Chapter 5

Exercise 1:

part a)

The full BET equation is as follows:

\[ \frac{P}{V_{ad}(P_e - P)} = \frac{1}{cV_m} + \left( \frac{c-1}{cV_m} \right) \frac{P}{P_e} \]  \hspace{1cm} (1)

After dividing both the numerator and denominator of the left hand side of equation (1) by \( P_e \),

\[ \frac{P/P_e}{V_{ad}(1 - P/P_e)} = \frac{1}{cV_m} + \left( \frac{c-1}{cV_m} \right) \frac{P}{P_e} \]  \hspace{1cm} (2)

By plotting \( \frac{P/P_e}{V_{ad}(1 - P/P_e)} \) vs \( P/P_e \) for sample 1, the following can be concluded (only the following data points were used in these calculations: 0.05 \( \leq \frac{P}{P_e} \leq 0.3 \)):

The regressed slope of the resulting line = \( \frac{c-1}{cV_m} = 0.035 \text{ g cm}^{-3} \)

The regressed y-intercept of the resulting line = \( \frac{1}{cV_m} = 9.15 \times 10^{-1} \text{ g cm}^{-3} \)

\( R^2 \) value of the fitted line = 0.99

Therefore \( c = 386.4 \) and \( V_m = 28.3 \text{ cm}^3 \text{ g}^{-1} \)

The one-point BET equation is as follows:

\[ \frac{P}{V_{ad}(P_e - P)} = \left( \frac{1}{V_m} \right) \frac{P}{P_e} \]  \hspace{1cm} (3)

where we assume that \( c \gg 1 \).

Choose one point to calculate \( V_m \). Choose \( P/P_e = 0.3 \).
At $P/P_\text{o} = 0.3$, $V_{\text{ad}} = 39.1 \text{ cm}^3 \text{ g}^{-1}$.

Therefore $V_{\text{m}} = V(1-P/P_\text{o}) = (39.1 \text{ cm}^3 \text{ g}^{-1})(0.7) = 27.4 \text{ cm}^3 \text{ g}^{-1}$.

Note that assuming $c >> 1$ was a good assumption, as seen from the calculations done using the full BET equation.

Now we need to calculate the surface area, $S_x$, for each solution.

The surface area is related to the number of molecules adsorbed in a monolayer, $N$, in the following way.

$$S_x = \frac{N}{\alpha} \quad (4)$$

where $\alpha$ is the cross-sectional area of the adsorbing gas (dinitrogen in this case).

$N = \frac{\text{# molecules adsorbed per monolayer}}{V} = \frac{V_{\text{m}}}{V}$ where $N_e$ is Avogadro’s number and $V$ is the volume of gas at STP (1 atm and 273 K) per mol, 22400 cm$^3$ mol$^{-1}$.

For dinitrogen, $\alpha = 0.162 \text{ nm}^2$.

For the full BET equation

$$S_x = \frac{28.3 \text{ cm}^3 \text{ g}^{-1}(6.02 \times 10^{23} \text{ molecules mol}^{-1})(0.162 \text{ nm}^2)}{22400 \text{ cm}^3 \text{ mol}^{-1}} = 123 \text{ m}^2 \text{ g}^{-1}.$$ 

Similarly for the one-point BET equation,

$$S_x = 119 \text{ m}^2 \text{ g}^{-1}.$$ 

These values are essentially the same (3% difference).

part b)

Repeat the same analysis as in part a) except on Sample 2.

Full BET equation:

c = 22.4

$V_{\text{m}} = 0.689 \text{ cm}^3 \text{ g}^{-1}$.
Note that this sample has a smaller BET constant than sample 1 (c is not much greater than 1 here).

For the one-point equation:
\[ V_n = V(1-P/P_a) = (0.89 \text{ cm}^3 \text{ g}^{-1})(1-0.3) = 0.623 \text{ cm}^3 \text{ g}^{-1}. \]

The surface areas for the full BET equation and the one-point equation are 3.00 m² g⁻¹ and 2.7 m² g⁻¹, respectively.

Due to the small BET constant, the two methods do not give the same answer (10% difference).

**Exercise 2:**

Note that:

# moles H chemisorbed irreversibly (strong sites) = 
\[ \text{# moles H chemisorbed in Run 1} - \text{# moles H chemisorbed in Run 2} \]

First, plot \( H/P_i \) vs \( P \) for each run; find the y-intercepts \( \left( \frac{H}{P_i} \right)_{P=0} \).

Dispersion = \( H/P_i \) irreversibly adsorbed = \( \frac{H}{P_i_{P=0,\text{Run 1}}} - \frac{H}{P_i_{P=0,\text{Run 2}}} = 0.93 - 0.34 = 0.59 \)

The average particle size is estimated using the following relationship, assuming that the particles are spherical:

Particle diameter (nm) = \( 1/\text{dispersion} \).

In this case the particle diameter is \( 1.69 \text{ nm} \).

**Exercise 3:**

The reaction investigated by A. Peloso is

\[ \text{CH}_3\text{CH}_2\text{OH (Et)} \quad \text{CH}_3\text{CHO} + \text{H}_2 \quad \text{(Ad)} \quad \text{(DH)} \quad (1) \]