

1) a) $\xi = 6\pi\eta R_{\text{sphere}}$

$F = \xi v$

η = friction factor - distance / time

$\xi \sim \frac{\text{force} \cdot \text{time}}{\text{distance}}$

$\eta = \frac{\tau}{\dot{\gamma}} = \frac{\text{force} / \text{distance}^2}{(\text{distance} / (\text{time} \cdot \text{distance}))} = \frac{\text{force} \cdot \text{time}}{\text{distance}^2}$

$R = \text{distance}$

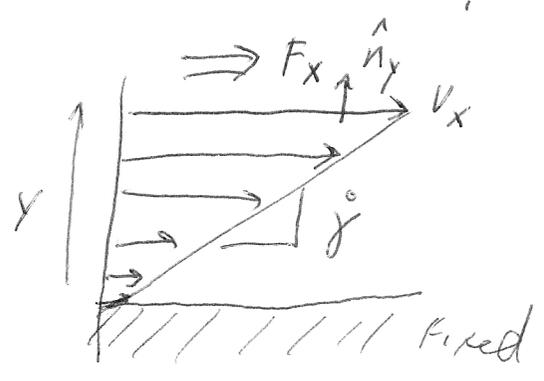
So $\xi = 6\pi\eta R$ has units of $\frac{\text{force} \cdot \text{time}}{\text{distance}}$ as required

b)

$D = \frac{kT}{6\pi\eta R}$

Diffusion is driven by temperature so it is natural that $D \sim T$. Larger particles diffuse slower, the exact functionality $D \sim \frac{1}{R}$ can be determined by a unit balance as in "d" or through a rather involved derivation.

c)



$\dot{\gamma}_{xy} = \frac{dv_x}{dy}$

$\tau_{xy} = \frac{dF_x}{dA_y}$

A_y is the area with normal \hat{n}_y in the y-direction.

d)

$$F_{\text{drag}} = \frac{\rho_{\text{fluid}} V^2 C_d A}{2}$$

ρ_{fluid} = fluid density

V^2 = speed of object (car)

C_d = drag coefficient

A = cross-sectional Area (Reference Area)

This definition relies on the existence of a boundary layer where there is a transition from laminar flow to turbulent flow at the surface of the object (car). For small objects at low speeds (e.g. dust or colloids)

few steps at the surface & there is no boundary layer so $F \sim v$ rather than $F \sim v^2$.

e) See b2

f) See b2

9.2 EXPERIMENTAL AND THEORETICAL TREATMENTS OF ADSORPTION: AN OVERVIEW

9.2a Adsorption Isotherms

Adsorption experiments are conducted at constant temperature, and an empirical or theoretical representation of the amount adsorbed as a function of the equilibrium gas pressure is called an *adsorption isotherm*. Adsorption isotherms are studied for a variety of reasons, some of which focus on the adsorbate while others are more concerned with the solid adsorbent. In Chapter 7 we saw that adsorbed molecules can be described as existing in an assortment of two-dimensional states. Although the discussion in that chapter was concerned with adsorption at liquid surfaces, there is no reason to doubt that similar two-dimensional states describe adsorption at solid surfaces also. Adsorption also provides some information about solid surfaces. The total area accessible to adsorption for a unit mass of solid—the specific area A_{sp} —is the most widely encountered result determined from adsorption studies. The energy of adsorbate-adsorbent interaction is also of considerable interest, as we see below.

9.2b Adsorption: Some Experimental Considerations

We saw in Chapter 6, Section 6.7, that solid surfaces are notoriously heterogeneous, particularly with respect to roughness and chemical composition. From the point of view of specific area determination, roughness is not too troublesome since the adsorbed gas molecules can generally cover the hills and valleys of the surface with ease. Pores with very small dimensions pose more of a problem. For now, we assume that such pores are absent; we take up the question of adsorption on porous solids in Section 9.7. Chemical heterogeneity affects the energetics of adsorption. For simplicity, we often assume that the surface is characterized by a single adsorption energy. Actually, a distribution of surface sites with differing adsorption energies may be present, and some indication of this may be extracted from adsorption data. As an approach to surface characterization, adsorption studies are indirect and give average rather than specific descriptions. We have already seen in Vignette I.8 that solid surfaces can be probed more directly for information on a molecular scale using scanning probe spectroscopy; we see below in this chapter (Section 9.8) how low-energy electron diffraction can be used to study the structure of surfaces on a molecular scale. For solids with high specific area, however, gas adsorption is the method of choice for quantifying this feature; we have more to say about it in Section 9.5.

