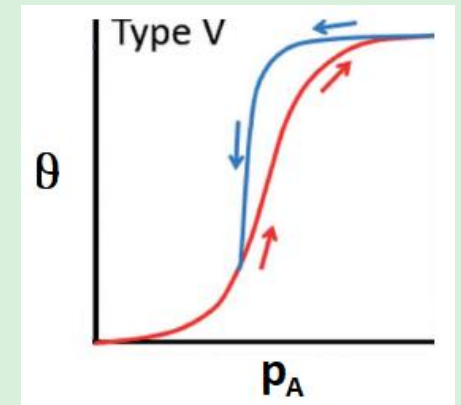
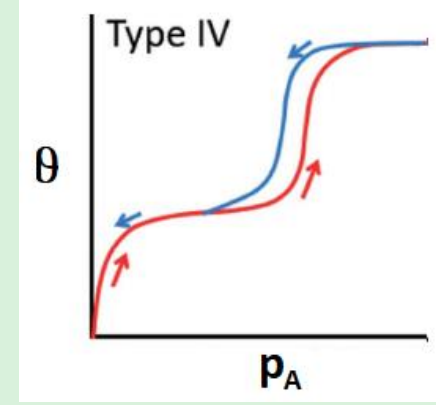
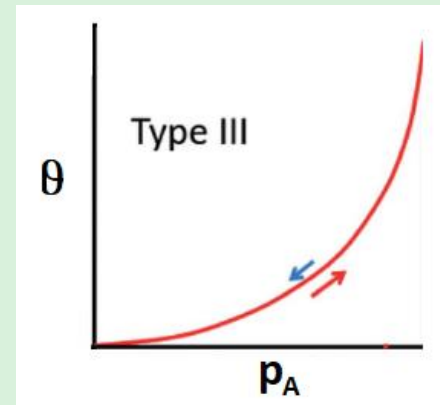
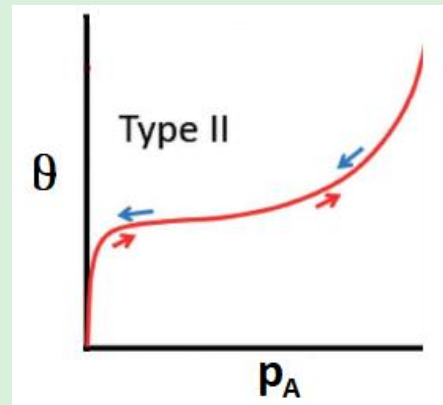
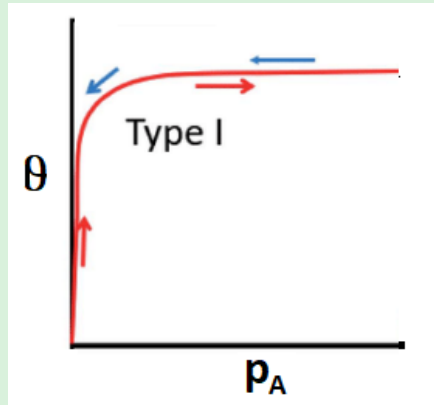


# Adsorption

Book: *Chemical Engineering Kinetics*, J. M. Smith, 3<sup>rd</sup> Edition (Chapter 7), 2<sup>nd</sup> Edition (Chapter 8,9)

# Experimental equilibrium adsorption data

Equilibrium adsorption data (equilibrium fractional coverage ( $\theta$ ) versus pressure) obtained from experiments show five different isotherms



Red lines indicate adsorption while the blue lines denote desorption

All curves are linear at low  $p_A$  and fit the equation  $\theta = K_A p_A$  or  $C_{AS} = K_A C_t p_A$

**Type I** fits the Langmuir isotherm over the whole range eg., activated carbon (surface area = 1000  $m^2/g$ ) having very narrow pores

**Type II** is seen in non-porous solids

**Type III** is seen in porous solids with the cohesive force between adsorbed molecule being greater than the adhesive force between adsorbent and adsorbed molecule eg., water vapour on graphite

**Type IV** is observed in porous solids with staged adsorption (first monolayer then build-up of other layers)

**Type V** is seen in porous solids with adhesive force between adsorbate molecule and adsorbent being greater than cohesive force between adsorbate molecules

# Freundlich isotherm

- The Freundlich equation is an empirical expression representing the isothermal variation of adsorption of a liquid or gas onto the surface of a solid material

