$, V_m corresponds to N, b corresponds to the binding constant K, and P corresponds to c_L.

- A modification of the Langmuir equation accounts for dissociation of surface-adsorbed molecules. Suppose a homonuclear diatomic molecule dissociates on the surface according to:

$$A_2 + 2S \rightleftarrows 2SA$$

- At equilibrium the rates for adsorption and desorption are equal

$$k_a P N^2 \left(1-f\right)^2 = -k_d N^2 f^2$$

Rearrange this to

$$\frac{k_a}{k_d} P\left(1-f\right)^2 = -f^2$$

and the fractional saturation is now

- $$f = \frac{b^{1/2} P^{1/2}}{1 + b^{1/2} P^{1/2}}$$

where $b = k_a/k_d$. For polyatomic molecules that dissociate into n fragments , the pressure is raised to the reciprocal of the number of fragments formed, i.e. $P^{1/n}$.

B. Heats of Adsorption

- A thermodynamic description of adsorption assumes the unadsorbed gas is in equilibrium with the adsorbed gas. If it is further assumed that the adsorbent, i.e. the surface, is thermodynamically inert in the sense that it is energetically unaffected by the adsorption of the gas, it follows that the adsorbed gas plus adsorbent can be treated as a single component system and the description of thermodynamic quantities is very straightforward.
- If the adsorbent is energetically inert, the criterion for equilibrium involves only the chemical potentials of the free gas and the surface-adsorbed gas:

$$\mu_{gas}\left(P,T\right) = \mu_{ads}\left(P,T\right)$$

- Suppose the state variables P and T are changed P→P+dP and T→T+dT. If the system is to remain in equilibrium we require:

$$d\mu_{gas}(P,T) = d\mu_{ads}(P,T)$$

$$-\bar{S}_{gas}dT + \bar{V}_{gas}dP = -\bar{S}_{ads}dT + \bar{V}_{ads}dP$$

which can be rearranged to obtain

$$\left(\frac{dP}{dT}\right)_{n_{ads}} = \frac{\bar{S}_{gas} - \bar{S}_{ads}}{\bar{V}_{gas} - \bar{V}_{ads}} = \frac{\bar{H}_{gas} - \bar{H}_{ads}}{T\left(\bar{V}_{gas} - \bar{V}_{ads}\right)} = -\frac{q_{st}}{T\Delta\bar{V}}$$

where q_{st} is the isosteric heat of adsorption, defined as the difference between the enthalpy of the free gas and the enthalpy of the adsorbed gas.

- Note the resemblance between this equation and the Clapeyron Equation in Chapter 7. The term isosteric refers to the fact that the surface coverage f is constant. If the free gas behaves ideally and the volume of the free gas greatly exceeds the volume of the adsorbed gas, the isosteric heat of adsorption can be related to the change in gas pressure with temperature:

$$\left(\frac{\partial \ln P}{\partial T}\right)_{n_{ads}} = -\frac{q_{st}}{RT^2}$$

- The isosteric heat of adsorption is also called the differential heat of adsorption q_d. Note that surface adsorption is exothermic so $\Delta\bar{H}<0$, but q_d is by convention positive. The differential heat of adsorption is related to the integral heat of adsorption Q by

$$Q = \int_0^{n_s} q_d \, dn_s = n_s\Delta\bar{H}$$

C.Derivation of the Differential Heat of Adsorption from Isotherm Equations

- Consider the equilibrium $A(g) \rightleftarrows A(adsorbed)$. The equilibrium constant $K_A = \frac{1}{P_0}$, where P_0 is the equilibrium pressure of the gas.
- Then the simple Langmuir isotherm equation is $\frac{v}{N} = \theta = \frac{K_A P}{1+K_A P} = \frac{P}{P_0 - P}, or \ldots P = P_0\left(\frac{\theta}{1-\theta}\right).$
- From the equations above the general form for an isotherm is $P = f(\theta)$. At equilibrium the chemical potential of the free gas is equal to the chemical potential of the adsorbed gas i.e. $\mu_{free} = \mu_{adsorbed}$
- From the relationship $\mu_{free} = \mu_{free}^0 + RT\ln P$, the equilibrium condition $\mu_{free} = \mu_{adsorbed}$, and the general isotherm equation $P = f(\theta)$, we obtain…

$$\mu_{adsorbed} = \mu_{free}^0 + RT\ln\left(f(\theta)\right)$$

- We can now obtain the molar enthalpy of adsorption using the Gibbs-Helmholtz equation… $\frac{\partial\left(\mu_{adsorbed}/T\right)}{\partial\left(1/T\right)} = \bar{H}_{adsorbed} = \bar{H}^{0}_{free\,gas} + R\left\{\frac{\partial \ln\left(f\left(\theta\right)\right)}{\partial\left(1/T\right)}\right\}$
- The differential heat of adsorption is then $\Delta\bar{H}_{diff} = \bar{H}^{0}_{free\,gas} - \bar{H}_{adsorbed} = -R\left\{\frac{\partial \ln\left(f\left(\theta\right)\right)}{\partial\left(1/T\right)}\right\}$