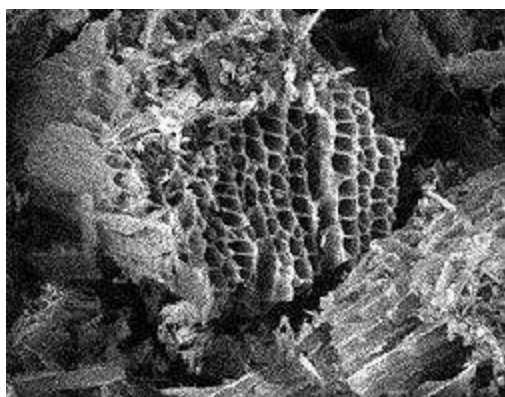


The Langmuir Adsorption Isotherm

In this laboratory exercise, we will generate a Langmuir Isotherm for the adsorption of Acetic Acid on the surface of *Norit A* Activated Charcoal. The surface area of the Activated Charcoal available for adsorption of Acetic Acid will be determined from the Isotherm data and other assumptions.

Activated Charcoal is particularly useful in purification processes involving impurity adsorption because of its high porosity, giving it an very high surface to mass ratio. It has been noted:



Adsorption by a solid is not a very important process unless the solid has a very large surface area compared to its mass. Consequently, charcoal made from bone, blood, or coconut shells is especially effective because it has a highly porous structure. Charcoal is activated by being heated to quite high temperatures in a vacuum or in a stream of dry air. This treatment probably desorbs the hydrocarbons that are adsorbed when the charcoal is first produced.

Physical Chemistry: Methods, Techniques, Experiments
by Rodney J. Sime

(Electron Micrograph of Activated Charcoal)

Norit, a producer of purification products, describes its production of activated charcoal:

Almost a century ago Norit began the production of activated carbon on an industrial scale. In the early days, the activated carbon was mainly used for the decolourisation of sugar syrup in the refining process for producing white sugar. Nowadays Norit is a global leader in purification solutions based on activated carbon technology. In steam activation as well as chemical activation we use a wide spectrum of raw materials, such as peat, wood, lignite, coal, coconut shells and even olive pits, to produce a vast array of activated carbon types.

...

In both powdered and granular form, Norit offers over 150 different varieties of activated carbon to ensure the precise fit for any application. This precise fit always translates into best performance, whether it's meeting critical product specifications, using the least amount of carbon to accomplish your task, or getting longer treatment cycles and fewer change outs. While all activated carbon may look the same to the naked eye, pore size and



structure makes a huge difference in how well impurities are adsorbed. That's why Norit has taken the time to test thousands of combinations of raw materials, activation methods, activity levels, and other factors.

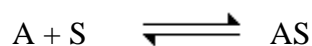
<http://www.norit.com/norit%20products/activated%20carbon/>

Surface adsorption to a solid falls into two broad categories; physisorption and chemisorption. Physisorption is a non-specific loose binding of the adsorbate to the solid via van der Waals type interactions. Multilayered adsorption is possible and it is easily disrupted by increasing temperatures. Chemisorption involves a more specific binding of the adsorbate to the solid. It is a process that is more akin to a chemical reaction and hence, only monolayer adsorption is possible. “The difference between physical and chemisorption is typified by the behavior of nitrogen on iron. At the temperature of liquid nitrogen, -190°C , nitrogen is adsorbed physically on iron as nitrogen molecules, N_2 . The amount of N_2 adsorbed decreases rapidly as the temperature rises. At room temperature iron does not adsorb nitrogen at all. At high temperatures, $\sim 500^{\circ}\text{C}$, nitrogen is chemisorbed on the iron surface as nitrogen atoms.” (Castellan 1983) The Langmuir Isotherm best describes chemisorption processes.

Irving Langmuir was awarded the Nobel Prize in 1932 for his investigations concerning surface chemistry. Langmuir's isotherm describing the Adsorption of Adsorbate (A) onto the surface of the Adsorbant (S) requires three assumptions:

- The surface of the adsorbant is in contact with a solution containing an adsorbate which is strongly attracted to the surface.
- The surface has a specific number of sites where the solute molecules can be adsorbed.
- The adsorption involves the attachment of only one layer of molecules to the surface, i. e. monolayer adsorption.