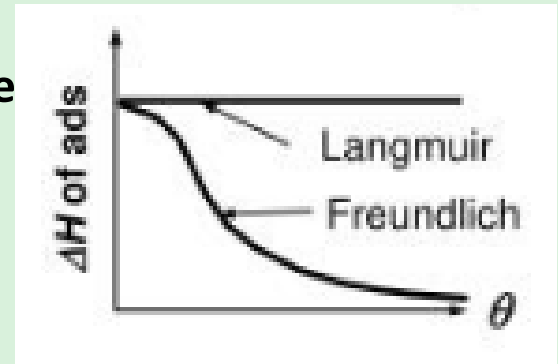
- Mathematically it can be expressed as  $\theta = K p_A^{1/n}$

where  $\theta$  = surface coverage;  $p_A$  = partial pressure of adsorbate gas;  $K, n$  = empirical constants at a particular temp,  $n > 1$

It is also expressed as  $\frac{x}{m} = K p_A^{1/n}$  where  $x$  = mass of adsorbate;  $m$  = mass of adsorbent

Linearized form is :  $\ln\theta = \ln K + \frac{1}{n} \ln p_A$  or  $\ln\left(\frac{x}{m}\right) = \ln K + \frac{1}{n} \ln p_A$

- Assumption: There is a **logarithmic change of adsorption enthalpy ( $\Delta H_a$ ) with surface coverage ( $\theta$ )** – surface is **heterogenous**
- Fits experimental data over a reasonable range of partial pressure (or concentration)
- Eg.,  $H_2$  adsorption on tungsten,  $SO_2$  adsorption on activated carbon



## Limitations of Freundlich Isotherm

Fails at high pressure - can give  $\theta > 1$  for high  $p_A$

Cannot be easily extended to more than one component

# Temkin isotherm

- Temkin isotherm is usually used for systems with **heterogeneous surface energy**
- This isotherm takes into account the effects of **indirect adsorbate-adsorbate interactions** on adsorption process
- Mathematically it is represented as  $\theta = k_1 \ln(k_2 p_A)$   
where  $\theta$  = surface coverage;  $p_A$  = partial pressure of adsorbate gas;  $k_1, k_2$  = adsorption constants

- The linear form of the equation is:

$$\theta = k_1 \ln(k_2) + k_1 \ln(p_A)$$

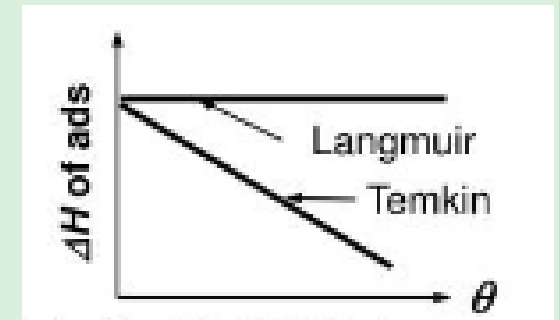
- Temkin found out experimentally the **heat of adsorption** of all molecules in the layer **decreases linearly** as a result of increase surface coverage due to adsorbate-adsorbate interactions

$$\Delta H_a = \Delta H_{ao}(1 - \alpha\theta)$$

## Limitations of Temkin Isotherm

Limiting value of  $\theta$  not predicted correctly

Cannot handle more than one component

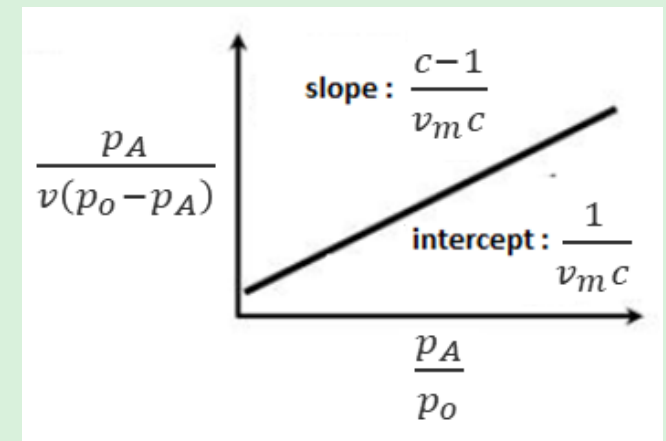


# BET (Brunauer-Emmett-Teller) isotherm

- Brunauer, Emmett and Teller derived the first isotherm for **multilayer adsorption**
- The theory of multilayer adsorption assumes that physisorption results in the formation of multilayer adsorption. After the **formation of the monolayer**, the **adsorption process can continue** with the formation of **multilayer** involving the second layer, third layer and so on.
- The **heat of adsorption** of additional layer equals to the **latent heat of condensation**
- The theory also assumes that the solid surface has **uniform sites of adsorption** and that **adsorption at one site does not affect adsorption at neighbouring sites**

