

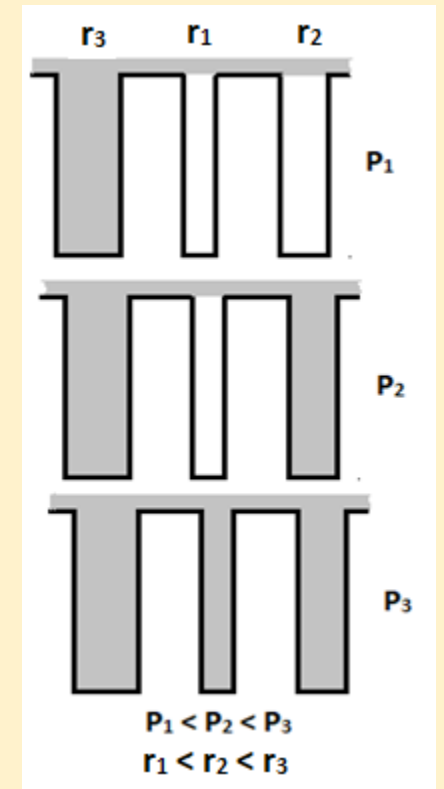
Solid catalysts

Pore volume distribution

- Effectiveness of the internal surface for catalytic reactions depend on both the (i) **volume of the void space (v_g)** and (ii) **the radius of the void regions**
- Knowing the pore size distribution gives an idea about accessibility of the reactants to the active sites. It is, therefore, necessary to know the distribution of the void volume in the catalyst according to the size of the pores
- The two methods for measuring the distribution of pore volumes are –
 - **Mercury penetration method or Hg porosimetry**
 - **Nitrogen desorption technique**

Mercury penetration method (Hg porosimetry)

- Here it is assumed that material is composed of a collection of cylindrical pores of radius, r
- Mercury has a significant surface tension and does not go into the pores at atmospheric pressure
- As pressure is increased, Hg is forced into the pores and the pressure required to force Hg into the pores depend on the pore radius



Mercury penetration method (Hg porosimetry)

- This method is used to **determine the pore volume and the pore size distribution of large pores** (radii > 100 Å)
- The relationship between the pore size and applied pressure, P is obtained from force balance (applied force = force due to surface tension)

$$\pi r^2 P = -2\pi r \sigma \cos\theta$$

where σ = surface tension

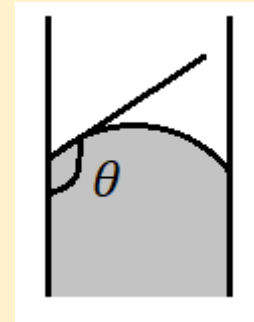
θ = contact angle between the liquid and pore walls

These values for Hg are typically, $\sigma = 480$ dyne/cm (0.48 N/m) in air at 293 K
and $\theta = 140^\circ$

$$r(\text{\AA}) = \frac{1.07 \times 10^6}{P(\text{psia})}$$

or

$$r(\text{nm}) = \frac{7.37 \times 10^8}{P(\text{Pa})}$$



At the maximum experimental pressure (system pressure) of 10^4 psia, $r = 107\text{\AA} = 10.7$ nm. This is the **minimum pore radius measured by this method**

Nitrogen desorption technique

- This method is used to determine the **distribution of pores with diameters smaller than 200 Å** (20 nm)
- In this method, the **Kelvin equation** is used to relate the pore radius to the ambient pressure
- The pore material is exposed to high pressures of N₂ such that $P/P_o \rightarrow 1$
- At high pressure, multilayer adsorption occurs and ultimately the adsorbed films are thick enough to bridge the pore.
- Further uptake of N₂ results in capillary condensation (occurs first in the smaller pores)
- If the pressure is then reduced in increments to get the desorption isotherm, where the largest pores will be emptied first (vapour pressure decreases with capillary size)
- The Kelvin equation gives the relationship between vapour pressure and the radius of the concave surface of the meniscus of liquid

$$r - \delta = \frac{-2\sigma v_l \cos\theta}{RT \ln(P/P_o)}$$

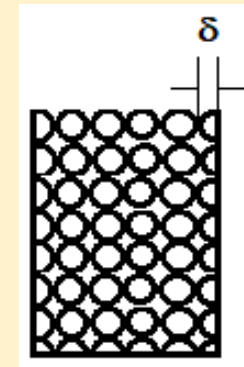
where σ = surface tension v_l = molal volume of the condensed liquid (eg. N₂)
 θ = contact angle between surface and condensate
 δ = thickness of the monolayer adsorbed on the pore wall

