

Adsorption Notes

R. K. Herz, ReactorLab.net, rherz@ucsd.edu

General Classification of adsorption

Physical adsorption - physisorption

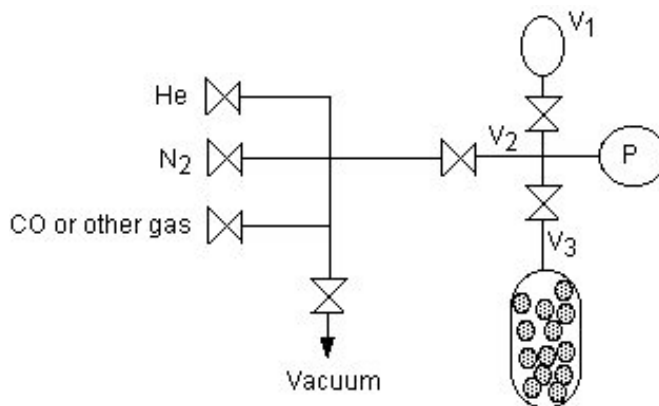
- dispersion forces - Van der Waals forces
- weak - only get high fractional coverage of surface at low temperatures
- not selective - same order of magnitude attraction between all molecules and surfaces
- use physisorption of a molecule to measure total surface area of high surface area materials
- may play a role in catalysis by affecting kinetics of entry and exit from chemisorption state as "precursor state"

Chemical Adsorption - chemisorption

- chemical bonds are formed between adsorbed molecule and surface atoms
- strong - can get high fractional coverage of surface at relatively high temperatures
- selective - bonds only form between certain molecules and certain surfaces
- use chemisorption to measure areas of specific materials in surfaces with complex composition

Adsorption measurements

This is a schematic of one version of an adsorption apparatus.



The circle labeled P is a capacitance manometer pressure gauge which has small internal volume. The sample is represented as the shaded circles in the sample cell. After introduction of a known mass of sample, the sample is degassed to remove water by pumping with the vacuum pump and heating the sample cell. For chemisorption measurements over supported metal catalysts, other pretreatments such as cleaning and reduction pretreatments can be performed.

The volume V_1 is known. The unknown volumes V_2 , which includes the internal volume of the pressure gauge, and V_3 , which is the void volume in the sample cell after the sample is loaded, are determined by filling V_1 with helium to known pressure, then expanding the helium, measuring the final pressure and using the ideal gas law. Helium will not chemisorb and will not physisorb to an appreciable extent except at temperatures near absolute zero.

Then the sample cell is evacuated and brought to the desired temperature. For physisorption measurements performed at liquid nitrogen temperature, a dewar containing liquid nitrogen is raised to cover the sample cell but not the valve above the sample cell.

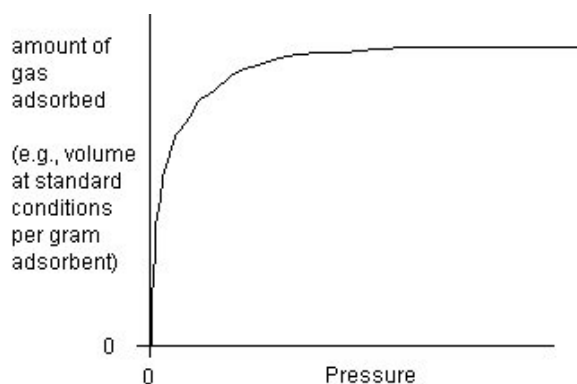
By opening and closing valves in the correct order, the gas to be adsorbed can be admitted to volume V_2 , the pressure recorded and the ideal gas law used to determine the moles of gas contained in V_2 . Then the valve between V_2 and V_3 is opened and time for equilibration is allowed. Then the pressure is recorded and the known volumes and temperatures and the ideal gas law can be used to determine the moles of gas remaining in the gas phase. The difference between the initial moles of gas in V_2 and the moles of gas remaining is the moles of gas molecules that have been adsorbed over the sample's surfaces. The valve between V_2 and V_3 is closed, more gas is admitted into V_2 and then the process is repeated with increasing pressures.

