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2

Adsorption on catalyst surface

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1

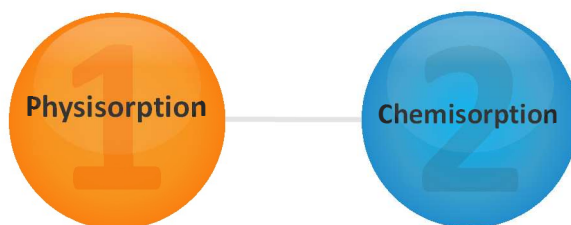
2.1 The extent of adsorption

- The extent of surface coverage is normally expressed as the fractional coverage, θ :

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}}$$

- The fractional coverage is often expressed in terms of the volume of adsorbate adsorbed by $\vartheta = V/V_{\infty}$,
- V_{∞} = the volume of adsorbate corresponding to complete monolayer coverage.

Adsorption on catalyst surface



Based on the type of bonding

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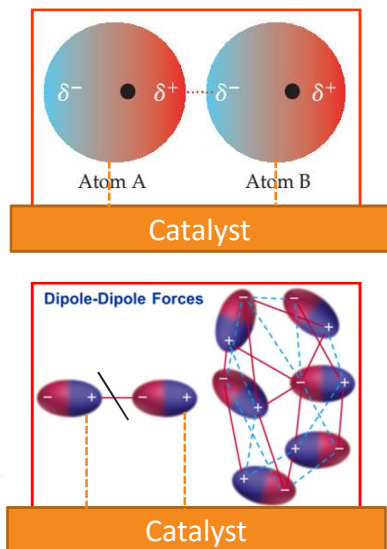


PHYSISORPTION

Physisorption (an abbreviation of 'physical adsorption'), there is a van der Waals interaction.

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Physical Adsorption



There is a van der Waals interaction (e.g. dispersion or a dipolar interaction between the adsorbate and the substrate).

Van der Waals interactions have a long range but are weak, and the energy released when a particle is physisorbed is of the same order of magnitude as the enthalpy of condensation.

Such small energies can be absorbed as vibrations of the lattice and dissipated as thermal motion, and a molecule across the surface will gradually lose its energy and finally adsorb to it in the process called accommodation.

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5

Enthalpy of physisorption measurement

Enthalpy of physisorption measurement

The enthalpy of physisorption can be measured by monitoring the rise in temperature of a sample of known heat capacity, and typical values are in the region of 20 kJ mol^{-1} (Table .1).

Adsorbate	$\Delta_{\text{ad}} H^\circ / (\text{kJ mol}^{-1})$
CH_4	-21
H_2	-84
H_2O	-59
N_2	-21

This small enthalpy change is insufficient to lead to bond breaking, so a physisorbed molecule retains its identity, although it might be distorted by the presence of the surface..

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6



CHEMISORPTION

In chemisorption (an abbreviation of 'chemical adsorption'), the molecules (or atoms) stick to the surface by forming a chemical (usually covalent) bond,

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Chemisorbed molecule

- The molecules (or atoms) stick to the surface by forming a **chemical (usually covalent) bond**.
- The molecules tend to find sites that maximize their **coordination number** with the substrate.
- **The enthalpy** of chemisorption is very much greater than that for physisorption, and typical values are in the region of **200 kJ mol⁻¹** (Table. 2).
- **The distance** between the surface and the closest adsorbate atom is also typically **shorter** for chemisorption than for physisorption.
- A chemisorbed molecule may be **torn apart** at the demand of the unsatisfied valences of the surface atoms.
- The existence of **molecular fragments** on the surface as a result of chemisorption is one reason why solid surfaces catalyse reactions.