- The equation for BET is given by 
$$\frac{p_A}{v(p_o - p_A)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p_A}{p_o}$$

where  $p_o$  = saturation vapour pressure of adsorbed gas at that temperature;  
 $p_A$  = partial pressure of gas A;  $c$  = constant for a particular system and temp;  
 $v_m$  = volume of gas adsorbed at monolayer;  
 $v$  = volume of gas adsorbed at partial pressure  $p_A$



- BET equation fits all known adsorption isotherms (types I to V) for various types of solid reasonably well
- BET isotherm **works best** in the  $\frac{p_A}{p_o}$  range of **0.05 - 0.35**
- The most significant contribution of BET isotherm is that it provides a **means of accurate determination of the surface area of a solid**

# Example

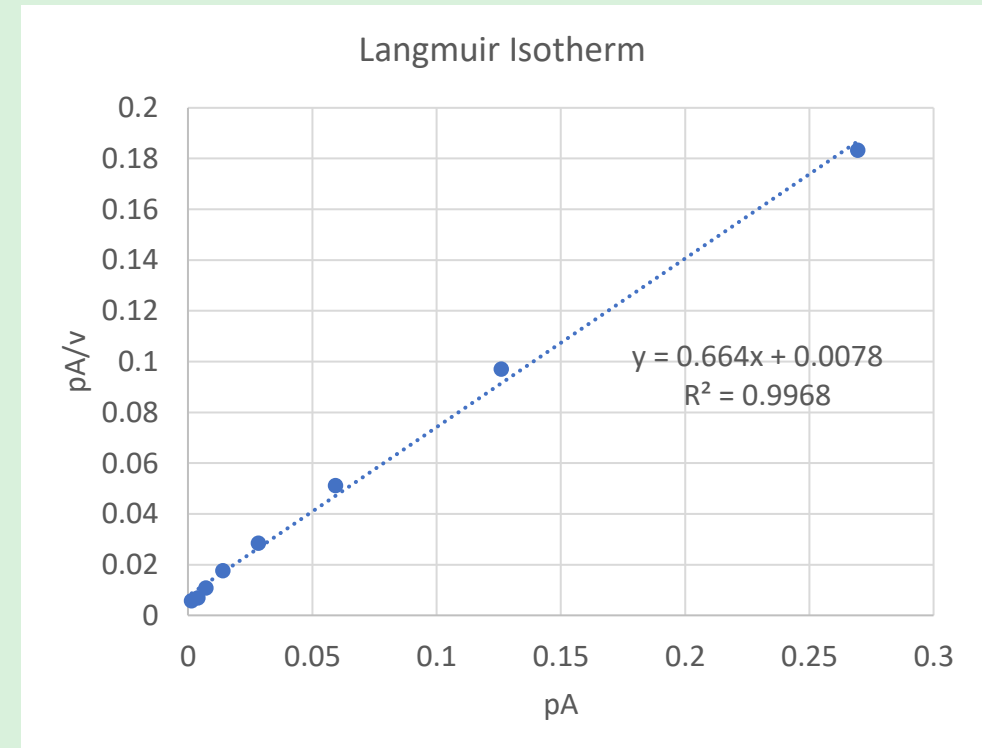
The chemisorption of hydrogen gas on copper powder and the equilibrium data from experiments at 25°C are as follows:

Hydrogen pressure, mm Hg	1.05	2.95	5.40	10.65	21.5	45.1	95.8	204.8
Volume adsorbed, cm <sup>3</sup> at 0°C and 1 atm	0.239	0.564	0.659	0.800	0.995	1.160	1.300	1.471

What kind of isotherm fits this data?