Commercial instruments are available which are automated. Some instruments have mass flow controllers and leak gas at a known, slow rate into (or out of) the sample cell as the pressure is continuously recorded. When the flow rate is sufficiently slow, adsorption equilibrium is closely approached during the experiment.

Chemisorption measurements and the Langmuir isotherm

Since chemisorption is selective, chemisorption of various gases can be used to get information about the surface areas contributed by the different components of a complex material. For example, chemisorption of CO, H₂ and/or O₂ is often used to estimate metal surface area in supported metal catalysts.

The "isotherm" measured at constant temperature will look similar to this:



Since only one layer of molecules can bond to the surface atoms, the amount of gas adsorbed approaches a maximum at relatively high pressure.

Often we are only interested in the maximum amount adsorbed. Knowing this amount, the ratio of adsorbed molecules to surface atoms at maximum coverage, the diameter of the surface atoms, and an assumed surface structure, we can compute the surface area of the material in m²/g.

There are a variety of models of chemisorption and associated isotherm equations which can be used to fit all of the experimental data over the full pressure range measured. Surfaces have a range of sites with different chemisorption bonding strengths, and there is a variety of isotherms which describe such adsorption, including: Elovich, Temkin, Freundlich, etc.

For surfaces with relatively uniform properties, the Langmuir adsorption isotherm can be used. The assumptions involved in the derivation of the Langmuir isotherm are:

- the surface is composed of an array of identical adsorption sites
- adsorbed molecules are distributed randomly over the surface
- there are no lateral (parallel to surface) interactions between sites or adsorbed molecules

The last assumption means that the chemisorption bonding energy and the heat (enthalpy) of adsorption are constant with coverage (amount adsorbed). At equilibrium, the rate of adsorption is equal to the rate of desorption:

$$k_{ads} P S_0 = k_{des} S_1$$

The variable S_i is the concentration of surface sites covered by i adsorbed molecules (number per amount of surface or adsorbent).

$$S_{tot} = S_0 + S_1$$

The total site concentration can be determined from the maximum amount that can adsorb. The fractional surface coverage, θ , is defined by

$$\theta \equiv \frac{S_1}{S_{tot}} = \frac{v}{v_m}$$

where v is the amount adsorbed in terms of the equivalent gas volume at standard temperature and pressure per gram of sample and v_m is the maximum amount which can adsorb.

$$\frac{S_0}{S_{tot}} = (1 - \theta)$$

$$k_{ads} P (1 - \theta) = k_{des} \theta$$

$$K \equiv \frac{k_{ads}}{k_{des}}$$

$$\theta = \frac{KP}{1 + KP}$$

This equation is the Langmuir isotherm. We can estimate v_m and K by plotting the inverse of the amount adsorbed vs. the inverse pressure and fitting a straight line to the data:

$$\frac{1}{v} = \left(\frac{1}{v_m} \right) + \left(\frac{1}{v_m K} \right) \frac{1}{P}$$

By performing chemisorption measurements and determining K values at different temperatures, we can estimate the heat (enthalpy) of adsorption by plotting $\ln K$ vs $1/T$.

$$K = \frac{k_{ads}}{k_{des}} = \frac{k_{ads}^0 e^{-E_{ads}/RT}}{k_{des}^0 e^{-E_{des}/RT}} = \left(\frac{k_{ads}^0}{k_{des}^0} \right) e^{-(E_{ads} - E_{des})/RT} = \left(\frac{k_{ads}^0}{k_{des}^0} \right) e^{-\Delta H_{ads}/RT}$$

$$\ln K = \ln \left(\frac{k_{ads}^0}{k_{des}^0} \right) - \left(\frac{\Delta H_{ads}}{R} \right) \frac{1}{T}$$

Usually $E_{ads} < E_{des}$ such that $\Delta H_{ads} < 0$. That is, chemisorption is usually exothermic, and the amount adsorbed at a constant pressure decreases with increasing temperature. The maximum amount adsorbed, v_m , should remain constant, although the pressure at which it will be closely approached will increase with increasing temperature. Often $E_{ads} = 0$.