9.2b.1 Experimental Determination of Adsorption Isotherms

Adsorption studies for the experimental determination of adsorption isotherms are conducted in a vacuum apparatus from which all gases can be removed prior to the addition of the adsorbate being studied. After the solid is introduced into the sample tube and the tube is attached to the vacuum line, it is generally pretreated by some sort of degassing procedure. This is a combination of heating and pumping to ensure the removal of physically adsorbed contaminants. Consideration must be given to the possibility of changing the solid when the temperature of degassing is selected. A heat treatment that is too vigorous may result in changes in any chemisorbed layer, which—from our point of view at least—amounts to a change in the adsorbent itself. If extensive enough, such changes may alter the surface area of a solid. Even less drastic changes are sufficient to alter the adsorption energy of a surface.

The range of pressures over which adsorption studies may be conducted is—in principle—from zero to p_0 , the saturation pressure or the normal vapor pressure of the material at the temperature of the experiment. At the low-pressure end of this range adsorption will be slight, so the determination of the isotherm involves measuring small differences in pressure at low pressures. This is not easy to do experimentally, although relatively modern low-pressure techniques have greatly extended this region. As the pressure approaches p_0 , adsorption often increases rapidly as if anticipating phase separation at the surface (resulting from multilayer adsorption in which most of the adsorbed molecules behave as if they were in the bulk liquid

state). As a matter of fact, if the solid is porous, the vapor may actually condense in the small pores at $p < p_0$ (see Section 9.7).

Figure 9.3 is a sketch of an apparatus that can be used to determine the equilibrium extent of gas adsorption as a function of pressure. We outline how such an experiment is conducted at ambient temperature, even though adsorption studies are frequently conducted at low temperatures, particularly when determination of A_p is the objective of the experiment. A known mass of adsorbent is introduced into the sample tube and degassed as described above. Then the following set of pressure-volume readings are made, described here in terms of Figure 9.3.

1. The sample tube and gas burette are evacuated and then a nonadsorbing gas—frequently helium—is introduced into the gas burette. The burette is graduated with respect to volume and also serves as one leg of a manometer so that both the volume and pressure of gas in the burette can be measured. Ambient temperature is assumed to apply throughout.
2. The three-way stopcock is opened to connect the gas burette with the sample tube. The new pressure and volume are read. From this, the volume of the dead space—the volume beyond the three-way stopcock that is not occupied by sample—can be determined (see Example 9.1).
3. The nonadsorbed gas is pumped out and replaced by the adsorbate. Its volume, pressure, and temperature are measured, and from these the number of moles of gas introduced (initially) into the apparatus can be determined.
4. The three-way stopcock is opened to connect the burette and sample tube, and volume and pressure are measured again. Since the dead space is known, the (final) number of moles of gas can be calculated. The difference between the initial and final number of moles gives the number of moles adsorbed.
5. This amount of adsorbed gas is in equilibrium with bulk gas at the pressure read in Step 4.

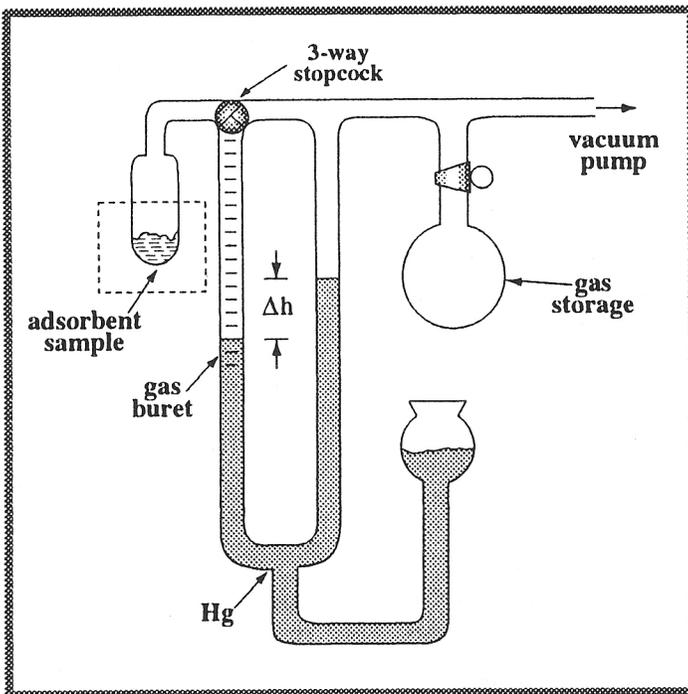


FIG. 9.3 Schematic illustration of a gas adsorption apparatus.

These steps describe the determination of a single point on an adsorption isotherm. By adjusting the mercury level, we can increase the pressure of the equilibrium gas with more adsorption occurring. Steps 3 and 4 are thus repeated until the full isotherm is mapped. Example 9.1 illustrates numerically how a point on the isotherm is established.