Langmuir Isotherm (Linear form):  $\frac{p_A}{v} = \frac{1}{K_A v_m} + \frac{1}{v_m} p_A$

pA (mm Hg)	pA (atm)	vol adsorbed, v (cm <sup>3</sup> )	pA/v
1.05	0.001381579	0.239	0.006
2.95	0.003881579	0.564	0.007
5.4	0.007105263	0.659	0.011
10.65	0.014013158	0.8	0.018
21.5	0.028289474	0.995	0.028
45.1	0.059342105	1.16	0.051
95.8	0.126052632	1.3	0.097
204.8	0.269473684	1.471	0.183



## Freundlich isotherm

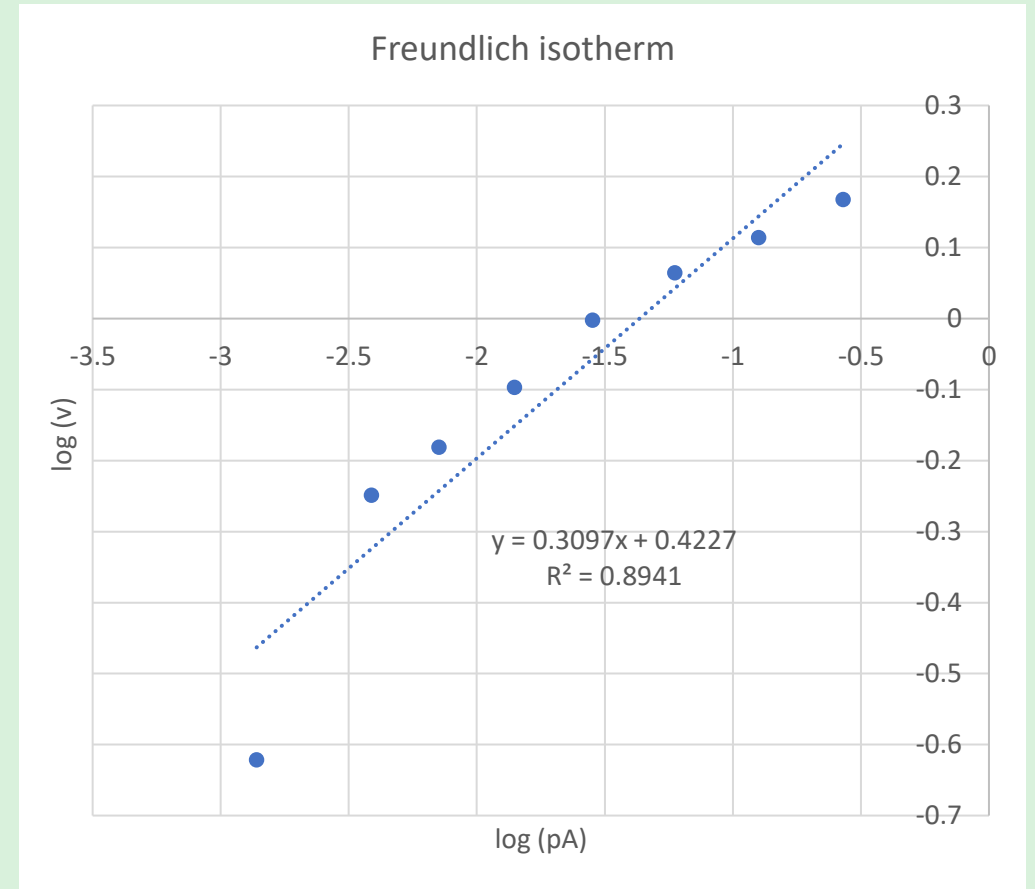
$$\theta = Kp_A^{1/n}$$

$$\frac{v}{v_m} = Kp_A^{1/n}$$

$$v = v_m K p_A^{1/n}$$

$$\log v = \log(Kv_m) + \frac{1}{n} \log p_A$$

pA (mm Hg)	pA (atm)	vol adsorbed, v (cm <sup>3</sup> )	log pA	log v
1.05	0.001381579	0.239	-2.85962429	-0.622
2.95	0.003881579	0.564	-2.41099158	-0.249
5.4	0.007105263	0.659	-2.14841983	-0.181
10.65	0.014013158	0.8	-1.85346398	-0.097
21.5	0.028289474	0.995	-1.54837513	-0.002
45.1	0.059342105	1.16	-1.22663705	0.064
95.8	0.126052632	1.3	-0.89944808	0.114
204.8	0.269473684	1.471	-0.56948364	0.168