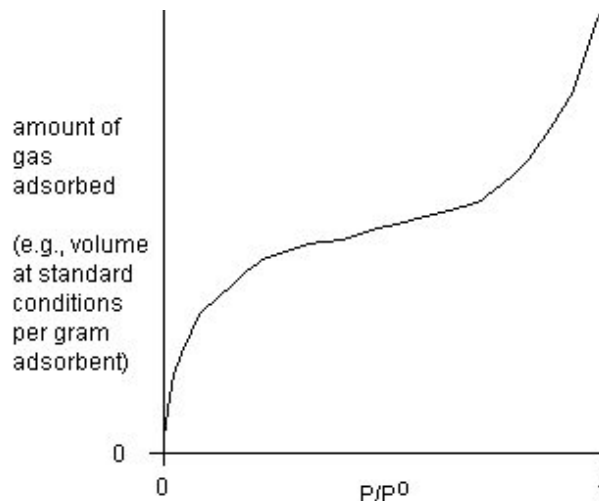
Endothermic adsorption can occur in association with large entropy changes, e.g., when there are large changes in protein configuration during protein adsorption on surfaces.

Measurement of total surface area using the BET method

The BET method is named after its developers, Stephen Brunauer, Paul Emmett, and Edward Teller [J. Am. Chem. Soc., vol. 60, p. 309 (1938)]. This method is used every day, all over the world to measure the total area of high surface area materials such as paint pigments, soils, food (breakfast cereals that snap, crackle and pop), adsorbents and catalysts.

In the BET method, a gas, often nitrogen, is physisorbed over a high surface area material at the normal boiling point temperature of liquid nitrogen (77 K).

The adsorption isotherm, or plot of amount adsorbed vs. gas pressure at constant temperature, often looks like this:

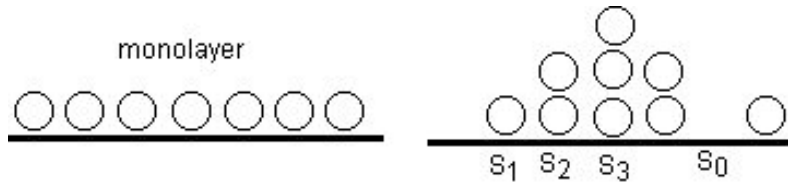


The shape of this isotherm is classified as a Type II isotherm. There are other shapes. P is the gas pressure and P^0 is the vapor pressure of the adsorbing gas at the measurement temperature. Sample chambers are often immersed in a liquid nitrogen bath for temperature control. For N_2 as the adsorbing gas, the vapor pressure P^0 is 1 atm at the liquid nitrogen normal boiling point of 77 K. When other gases are adsorbed at 77 K, their vapor pressure at 77 K will not be 1 atm.

The objective is to analyze these data in order to determine the amount of gas that would be adsorbed over the surface in one complete monolayer. With monolayer coverage, the surface is completely covered with one and only one layer of adsorbed molecules. In a physisorbed monolayer, the molecules are closely packed together. Once we know the monolayer coverage amount, e.g., moles of N_2 adsorbed in a monolayer per gram of sample,

we can use the Van der Waals diameter of N_2 and an assumed close-packed arrangement to compute the surface area occupied by an adsorbed N_2 molecule and, finally, the total surface area of the material in m^2/g .

With physisorption, the attractive forces between the adsorbed molecules and the surface are usually only a little stronger than between the adsorbed molecules when they are in the liquid phase. Thus, multilayer adsorption occurs over parts of the surface before a complete monolayer of adsorbed molecules is formed.



In the schematics above, the surface is shown as a flat plane but we know that it is really a layer of surface atoms of the solid material. The variable S_i is the concentration of surface sites covered by i adsorbed molecules (number per amount of surface or adsorbent).

Our goal is to determine the amount of gas adsorbed in a monolayer over our sample but the adsorption doesn't occur that way. Thus, we need a model of multilayer adsorption and some math.

Here are the equations that lead to development of the BET isotherm equation. At equilibrium, the rate of adsorption from the gas into sites of type S_1 equals the rate of desorption from sites of type S_1 :

$$a_1 P S_0 = b_1 e^{-Q_1/RT} S_1$$

where a_1 and $(b_1 e^{-Q_1/RT})$ are the adsorption and desorption rate coefficients, respectively, and Q_1 is the heat of adsorption of molecules in direct contact with the surface. For molecules adsorbed into higher layers:

$$a_i P S_{i-1} = b_i e^{-Q_v/RT} S_i$$

where Q_v is the heat of vaporization of the liquid phase of the adsorbing molecules.

