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 — $\theta \to 1$; $\theta \equiv v/v_{\text{monolayer}} \to v = v_{\text{m}}\, bP/(1 + bP)$.

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*:

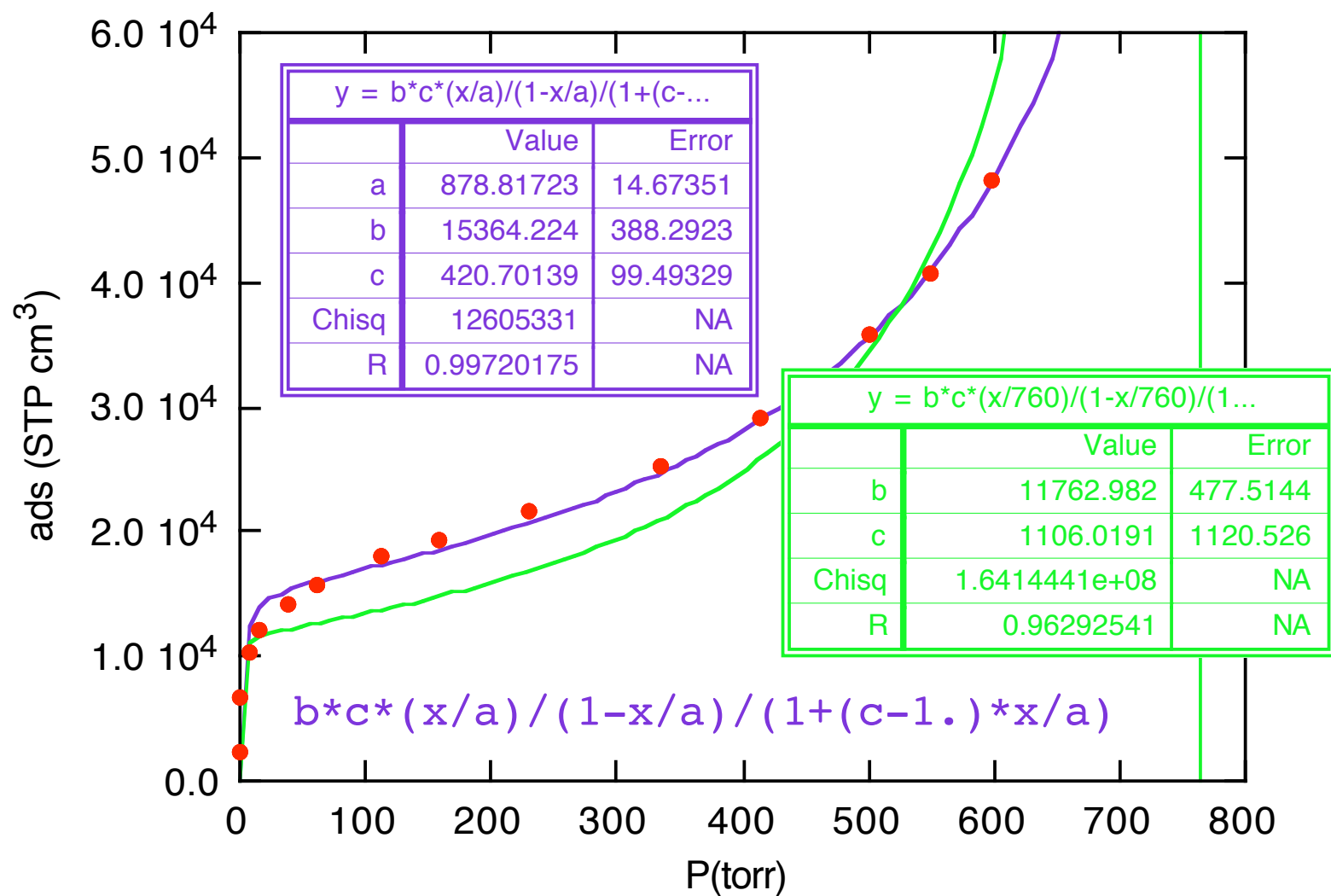$$\frac{x}{v\,(1-x)} = \frac{1}{v_m\, c} + \frac{(c-1)x}{v_m\, c}$$

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 $P_1 V_1 = P_2 V_2$ (Boyle's Law).

