

### **Adsorption using Argon and Krypton**

Krypton is used as adsorbate at 77 K for low surface area analysis while, Argon adsorption at 77 K and liquid argon temperature (87K) is often used for micro and mesopores analysis.

To measure very low surface area the number of molecules trapped in the void volume of sample cell needs to be reduced. The number of molecules left in void volume can be reduced by using adsorbate such as Krypton with low vapor pressure at liquid nitrogen temperature. The saturation pressure of Krypton at liquid nitrogen temperature is 0.35 kPa which is much lower compared to that of N<sub>2</sub> (101.3 kPa). Consequently the number of Krypton molecules in free space of sample cell, at any given relative pressure, is significantly reduced compared to that of nitrogen at liquid nitrogen temperature, though amount of adsorption will be only slightly less. Hence, Krypton adsorption at 77 K is much more sensitive and can be applied to measure surface areas down to 0.05 m<sup>2</sup>. The cross sectional area used for Krypton is 0.202 nm<sup>2</sup>.

For analysis of ultramicropores less 0.7 nm, the nitrogen adsorption at 77 K is not satisfactory. The pore width of 0.7 nm corresponds to bilayer thickness of nitrogen molecule. For ultramicropores, pore filling occurs at relative pressure of 10<sup>-7</sup> to 10<sup>-5</sup>, where the rate of diffusion and attainment of adsorption equilibration is very slow. Consequently measurement becomes time consuming and may also cause non-equilibrated adsorption isotherms with erroneous results. On the other hand argon fills the micropores of dimension 0.4-0.8 nm in most cases at much higher relative pressure as compared to nitrogen. This leads to accelerated diffusion and equilibration process and result in reduction of analysis time as well as increase in accuracy. Argon adsorption is advantageous for pore size analysis of zeolites and other microporous materials.

The typical surface area values of different supports and catalysts are summarized in Table 1.

Table 1. Typical surface area values of different support and catalyst.

Support/catalyst	BET surface area m <sup>2</sup> /g	Application
Activated carbon	500-2000	Used as support for various process
Zeolites	500-1200	Used as catalyst and support
Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> -Zeolites	100-600	Fluid catalytic cracking catalysts
Ni/Al <sub>2</sub> O <sub>3</sub>	100-150	Methanation catalyst
Cu/Zn/Al <sub>2</sub> O <sub>3</sub>		Methanol synthesis catalyst
MnO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	140-180	Catalyst for total oxidation of volatile organic carbon
Fe/K/Al <sub>2</sub> O <sub>3</sub>	20	Ammonia synthesis catalyst

### Determination of surface area using BET Equation

As discussed earlier (lecture 4), the BET equation describes the relationship between volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage. BET equation can be written in the form :

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p}{p_0} \quad \text{----- (1)}$$

p = partial pressure ; p<sub>0</sub> = saturation pressure at the experimental temperature ;

v = volume adsorbed at p; v<sub>m</sub> = volume adsorbed at monolayer coverage ; c = constant

Monolayer coverage is determined using BET equation. The  $\frac{p}{v(p_0 - p)}$  is plotted as a function of  $\frac{p}{p_0}$ . The plot is linear in the range of relative pressures  $\frac{p}{p_0} = 0.05 - 0.3$ . At higher relative pressure  $p/p_0$ , the BET plot deviates from linearity as non-ideality or pore condensation was not accounted for the derivation of BET equation.

Slope and intercept of this linear plot is used for determination of monolayer capacity  $v_m$ .