The main ideas involved here are:

- all surface sites are identical
- there are no lateral interactions that affect adsorption and desorption
- the attractive force between molecules in direct contact with the surface is different (stronger) than the force between molecules in the first layer and the second layer, the second layer and the third, etc.
- the attractive force between molecules in the multilayers (between first layer and second layer, between second layer and third, etc.) are the same as between these molecules when they are in the liquid phase.

Define the variables x , y , and c .

$$x = \frac{S_2}{S_1} = \frac{S_3}{S_2} = \frac{S_i}{S_{i-1}} = \left(\frac{a_i}{b_i} \right) P e^{Q_v/RT}$$

$$y = \frac{S_1}{S_0} = \left(\frac{a_1}{b_1} \right) P e^{Q_1/RT}$$

$$c = \frac{y}{x} = \left(\frac{a_1 b_i}{a_i b_1} \right) e^{(Q_1 - Q_v)/RT} \approx e^{(Q_1 - Q_v)/RT}$$

$$x^{i-1} = \frac{S_i}{S_1} \quad \text{e.g.,} \quad x^2 = \left(\frac{S_2}{S_1} \right) \left(\frac{S_3}{S_2} \right) = x^{3-1} = \frac{S_3}{S_1}$$

$$S_i = x^{i-1} S_1 = y x^{i-1} S_0 = c x^i S_0$$

The number concentration of total molecules adsorbed, n , divided by the number concentration with only a hypothetical monolayer adsorbed, n_m , is:

$$\frac{n}{n_m} = \frac{\sum_{i=0}^{\infty} i S_i}{\sum_{i=0}^{\infty} S_i} = \frac{c S_0 \sum_{i=1}^{\infty} i x^i}{S_0 + S_0 c \sum_{i=1}^{\infty} x^i} = \frac{c \sum_{i=1}^{\infty} i x^i}{1 + c \sum_{i=1}^{\infty} x^i}$$

This last result can be solved by us at WolframAlpha.com (not available to BE & T in 1938!):

Solve (c*(sum(i*x^i) from i=1 to i=inf))/(1+c*(sum(x^i) from i=1 to i=inf))

$$\frac{n}{n_m} = \frac{\frac{cx}{(1-x)^2}}{1 + \frac{cx}{(1-x)}} = \frac{cx}{(1-x)[1+(c-1)x]}$$

This is the BET isotherm equation. We can measure n as a function of gas pressure at constant temperature. We want to use these measurements to find n_m . The theory now relates the variable x to the gas pressure divided by the vapor pressure of the gas molecules at the measurement temperature:

$$x = \frac{P}{P^0}$$

How do we get this? From above:

$$x = \frac{P}{P^0} = \left(\frac{a_i}{b_i} \right) P e^{Q_v/RT}$$

$$\frac{1}{P^0} = \left(\frac{a_i}{b_i} \right) e^{Q_v/RT}$$

$$a_i P^0 = b_i e^{-Q_v/RT}$$

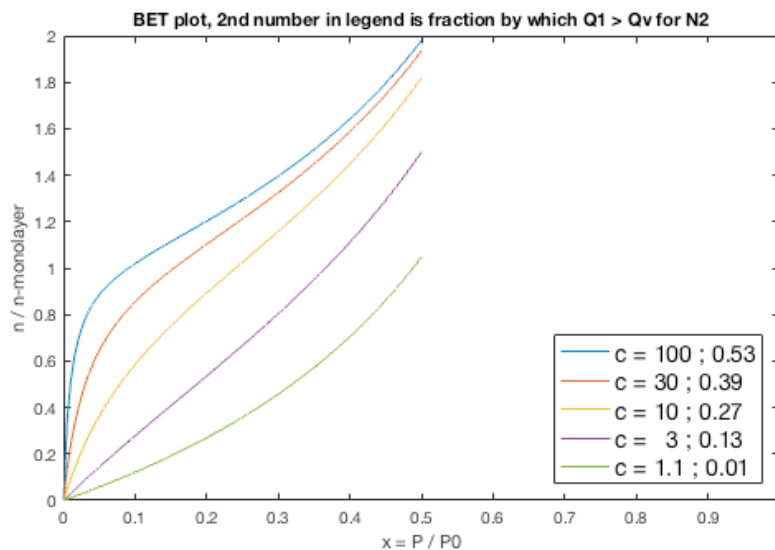
This says that, at equilibrium, the rate of adsorption from the gas into the surface of a liquid of the adsorbing molecules is equal to the desorption rate from the liquid surface.