For N₂, the surface is completely wetted (unlike Hg) and $\theta = 0^\circ$ and $\cos\theta = 1$

$$\delta(\text{Å}) = 7.34 \left(\log \frac{P_o}{P} \right)^{1/3}$$

For N₂, at -195.8° C (NBP)

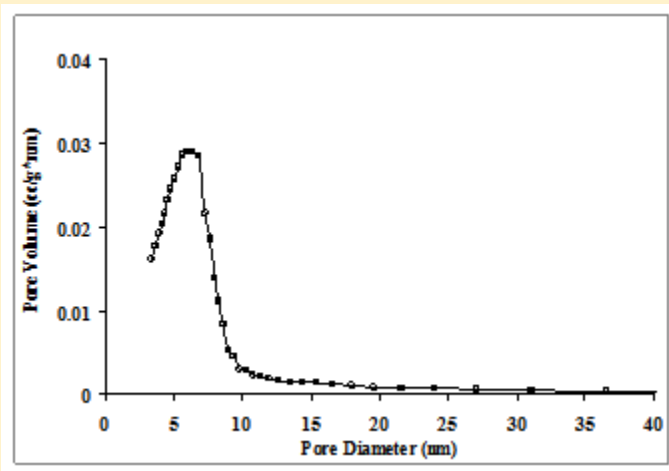
$$(r - \delta)(\text{Å}) = 9.52 \left(\log \frac{P_o}{P} \right)^{-1}$$



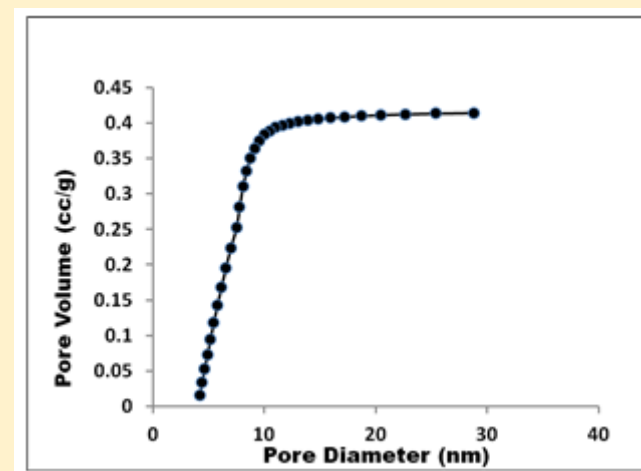
Some of the N₂ is adsorbed on the surface and is not present because of capillary condensation. Hence, Kelvin equation has to be corrected for the thickness of the adsorbent layer

Nitrogen desorption technique

- For a chosen $\frac{P}{P_0}$, the equation $\left[(r - \delta)(\text{\AA}) = 9.52 \left(\log \frac{P_0}{P} \right)^{-1} \right]$ gives the **pore radius above which all the pores will be empty**, pore radius less than this will be filled by condensed vapour
- If the amount of desorption is measured at different $\frac{P}{P_0}$, the pore volume corresponding to various radii can be evaluated
- Differentiation of the curve for the cumulative pore volume versus radius gives the distribution of the pore volume
- **By combining the Hg porosimetry and N₂ desorption technique**, pore volume information can be obtained **over the complete range of radii** in a catalyst pellet containing macro and micro pores



Differential pore volume distribution



Cumulative pore volume distribution

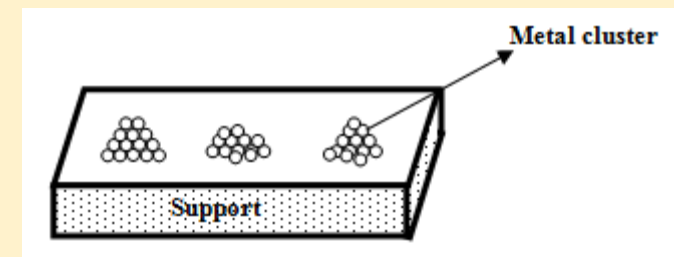
Dispersed state of the active agent

- A large majority of catalytic reactions involve metallic systems as the active species
- The **location and state of the active metal on the support largely depend on the preparation method of the catalyst**