The intercept and slope from the plot is given as

$$\text{Intercept} = \frac{1}{cv_m} \quad \text{Slope} = \frac{(c-1)}{cv_m}$$

Then the monolayer volume  $v_m$  is given as ,  $v_m = \frac{1}{\text{slope} + \text{intercept}} (STP)$

The total number of  $N_2$  molecules adsorbed corresponding to monolayer volume  $v_m$  can be calculated as

$$\text{No. of } N_2 \text{ molecules} = \frac{v_m (m^3) \times 6.02 \times 10^{23} (\text{molecules} / \text{mol})}{0.0224 (m^3 / \text{mol})}$$

Now , each adsorbed  $N_2$  molecule occupies an area of surface comparable to its cross section area of  $0.162 \text{ nm}^2$ .

$$SA(m^2) = \left[ \frac{v_m (m^3) \times 6.02 \times 10^{23} (\text{molecules} / \text{mol})}{(0.0224 m^3 / \text{mol})} \right] \times 16.2 \times 10^{-20} (m^2 / N_2 \text{ molecule})$$

Or  $SA(m^2) = v_m (m^3) \times 4.36 \times 10^6 (m^{-1}) = 4.36 \times 10^6 v_m$

**Solved problem :**

1. Nitrogen was employed to determine the surface area of 1.0 g sample of silica gel and results obtained shown in table below. The sample of silica gel was maintained at the normal boiling point of liquid nitrogen (77K). One molecule of nitrogen occupies  $16.2 \times 10^{-20} \text{ m}^2$  area of plane surface. Calculate the specific surface area of silica gel by the BET method. The saturated vapor pressure  $p_0$  of nitrogen at 77K is 101.3 kPa.

Equilibrium Pressure, p [kPa]	5.0	6.3	7.5	9.0	11.2
Volume adsorbed, (STP), $V \times 10^6$ [m <sup>3</sup> ]	6.7	7.0	7.2	7.4	7.7

**Solution :**

The BET equation in following form is used. 
$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{p}{p_0}$$

The  $\frac{p}{V(p_0 - p)}$  is plotted as function of  $\frac{p}{p_0}$ . The plot is shown in Fig. 3.

Table 1. Calculation for plot of BET equation

$v$ $m^3$	$p$ $kPa$	$p_o$ $kPa$	$p/p_o$	$p/[v(p_o - p)]$ $m^{-3}$
6.7E-06	5	101.3	0.049	7.75E+03
7.0E-06	6.3	101.3	0.062	9.47E+03
7.2E-06	7.5	101.3	0.074	1.11E+04
7.4E-06	9	101.3	0.089	1.32E+04
7.7E-06	11.2	101.3	0.111	1.61E+04

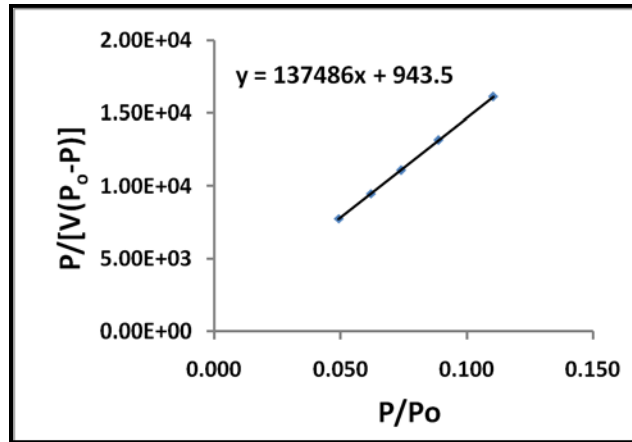


Fig. 3. Linear plot of BET equation

Intercept =  $943.5 \text{ m}^{-3}$  ; Slope =  $137486 \text{ m}^{-3}$

$$\text{Monolayer volume } V_m = \frac{1}{\text{slope} + \text{intercept}} = \frac{1}{137486 + 943.5} = 7.22 \times 10^{-6} \text{ m}^3 \text{ (STP)}$$

Then surface area for 1 gm sample can be determined as :

$$SA = \left[ \frac{7.22 \times 10^{-6} \text{ m}^3 \times 6.02 \times 10^{23} \text{ molecules / mol}}{22400 \times 10^{-6} \text{ m}^3 / \text{mol}} \right] \times 16.2 \times 10^{-20} \text{ m}^2 / N_2 \text{ molecule}$$

$$= \mathbf{31.4 \text{ m}^2}$$

As initially 1 gm sample was used, specific surface area of sample = 31.4 m<sup>2</sup>/g

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