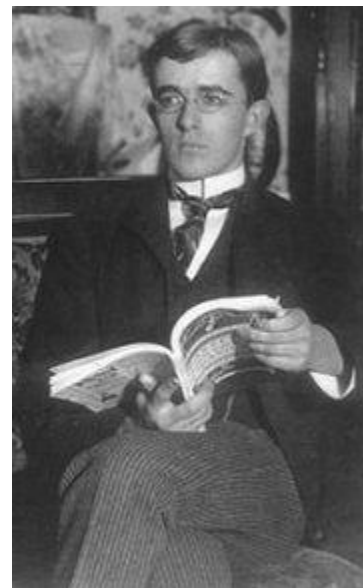
The chemical reaction for monolayer adsorption can be represented as follows:



where AS represents a solute molecule bound to a surface site on S. The equilibrium constant K_{ads} for this reaction is given by:

$$K_{\text{ads}} = \frac{[\text{AS}]}{[\text{A}][\text{S}]} \quad (\text{Eq. 1})$$

[A] denotes the concentration of A, while the other two terms [S] and [AS] are two-dimensional analogs of concentration and are expressed in units such as mol/cm^2 . The principle of chemical equilibrium holds with these terms. The complete form of the Langmuir isotherm considers (Eq. 1) in terms of surface coverage θ which is defined as the fraction of the adsorption sites to which



a solute molecule has become attached. An expression for the fraction of the surface with unattached sites is therefore $(1 - \theta)$. Given these definitions, we can rewrite the term $[AS]/[S]$ as

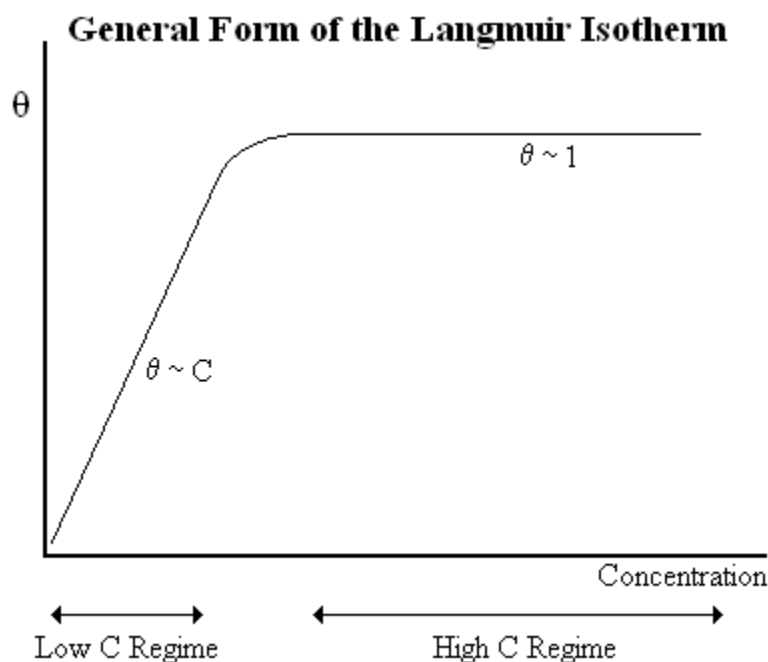
$$\frac{[AS]}{[S]} = \frac{\theta}{1 - \theta} \quad (\text{Eq. 2})$$

Now we express $[A]$ as C and rewrite (Eq. 1) as:

$$K_{\text{ads}} = \frac{\theta}{C(1 - \theta)} \quad (\text{Eq. 3})$$

Rearranging, we obtain the final form of the Langmuir adsorption isotherm:

$$\theta = \frac{K_{\text{ads}}C}{1 + K_{\text{ads}}C} \quad (\text{Eq. 4})$$



If we define Y as the amount of adsorption in units of moles adsorbate per mass adsorbant, and Y_{max} and the maximal adsorption, then:

$$\theta = Y/Y_{\text{max}} \quad (\text{Eq. 5})$$

and the isotherm can be expressed as:

$$\frac{C}{Y} = \frac{1}{K_{\text{ads}}Y_{\text{max}}} + \frac{C}{Y_{\text{max}}} \quad (\text{Eq. 6})$$

This is the form of the isotherm we will use for our Charcoal-Acetic Acid system.

At lower concentrations, an alternate isotherm developed by Herbert F. Freundlich frequently describes the data better. The Freundlich Isotherm is:

$$Y = k C^{1/n} \quad (\text{Eq. 7})$$

where the Freundlich parameters k and n are empirically determined. A plot of $\log Y$ vs. $\log C$ allows for a determination of these parameters.



Journal of Chemical Education, 1934

We will prepare our Acetic Acid-Charcoal isotherm by allowing Acetic Acid solutions of various concentrations to equilibrate for about a week with a given mass of *Norit A*. The amount of Acetic Acid (HAc) not adsorbed to the *Norit A* will be determined by titration with Sodium Hydroxide (NaOH).



This will allow us to easily determine the amount of Acetic Acid that has adsorbed to a given mass of the Charcoal.

