Physisorption

A. Theory — Chemisorption: The Langmuir Isotherm

Theory for *physisorption* (the BET isotherm — for weak, or physical adsorption) is beyond the scope of this course. However, many elements of the theory arise also in the simpler theory of *chemisorption* (for strong binding to surfaces). Thus we will examine chemisorption.

1. *Assumptions*: (a) one available adsorption site for each adsorbed molecule, and one adsorbed layer; (b) rate of adsorption = rate of desorption.

2. *Definitions*: (a) N = # sites; θ = fractional occupancy. (b) k_a = adsorption rate constant; k_d = desorption rate constant; P = gas pressure.

3. *Rates*: adsorption = $k_a\, P\, (1 - \theta)\, N$; desorp. = $k_d\, \theta\, N$

4. *Results*: $\theta = k_a\, P/(k_d + k_a\, P) = bP/(1 + bP)$; $b \equiv k_a/k_d$.

5. *Application*: low P — $\theta \propto P$; high P — $\theta \rightarrow 1$; $\theta \equiv v/v_{\text{monolayer}} \rightarrow v = v_{\text{m}}\, bP/(1 + bP)$.

B. Physisorption — BET Model

1. *Differences*: (a) Binding interactions much weaker;
   (b) Multiple adsorption layers permitted;
   (c) 1st adsorption layer different from others.

2. *Results*: $$v = \frac{v_m\, c\, x}{(1-x)\,[1+(c-1)\,x]}$$

   $x = P/P_0$ (P_0 = vapor P); c = constant.

C. Linearization

1. Not really necessary, with nonlinear LS available; but still often done.

2. *Langmuir*: $1/v = 1/v_m + 1/(v_m\, b\, P)$

3. *BET*: $$\frac{x}{v\,(1-x)} = \frac{1}{v_m\, c} + \frac{(c-1)\,x}{v_m\, c}$$

D. Measurements

1. *V Calibration*: Need *V*s of vacuum system parts, and "cold volume" of cell; start with calibration cell of known *V* and use $P_1V_1 = P_2V_2$ (Boyle's Law).

2. *T of bath*: Measure P_0 of liq N_2 → get *T* of bath.

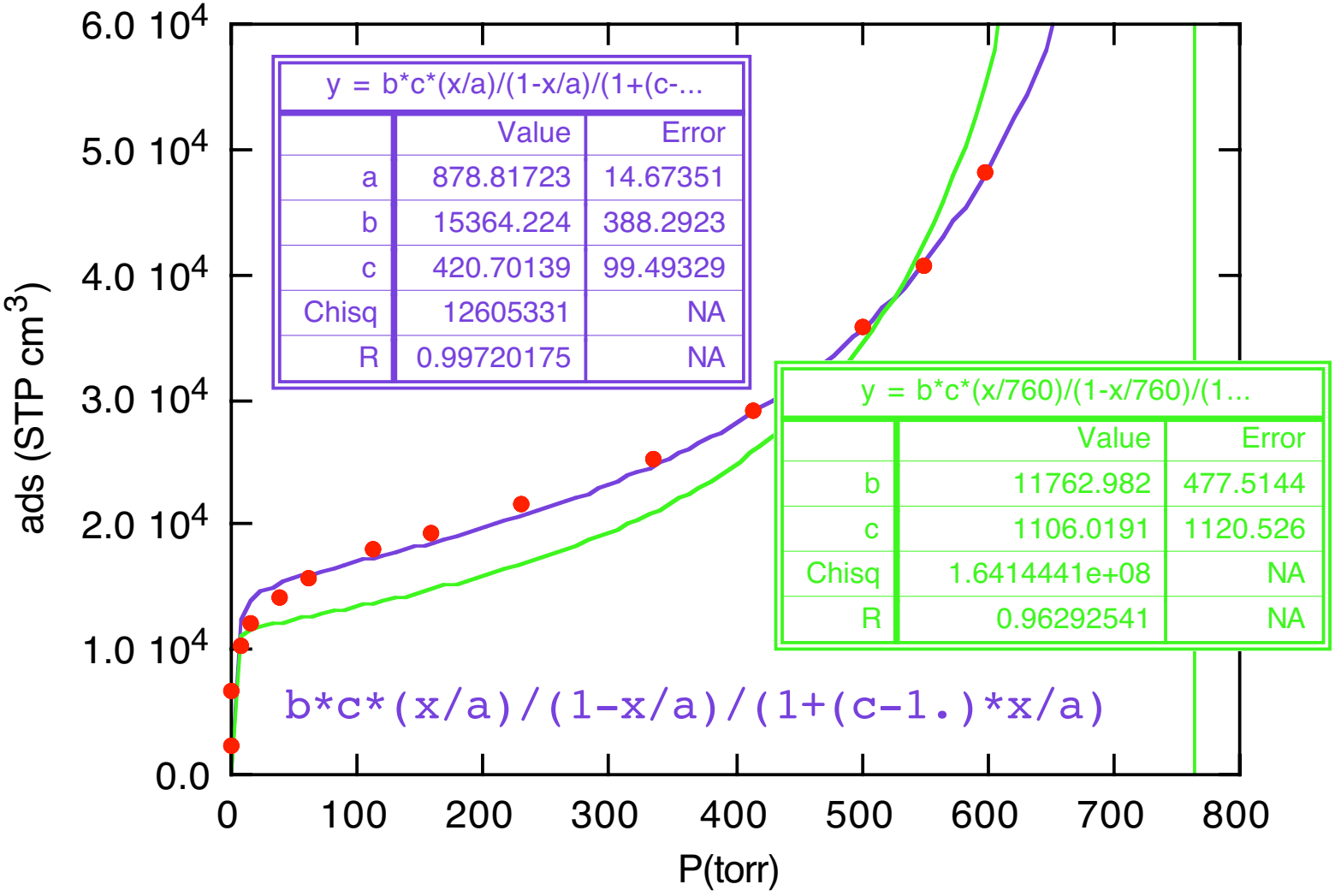
3. *v*: Add gas to vacuum manifold & measure *P*; open valve to cell, equilibrate, remeasure *P*;. repeat for each data point.

4. *units*: Traditionally *v* is given in STP cm^3.

E. Analysis

1. Analyze using KG to fit both versions of equation.
2. Can treat P_0 as an adjustable parameter, or as known.

F. Illustrations



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