2. *T of bath*: Measure P_0 of liq $N_2 \rightarrow$ 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.

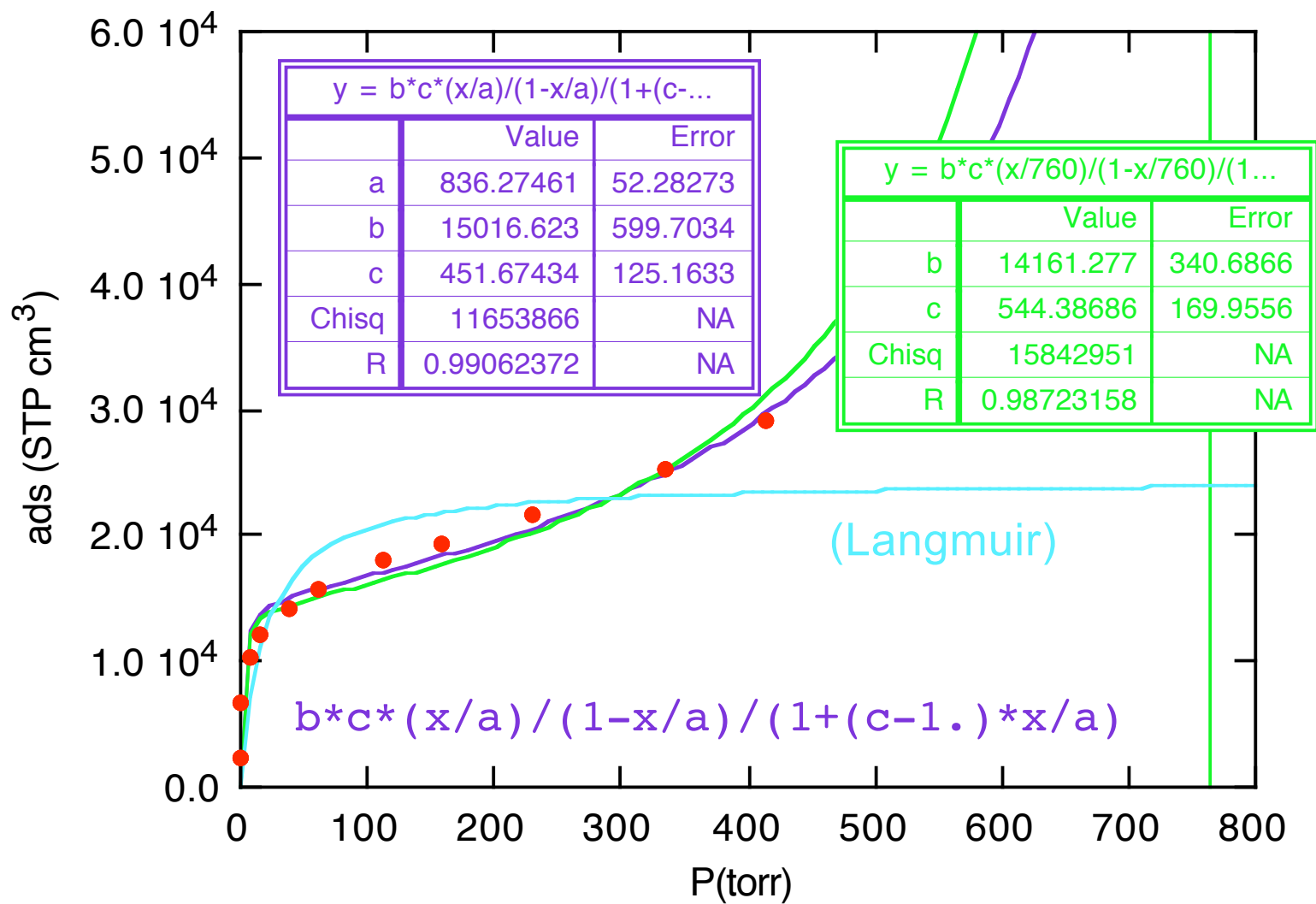4. *units*: Traditionally *v* is given in STP cm^3.