Chemisorbed molecule

Table 2
Maximum
observed
enthalpies of
chemisorption,
kJ/mol

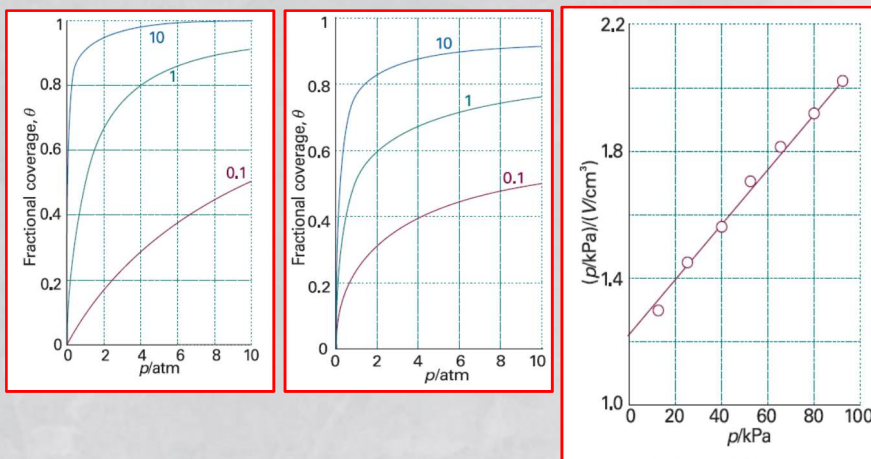
Adsorbate	Adsorbent (substrate)		
	Cr	Fe	Ni
CH ₄	-427	-285	-243
CO		-192	
H ₂	-188	-134	
NH ₃		-188	-155

- Chemisorption **must be exothermic**, except in special cases.

Chemisorbed molecule

- A **spontaneous process requires $\Delta G < 0$** , because the translational freedom of the adsorbate is reduced when it is adsorbed, ΔS is negative. Therefore, in order for $\Delta G = \Delta H - T\Delta S$ to be negative, ΔH must be negative (that is, the process is exothermic).
- The **enthalpy of adsorption** depends on the extent of surface coverage, mainly because the adsorbate particles interact.
- If the **particles repel each other** (as for CO on palladium) the adsorption becomes less exothermic (the enthalpy of adsorption less negative) as coverage increases.
- If the **adsorbate particles attract one another** (as for O₂ on tungsten), then they tend to cluster together in islands, and growth occurs at the borders.

2.3 Adsorption isotherms: The Langmuir adsorption isotherm



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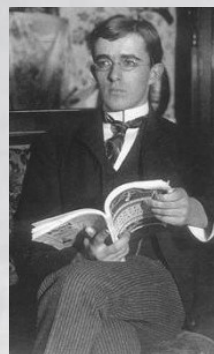
11

2.3 Adsorption isotherms: The Langmuir adsorption isotherm

Assumptions:

1. Adsorption cannot proceed beyond monolayer coverage.
2. All sites are equivalent and the surface is uniform.
3. Adsorption of a molecule at a site is independent of the occupation of neighboring sites.

The dynamic equilibrium is

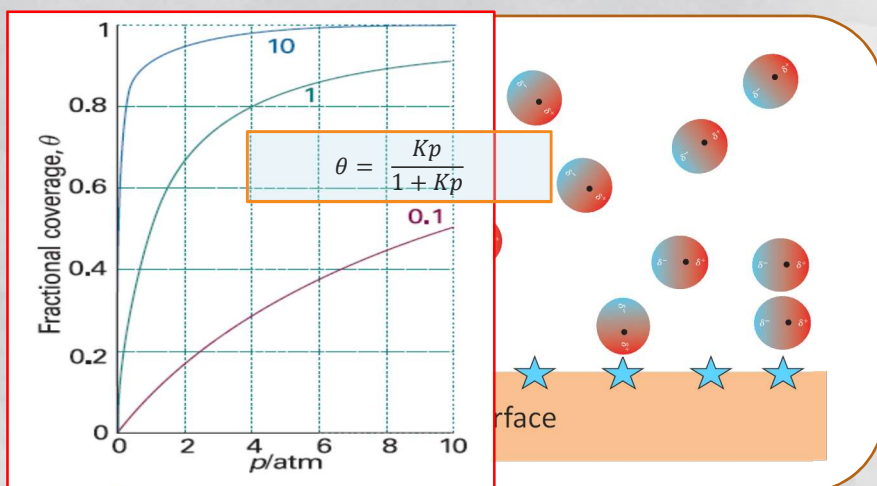


American chemist and physicist Irving
Langmuir (1881 - 1957).