## Temkin isotherm

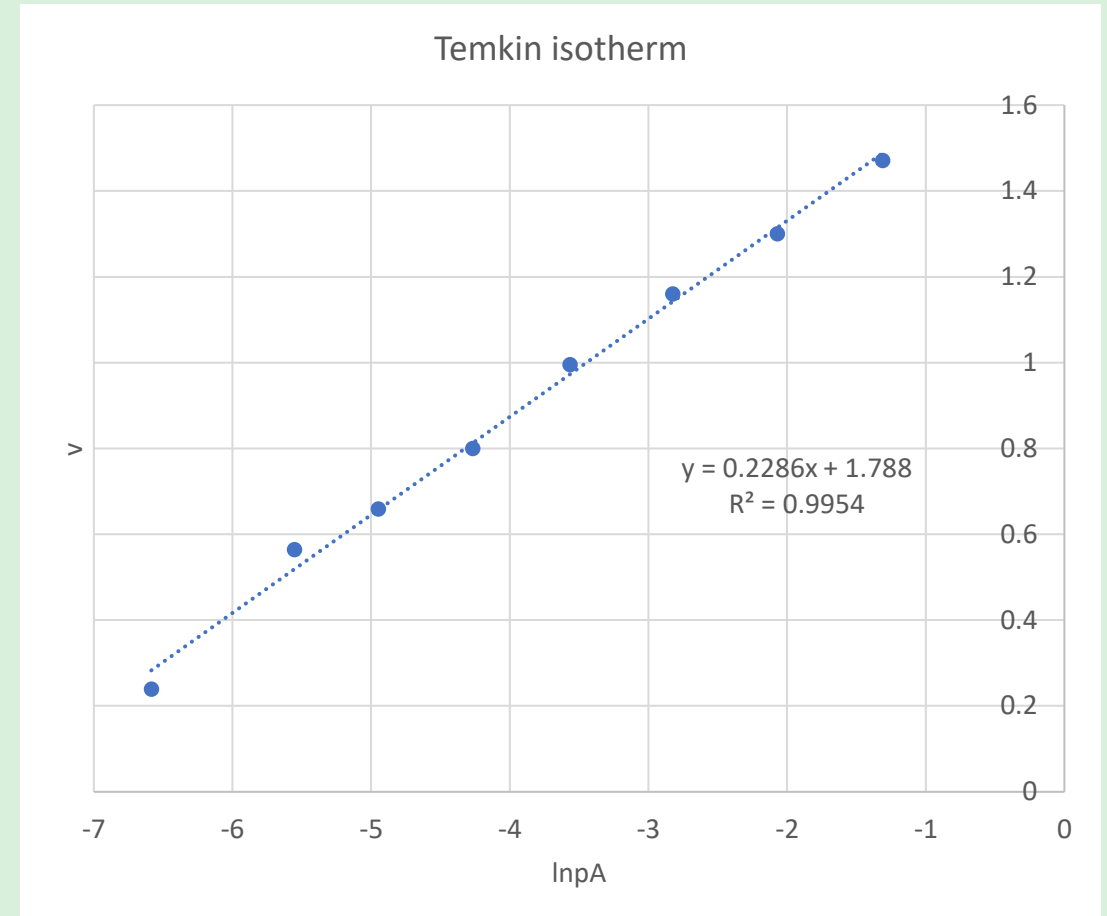
$$\theta = k_1 \ln(k_2 p_A)$$

$$\frac{v}{v_m} = k_1 \ln(k_2 p_A)$$

$$v = v_m k_1 \ln(k_2 p_A)$$

$$v = v_m k_1 \ln(k_2) + v_m k_1 \ln(p_A)$$

pA (mm Hg)	pA (atm)	vol adsorbed, v (cm <sup>3</sup> )	ln pA
1.05	0.001381579	0.239	-6.58452827
2.95	0.003881579	0.564	-5.55151326
5.4	0.007105263	0.659	-4.94691948
10.65	0.014013158	0.8	-4.26775854
21.5	0.028289474	0.995	-3.5652655
45.1	0.059342105	1.16	-2.82443619
95.8	0.126052632	1.3	-2.07105575
204.8	0.269473684	1.471	-1.31128454



It can be seen from the plots that both Langmuir and Temkin isotherms fit the data reasonably well