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

(Delete some high-P points)

ads (STP cm^3) vs **P(torr)**

$y = b*c*(x/a)/(1-x/a)/(1+(c-...$

	Value	Error
a	836.27461	52.28273
b	15016.623	599.7034
c	451.67434	125.1633
Chisq	11653866	NA
R	0.99062372	NA

$y = b*c*(x/760)/(1-x/760)/(1...$

	Value	Error
b	14161.277	340.6866
c	544.38686	169.9556
Chisq	15842951	NA
R	0.98723158	NA

(Langmuir)

b*c*(x/a)/(1–x/a)/(1+(c–1.)*x/a)

L-V Equilibrium in a Binary System

A. **Ideal Solution Theory (Raoult's Law)**
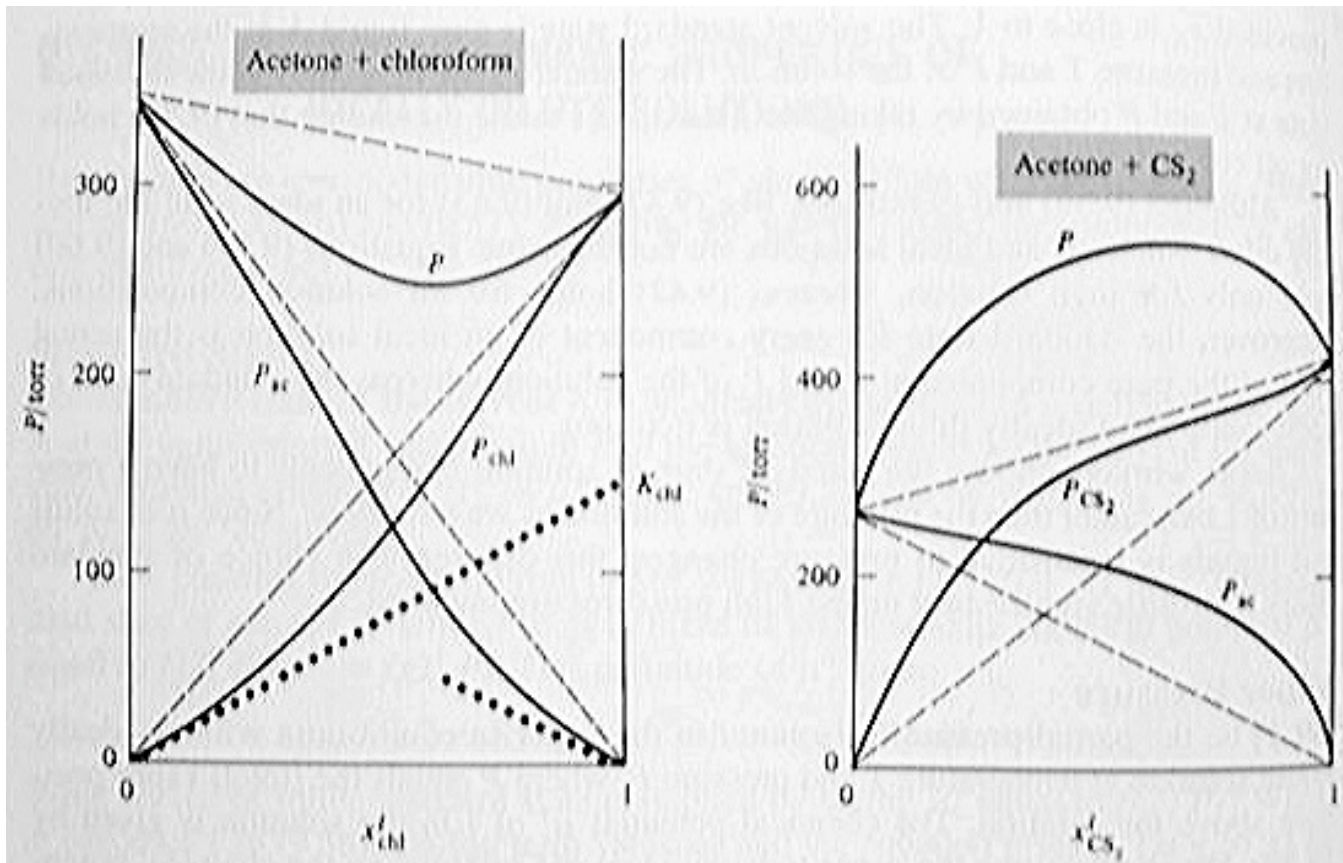
  1. $P_{i,\text{id}} = x_{i,\ell} \, P_i^*(T)$ x = mole fraction; ℓ = liq.; * = pure;