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2

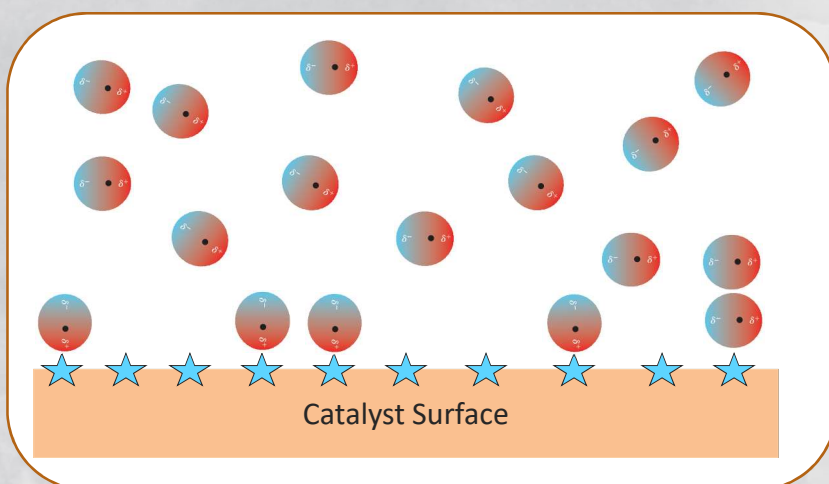
2.3 Adsorption isotherms: The Langmuir adsorption isotherm



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13

2.3 Adsorption isotherms: The Langmuir adsorption isotherm

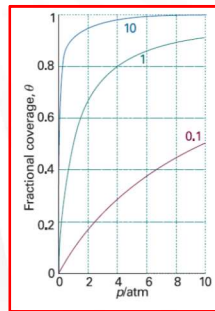


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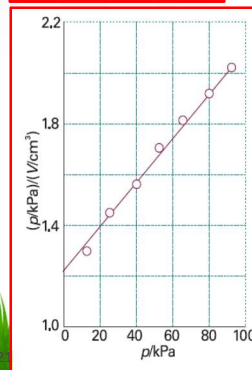
14

Application of the Langmuir equation

$$\theta = \frac{Kp}{1 + Kp}$$



$$\frac{P}{V} = \frac{P}{V_{\infty}} + \frac{1}{KV_{\infty}}$$



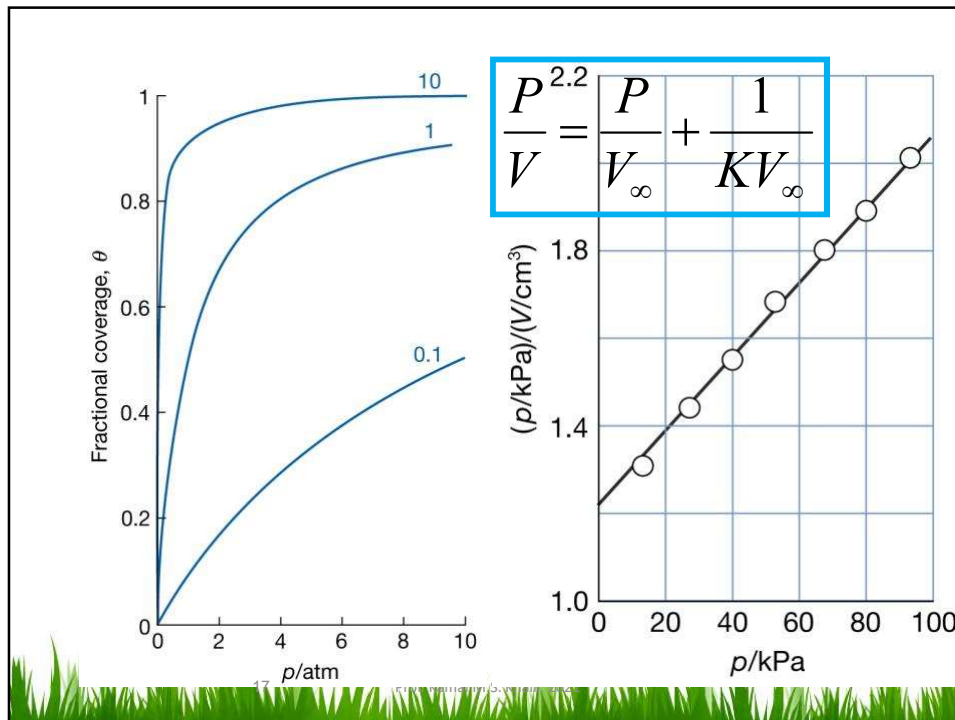
Test for The Langmuir adsorption isotherm

