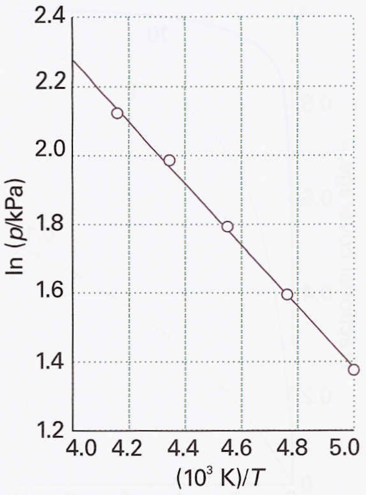

Fig. 25.18 The isosteric enthalpy of adsorption can be obtained from the slope of the plot of ln p against $1/T$, where p is the pressure needed to achieve the specified surface coverage. The data used are from Example 25.2.

It follows from eqn 25.7 that

$$\left(\frac{\partial \ln p}{\partial T}\right)_\theta = -\left(\frac{\partial \ln K}{\partial T}\right)_\theta = -\frac{\Delta_{\text{ad}}H^\ominus}{RT^2}$$

With $\mathrm{d}(1/T)/\mathrm{d}T = -1/T^2$, this expression rearranges to

$$\left(\frac{\partial \ln p}{\partial(1/T)}\right)_\theta = \frac{\Delta_{\text{ad}}H^\ominus}{R}$$

Therefore, a plot of ln p against $1/T$ should be a straight line of slope $\Delta_{\text{ad}}H^\ominus/R$.

Answer We draw up the following table:

T/K	200	210	220	230	240	250
$10^3/(T/\text{K})$	5.00	4.76	4.55	4.35	4.17	4.00
$\ln(p/\text{kPa})$	1.39	1.60	1.80	1.97	2.14	2.29

The points are plotted in Fig. 25.18. The slope (of the least squares fitted line) is −0.904, so

$$\Delta_{\text{ad}}H^\ominus = -(0.904 \times 10^3\ \text{K}) \times R = -7.52\ \text{kJ mol}^{-1}$$

The value of K can be used to obtain a value of $\Delta_{\text{ad}}G^\ominus$, and then that value combined with $\Delta_{\text{ad}}H^\ominus$ to obtain the standard entropy of adsorption. The expression for $(\partial \ln p/\partial T)_\theta$ in this example is independent of the model for the isotherm.

Self-test 25.2 Repeat the calculation using the following data:

T/K	200	210	220	230	240	250
p/kPa	4.32	5.59	7.07	8.80	10.67	12.80

[$-9.0\ \text{kJ mol}^{-1}$]

(b) The BET isotherm

If the initial adsorbed layer can act as a substrate for further (for example, physical) adsorption, then, instead of the isotherm levelling off to some saturated value at high pressures, it can be expected to rise indefinitely. The most widely used isotherm dealing with multilayer adsorption was derived by Stephen Brunauer, Paul Emmett, and Edward Teller, and is called the **BET isotherm**:

$$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \quad \text{with} \quad z = \frac{p}{p^*} \tag{25.8}$$

In this expression, p^* is the vapour pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid, V_{mon} is the volume corresponding to monolayer coverage, and c is a constant which is large when the enthalpy of desorption from a monolayer is large compared with the enthalpy of vaporization of the liquid adsorbate:

$$c = \mathrm{e}^{(\Delta_{\text{des}}H^\ominus - \Delta_{\text{vap}}H^\ominus)/RT} \tag{25.9}$$

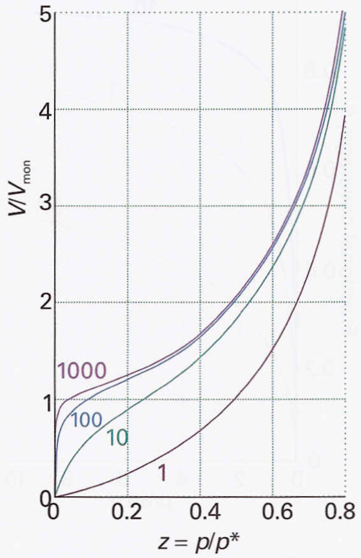

Fig. 25.19 Plots of the BET isotherm for different values of c. The value of V/V_{mon} rises indefinitely because the adsorbate may condense on the covered substrate surface.