                                       i = A or B for *binary* system.

  2.   Typically used for mixtures of volatile components.

  3.   Far less reliable than ideal gas theory for gases.

  4.   BUT, R's Law *does* hold for component A when $x_{\text{A},\ell} \rightarrow 1$.

  5.   Then *Henry's Law* holds for other component:

$$P_\text{B} = k_{\text{H,B}} \, x_{\text{B},\ell} \quad (\text{as} \ \ x_{\text{A},\ell} \rightarrow 1)$$

B. **Real Solution**

  1. $P_i = a_i \, P_i^*(T)$, with $a_i = \gamma_i \, x_{i,\ell}$ [activity & act. coef.]

  2. $\gamma_i \rightarrow 1$ as $x_{i,\ell} \rightarrow 1$, so $a_i \rightarrow x_{i,\ell}$.

  3.   This is called *Convention I* in Levine.

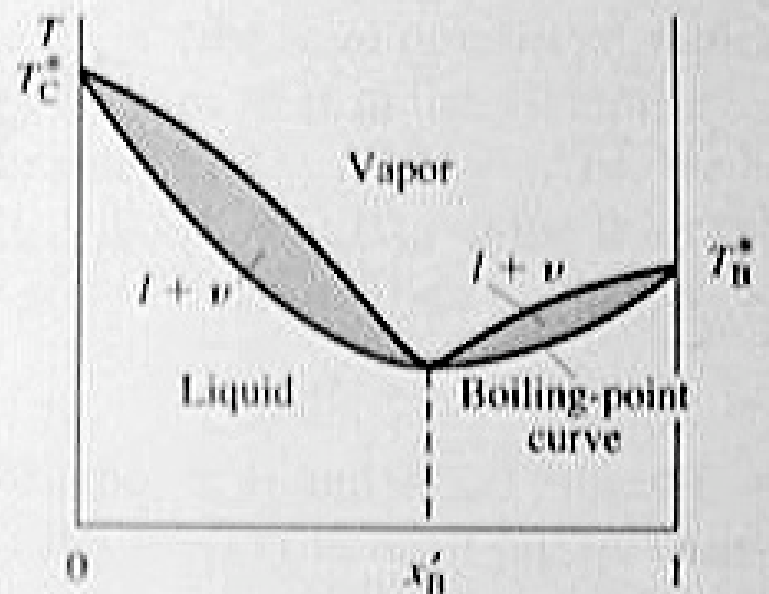 4.   Vapor: $P_i = x_{i,v} \, P$ (Dalton's Law of Partial Ps)

C. Deviations from Ideality

1. Accommodated by activity coefficient "fudge factor."
2. Distinguish *positive* and *negative deviations*.
3. Extreme → *azeotropes*, compound formation, *immiscibility*.