* * *

EXAMPLE 9.1 Construction of Adsorption Isotherms: The following pressure-volume (p - V) data were collected at a temperature of 22°C. The V 's are volumes in the gas burette, and the numerical subscripts refer to the steps itemized above.

With helium, $p_1 = 21.71$ torr, $V_1 = 12.90$ cm³, $p_2 = 16.50$ torr, $V_2 = 10.90$ cm³. With adsorbate, $p_3 = 12.85$ torr, $V_3 = 13.70$ cm³, $p_4 = 3.24$ torr, $V_4 = 5.00$ cm³. What is the volume of the dead space? How many moles are adsorbed at the final equilibrium pressure, 3.24 torr?

Solution: Successive applications of the ideal gas law allow us to calculate the desired quantities.

The total volume to which the gas has access after the stopcock is opened is the sum of the burette volume and the dead space V_d . Therefore $V_d + V_2 = p_1 V_1 / p_2 = (21.71)(12.90) / (16.50) = 16.97$, or $V_d = 6.07$ cm³. It is convenient to use $R = 62,360$ cm³ torr K⁻¹ mole⁻¹ as the value of the gas constant in these calculations. The initial moles of adsorbate are given by $n_i = p_3 V_3 / RT = (12.85)(13.70) / (62360)(295) = 9.57 \cdot 10^{-6}$. After adsorption equilibrium is established, $n_f = p_4 (3.24)(5.00 + 6.07) / (62360)(295) = 1.95 \cdot 10^{-6}$. The difference $n_i - n_f = (9.57 - 1.95) \cdot 10^{-6} = 7.62 \cdot 10^{-6}$ mole gives the amount adsorbed at an equilibrium pressure of 3.24 torr. ■

* * *

The adsorption isotherm is to be determined at some temperature other than room temperature—liquid nitrogen temperature, for example—the sample tube is placed in a suitable thermostat. This is indicated by the dotted line in Figure 9.3. In this case two sets of readings are made with the nonadsorbed gas, one at room temperature and one with the thermostat in place. In this way the partitioning of the dead space between the two temperature regions can be determined. Several additional considerations should be cited that are important in actual practice:

1. The gases used for adsorption must be of high purity.
2. The gas burette should itself be thermostated unless the laboratory has very good temperature control.
3. The nonideality for the adsorbate at low temperatures must be taken into account unless the volume of the low-temperature dead space is minimized.
4. Sufficient time must be allowed for equilibrium to be established. A way of checking this experimentally is to lower the pressure and observe that desorption follows the same curve as adsorption.

b.2 Classification of Adsorption Isotherms

Experimental gas adsorption isotherms are traditionally classified into one of the five types shown in Figure 9.4.

- The Type I isotherm is reminiscent of Figure 7.16, the *Langmuir isotherm*. The plateau is interpreted as indicating monolayer coverage. We see that this type of behavior implies a sufficiently specific interaction between adsorbate and adsorbent to be more typical of chemisorption than physical adsorption.
- Type II adsorption, by contrast, is widely observed with physical adsorption and is interpreted to mean multilayer adsorption.
- We see in Section 9.5b (Example 9.5) that Type III behavior occurs when the heat of liquefaction is more than the heat of adsorption.
- Types IV and V are analogs of Types II and III, except for the leveling off that occurs at pressures below p_0 . These cases are associated with porous solids in which the adsorbate condenses in the small pores at $p < p_0$.

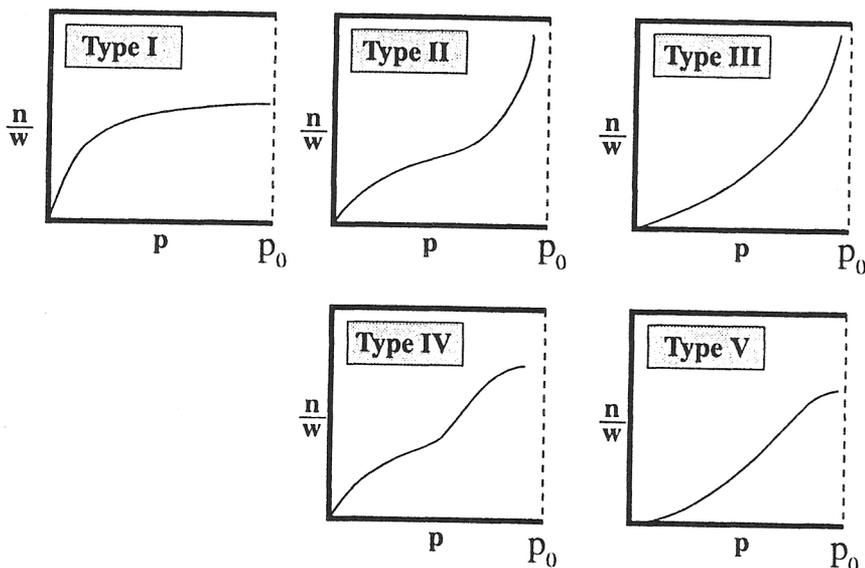


FIG. 9.4 Qualitative shapes of the five general types of gas adsorption isotherms. (See text for a discussion of their physical significance.)