Procedure

Week 1

Prepare about 1L of 0.1M NaOH from a 6M stock solution and store it in a tightly stoppered plastic bottle. Standardize this NaOH solution against Potassium Hydrogen Phthalate (KHP) using Phenolphthalein to detect the endpoint. Your titration should be done in triplicate.

Prepare about 1L of 0.4M Acetic Acid. Determine its exact concentration by titrating this solution with the NaOH standard. Again, this should be done in triplicate.

Weigh about 1.5g Charcoal into 6 stopper 250 mL Erlenmeyer flasks. This should be recorded to ± 1 mg.

Prepare a series of Acetic Acid solutions according to the second column in the table below:

<u>Sample</u>	<u>Vol.(mL) 0.4 M Acetic Acid Diluted to 100 mL</u>	<u>Aliquot for Analysis (mL)</u>
1	100	10
2	75	10
3	50	10
4	25	25
5	10	25
6	5	25

For each sample above, add 100 mL of the solution to a charcoal sample. Promptly stopper the flask tightly. Swirl the flasks vigorously and then place them into the shaker bath at 25°C. Let them agitate until next week.

Pre-Lab Preparation

- 1. Determine how to prepare the stock 0.4M Acetic Acid solution.**
- 2. Determine the dilution factor for the preparation of the 0.1M NaOH solution.**
- 3. Determine the amount of KHP needed for the standardization.**

Week 2

Filter your charcoal solutions (discard the first 10 ml of filtrate to clean the filter flask of any contaminants and to saturate with acid any adsorption sites which might be on the filter paper) using a long-stem gravity funnel. A moderately "fast" filter paper can be used for this filtration.

For each sample, titrate an aliquot, whose volume is recommended above, with the standardized NaOH solution using Phenolphthalein to detect the endpoint. Perform your titrations in triplicate.

Data Analysis

All results must be accompanied by an appropriate error estimate.

1. Determine the concentration of the NaOH solution from your standardization data.
2. Using your titration data, for each sample:
Calculate the number of moles of acetic acid in the solution *before* adsorption.
(Recall, you diluted the 0.4M Acetic Acid according to the above tabulated scheme.)

Calculate the number of moles of acetic acid in the solution *after* adsorption.
(Recall, you only titrated an aliquot of the original solution, as specified in the above tabulation.)
3. Determine Y for each sample. Include appropriate error estimates for each Y value.
4. Plot your isotherm; Y vs. C . Include appropriate error bars for Y .
5. Plot the isotherm in the form of (Eq. 6) and determine the Langmuir parameters Y_{\max} and K_{ads} . Include appropriate error estimates for each parameter.
6. Make the suggested plot to determine the Freundlich parameters k and n . Again, include appropriate error estimates for each parameter.
7. Re-plot your isotherm; Y vs. C . Include the Langmuir and Freundlich isotherms, in each case generated using the parameters determined above. Comment on the quality of the Langmuir and Freundlich isotherms.
8. Assume the surface area occupied by one acetic acid molecule on the surface of the charcoal is 21\AA^2 . Determine the surface area of 1 g of charcoal. Express your result in m^2/g . Is your number reasonable? Compare your result with that of the literature.

References

- Adamson, Arthur W. (1979). "A Textbook of Physical Chemistry," 2nd Ed. Academic Press, New York.
- Castellan, Gilbert W. (1983). "Physical Chemistry," 3rd Ed. Addison-Wesley.
- Duff, David G., Ross, Sheina M.C. and Vaughan, D. Huw "Adsorption from Solution: An Experiment to Illustrate the Langmuir Isotherm" *J. Chem. Ed.* **65** 815 (1988).
- Dunicz, Boleslaw Ludwik "Surface Area of Activated Charcoal by Langmuir Adsorption Isotherm" *J. Chem. Ed.* **38** 357 (1961).
- Hanson, Robert S. and Craig, Roy P. "The Adsorption of Aliphatic Alcohols and Acids from Aqueous Solutions by Non-Porous Carbons" *J. Phys. Chem.* **58** 211 (1954).
- Levine, Ira N. (2009) "Physical Chemistry," 6th Ed. McGraw-Hill, Boston.
- Moore, Walter J. (1972). "Physical Chemistry," 4th Ed. Prentice-Hall, New Jersey.
- Sime, Rodney J. (1990). "Physical Chemistry: Methods, Techniques and Experiments." Saunders College Publishing, Philadelphia.
- unauthored, "Professor Herbert Freundlich, 1880- " *J. Chem. Ed.* **11** 257 (1934).
- <http://www.norit.com/>; accessed September 5, 2010.