P

P_{max}

Liquid

P_C^*

$l + v$

$l + v$

Vapor

P_B^*

0 $x_{B,1}$ 1

(a)

T

T_C^*

Vapor

$l + v$

$l + v$

T_B^*

Liquid   Boiling-point curve

0 x_B' 1
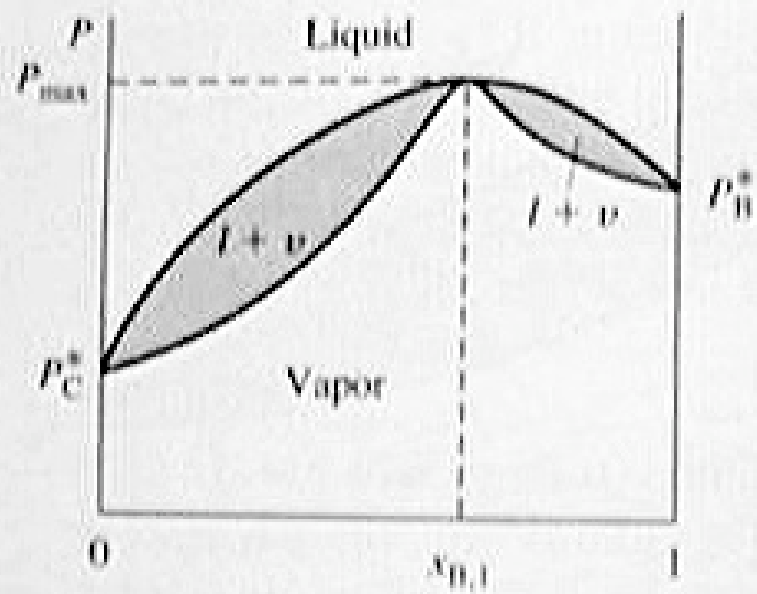
(b)

D. Experiment

1. Use refractive index to determine mixture compositions.

2. Prepare calibration curve by measuring RI for several (8-10) prepared samples. (Start with 6 and expand.)

3. Starting with mixture on vacuum line, establish ℓ-v equilibrium, measuring P and capturing ~2 L of vapor in storage bulb.

4. Transfer vapor to sample cell by freezing out with liq N_2.

5. Measure RI for *both* samples -- but allow to warm to room T first. (The composition of the ℓ sample changes with vaporization.)

6. Try to get results for 6 mixtures, plus both pure components (P^* only); but 4 mixtures will suffice if pressed for time.

7. In the estimation of γ_A and γ_B, data noise tends to be amplified; follow the fitting procedures and use your smooth fitted curves for this determination.

Today's Practice Quiz

1. If 1.0 gal of gasoline powers a car for 35 miles, then driving under the same conditions, 5.0 gal should power the same car for
   a. 7 miles   b. 35 miles   (c.) 175 miles   d. 350 miles   e. none of these

2. Suppose that 1.0 gal of gasoline powers a car for 30 miles. A second fuel has a combustion energy content 50% greater than that of gasoline. How much of this second fuel would be needed to power the car for 180 miles, driving under the same conditions:
   a. 1.0 gal   (b.) 4.0 gal   c. 6.0 gal   d. 9.0 gal   e. none of these

3. Still comparing these two fuels, if 1.00 g of gasoline raises the temperature of 1.00 kg of water by 2.00 K, by how much would 0.80 g of the second fuel raise the temperature of 2.00 kg of water?
   a. 0.50 K   (b.) 1.20 K   c. 2.40 K   d. 3.00 K   e. none of these

4. Calculate Δn_g for the combustion of 1.00 mol of n-propanol (C_3H_7OH) at 25°C to produce $CO_2(g)$ and $H_2O(\ell)$.
   a. 0.0 mol   b. 1.0 mol   c. 1.5 mol   d. 2.5 mol   (e.) none of these

5. The heat exchanged with the surroundings in a process carried out at constant pressure is
   a. w (b.) ΔH c. ΔE d. $C_P \Delta T$ e. none of these