If the specific area of the solid is the information sought, it is the amount of adsorption at monolayer coverage that must be measured. This is readily available in Type I adsorption, but requires considerable interpretation when multilayer adsorption takes place. Once determined, however, the number of molecules required to saturate a surface times the area occupied per molecule gives the surface area of a sample. This divided by the mass of the sample gives A_{sp} . In addition, once the adsorption at monolayer coverage is identified, all other extents of adsorption can be expressed as fractions or multiples of the monolayer.

9.2c Adsorption Isotherms: Theoretical Considerations

This makes a convenient point of contact with theory since models for adsorption inevitably subdivide the surface into an array of adsorption sites that gradually fill as the pressure increases. If θ is defined as the fraction of sites filled, then $\theta = 1$ corresponds to monolayer coverage, with $\theta < 1$ or $\theta > 1$ to submonolayer and multilayer coverages, respectively. Theoretical isotherms predict how θ varies with p in terms of some particular model for adsorption. It turns out that a set of experimental points can often be fitted by more than one theoretical isotherm, at least over part of the range of the data; that is, theoretical isotherms are not highly sensitive to the model on which they are based. A comparison between theory and experiment with respect to the temperature dependence of adsorption is somewhat more discriminating than the isotherms themselves.

Since it is relatively easy to fit experimental adsorption data to a theoretical equation, there is some controversy as to what constitutes a satisfactory description of adsorption. From a practical point of view, any theory that permits the amount of material adsorbed to be related to the specific surface area of the adsorbent and that correctly predicts how this adsorption varies with temperature may be regarded as a success. From a theoretical point of view, what is desired is to describe adsorption in terms of molecular properties, particularly in terms of an equation of state for the adsorbed material, where the latter is regarded as a two-dimensional state of matter.

As we see in the course of the chapter, these two approaches frequently clash. The adsorption isotherm of Brunauer, Emmett, and Teller (BET), which is discussed in Section 9.5, is an excellent example of this. The model on which the BET isotherm is based has been criticized by many theoreticians. At the same time, the isotherm itself has become virtually

- 2) a) Dipole - Dipole
- Dipole - Induced Dipole
- Induced Dipole - Induced Dipole
- See Schaefer Colloids ppt

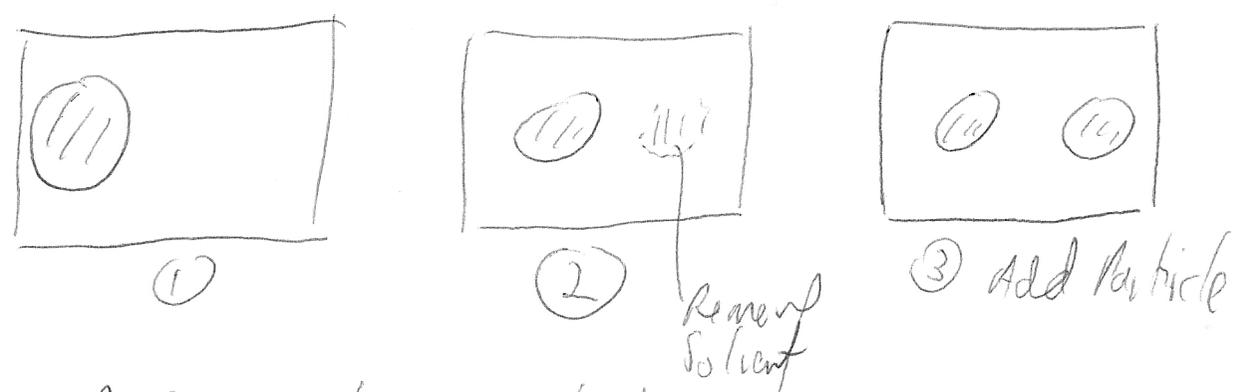
b) See Wiki 6-12 Link

c) See Schaefer Colloids & Hamaker Const.

d) Plate equation is per area

e)

3) a.) Hamaker is composed of Van der Waals forces so it depends on μ & α for the material (See Schaefer Colloids ppt). Consider a 2 step process



Dodecane has α but no μ
 Water has μ but no α

b.) Dodecane would be the best solvent for a stable colloidal dispersion since it has almost 0 for the Hamaker constant.

c) No, it is based on van der Waals Forces. ④

d) see with double layer + "b"

e)