Exploration Using eqn 25.8, generate a family of curves showing the dependence of $zV_{\text{mon}}/(1-z)V$ on z for different values of c.

Figure 25.19 illustrates the shapes of BET isotherms. They rise indefinitely as the pressure is increased because there is no limit to the amount of material that may condense when multilayer coverage may occur. A BET isotherm is not accurate at all pressures, but it is widely used in industry to determine the surface areas of solids.

Example 25.3 *Using the BET isotherm*

The data below relate to the adsorption of N_2 on rutile (TiO_2) at 75 K. Confirm that they fit a BET isotherm in the range of pressures reported, and determine V_{mon} and c.

p/kPa	0.160	1.87	6.11	11.67	17.02	21.92	27.29
V/mm^3	601	720	822	935	1046	1146	1254

At 75 K, $p^* = 76.0$ kPa. The volumes have been corrected to 1.00 atm and 273 K and refer to 1.00 g of substrate.

Method Equation 25.8 can be reorganized into

$$\frac{z}{(1-z)V} = \frac{1}{cV_{\text{mon}}} + \frac{(c-1)z}{cV_{\text{mon}}}$$

It follows that $(c-1)/cV_{\text{mon}}$ can be obtained from the slope of a plot of the expression on the left against z, and cV_{mon} can be found from the intercept at $z = 0$. The results can then be combined to give c and V_{mon}.

Answer We draw up the following table:

p/kPa	0.160	1.87	6.11	11.67	17.02	21.92	27.29
$10^3 z$	2.11	24.6	80.4	154	224	288	359
$10^4 z/(1-z)(V/\text{mm}^3)$	0.035	0.350	1.06	1.95	2.76	3.53	4.47

These points are plotted in Fig. 25.20. The least squares best line has an intercept at 0.0398, so

$$\frac{1}{cV_{\text{mon}}} = 3.98 \times 10^{-6}\ \text{mm}^{-3}$$

The slope of the line is 1.23×10^{-2}, so

$$\frac{c-1}{cV_{\text{mon}}} = (1.23 \times 10^{-2}) \times 10^3 \times 10^{-4}\ \text{mm}^{-3} = 1.23 \times 10^{-3}\ \text{mm}^{-3}$$

The solutions of these equations are $c = 310$ and $V_{\text{mon}} = 811$ mm^3. At 1.00 atm and 273 K, 811 mm^3 corresponds to 3.6×10^{-5} mol, or 2.2×10^{19} atoms. Because each atom occupies an area of about 0.16 nm^2, the surface area of the sample is about 3.5 m^2.

Self-test 25.3 Repeat the calculation for the following data:

p/kPa	0.160	1.87	6.11	11.67	17.02	21.92	27.29
V/cm^3	235	559	649	719	790	860	950

[370, 615 cm^3]

When $c \gg 1$, the BET isotherm takes the simpler form

$$\frac{V}{V_{\text{mon}}} = \frac{1}{1-z} \tag{25.10}$$

This expression is applicable to unreactive gases on polar surfaces, for which $c \approx 10^2$ because $\Delta_{\text{des}}H^\ominus$ is then significantly greater than $\Delta_{\text{vap}}H^\ominus$ (eqn 25.9). The BET isotherm

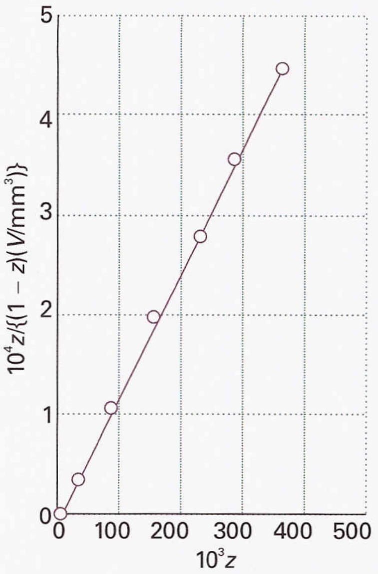

Fig. 25.20 The BET isotherm can be tested, and the parameters determined, by plotting $z/(1-z)V$ against $z = p/p^*$. The data are from Example 25.3.