Rearranging the isotherm equation,

$$\frac{x}{n(1-x)} = \left[\frac{1}{cn_m} \right] + \left[\frac{c-1}{cn_m} \right] x$$

we see that we can plot measurements of $x/(n(1-x))$ vs. $x = P/P^0$ and estimate values of c and n_m from the slope and intercept of a straight-line fit to the data. The fit usually applies only in the the pressure ratio range P/P^0 from 0.05 to 0.3. One reason is that at higher pressure ratios, condensation and filling of small pores will start to occur.

The number concentration of gas molecules adsorbed is proportional to the volume of gas at standard temperature and pressure that is adsorbed per gram of sample, v . We often see plots of v vs. P/P^0 . Below is a plot of n/n_m vs. P/P^0 for different values of c . The second number in each line of the legend is the fraction by which Q_l is greater than Q_v .



For c values of order magnitude 100 and in the pressure ratio range P/P^0 from 0.05 to 0.3, the following equation provides a reasonable fit:

$$\frac{n}{n_m} \approx \frac{1}{1-x}$$

$$n \approx 0 + n_m \left(\frac{1}{1-x} \right)$$

Plot measurements of n vs. $1/(1-x)$ and fit a straight line through the origin. The slope of the line provides an estimate of n_m .

The "single-point method" uses a measurement of $v \propto n$ at one value of $x = P/P^0$. This is convenient for an apparatus which uses flowing N_2 (or other gas) in nonphysisorbing He at one mole fraction at atmospheric

pressure. This type of apparatus is less expensive than the apparatus shown above which can measure many points on an isotherm.

The sample is contained in a glass U-tube. After a cleaning pretreatment, the U-tube is immersed in liquid nitrogen and the sample is equilibrated in a flow of the gas. The inlet and outlet gas flow through the two sides of a thermal conductivity detector, such as are found in gas chromatographs. Then the sample is rapidly warmed and the N_2 that desorbs is measured as a peak by the detector. The area of the peak that is recorded is proportional to the amount of N_2 that desorbs, and can be determined by calibration of the detector.

By using an adsorbing gas with a lower vapor pressure at liquid nitrogen temperature, such as Ar or Kr, one can get greater sensitivity. This is because a smaller mole fraction of that gas in He can be used, thus providing a larger signal from the thermal conductivity detector when desorption occurs.

```
% MATLAB listing for BET plot
```

```
x = linspace(0,0.5,100);  
c = [100 30 10 3 1.1];
```

```
for j = 1:length(c)  
    nnm = c(j)* x ./ ((1-x) .* (1+(c(j)-1)*x));  
    plot(x,nnm)  
    axis([0,1,0,2]);  
    hold on  
end  
hold off
```

```
% curves listed in Legend top to bottom in order curves plotted in for repeat
```

```
legend({'c = 100 ; 0.53', 'c = 30 ; 0.39', 'c = 10 ; 0.27', 'c = 3 ; 0.13', 'c = 1.1 ; 0.01'},...  
       'FontSize',14,'Location','SouthEast')
```

```
title('BET plot, 2nd number in legend is fraction by which  $Q_1 > Q_v$  for  $N_2$ ')
```

```
ylabel('n / n-monolayer')  
xlabel('x = P / P0')
```

```
% c = exp(deltaQ/R/T)
```

```
% dQ = RTln(c) =  $Q_1 - Q_v$ 
```

```
T = 77; % K
```

```
R = 0.00831446; % kJ/K/mol
```

```
Qv = 5.56; % kJ/mol, heat of vaporization of  $N_2$ 
```

```
dQ = R*T*log(c) % log is natural ln in Matlab (log10 is log base 10)
```

```
fQ = dQ/Qv
```