When prepared by impregnation method, more active metals are expected to concentrate on the surface of support, whereas in bulk preparation method active metals are trapped more within the bulk matrix

- Often these metals exist as clusters on the support surface and thereby, **only a fraction of the total deposited metal is actually exposed to the incoming reactant molecules** for participation in a reaction
- Thus, the dispersion of the metal on the supported catalysts is of primary importance

$$Dispersion = \frac{\text{number of surface metal atoms}}{\text{total number of metal atoms}} = \frac{N_s}{N}$$



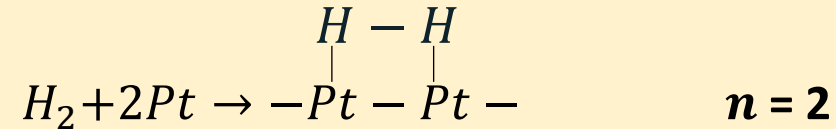
- Estimation of **metal dispersion, metal surface area, crystallite size** can be carried out using methods such as **chemisorption, TEM and XRD**

Chemisorption

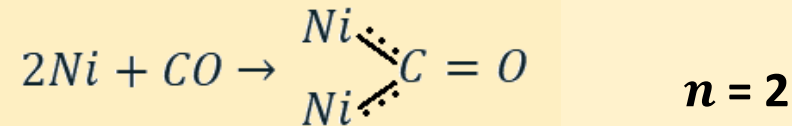
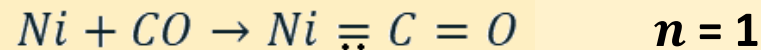
- **Chemisorption technique** gives direct measurement of the **number of exposed surface atoms**. This method measures **quantity of gas adsorbed selectively on the metal at monolayer coverage**
- This technique can be used to **determine the dispersion of metal in catalysts** and estimate the active area of surface metal species
- The sample is exposed to a gas that can chemisorb on the active metal. At monolayer coverage, the average number of surface metal atoms associated with adsorption of each gas molecule is determined
- The adsorbate gas is chosen for a given catalyst such that there is **irreversible (or weakly reversible) chemisorption on the metal and minimum or no adsorption on the support**
- H₂ and CO are the most commonly used adsorbate gases.
- Knowledge of the **stoichiometry of the chemisorption reaction** is required for accurate determination of metal dispersion and the active metal area
- Stoichiometry of the gas adsorption depends on the gas and the metal surface

- **Chemisorption stoichiometry (n)** is defined as the **number of metal atoms to which one adsorbate gas molecule can attach**

(1) Adsorption of H_2 on Pt is **dissociative adsorption**



(2) Adsorption of CO on Ni is **non-dissociative adsorption**



- The number of surface metal atoms (N_s) was calculated from

$$N_s = \frac{v}{v_m} \times N_o \times n$$

v = volume of gas chemisorbed

v_m = molar volume of gas

n = stoichiometry of chemisorption

N_o = Avogadro number

- The total number of metal atoms in the catalyst (N) can be calculated from the metal content of the catalyst

$$Dispersion = \frac{\text{number of surface metal atoms}}{\text{total number of metal atoms}} = \frac{N_s}{N}$$

- Surface area of the active metal sites (S_M), $S_M = N_s \times S$ where S = surface area occupied by one metal atom

4) Quality of the active surface

Acidity of the catalyst

- The acidic sites are **titrated with an organic base** (quinoline, pyridine etc) or ammonia gas
- Total uptake of base is a measure of its acidity
- Temperature programmed desorption (TPD) studies can be used to estimate the acidic and basic sites on the catalyst surface by measuring the desorbed molecules from the sample surface
- Eg., TPD of NH_3 is used to study acidic sites on the surface of Al_2O_3 catalyst

Electron paramagnetic resonance (EPR) spectroscopy

- EPR is a spectroscopic technique for **studying materials with unpaired electrons**
- The **electron spins are excited** in this method
- It is a particularly useful tool to **investigate the electronic structure of catalysts**, which is fundamental to understand their reactivity
- Presence of unpaired electrons determines how the catalyst interacts with the reactant species