$$\theta = \frac{Kp}{1 + Kp}$$

$$Kp = Kp\theta + \theta$$

$$Kp = Kp \frac{V}{V_{\infty}} + \frac{V}{V_{\infty}}$$

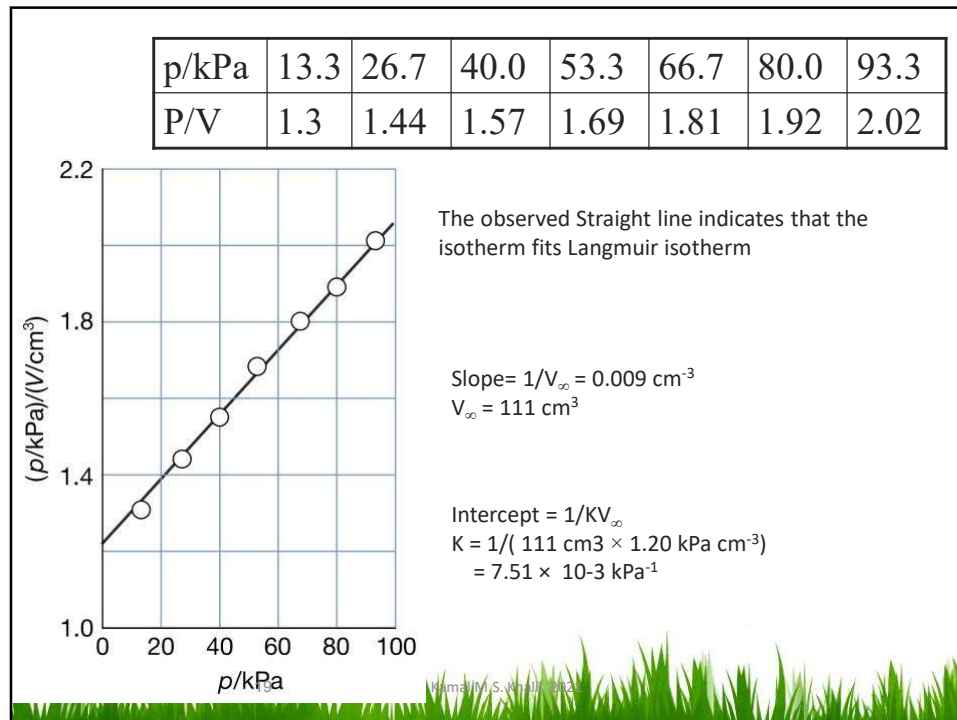
$$\frac{P}{V} = \frac{P}{V_{\infty}} + \frac{1}{KV_{\infty}}$$



The Langmuir adsorption isotherm

Example 28. 1:

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
V/cm	10.2	18.6	25.5	31.5	36.9	41.6	46.1
P/V	1.3	1.44	1.57	1.69	1.81	1.92	2.02



The Langmuir adsorption isotherm

$$\theta = \frac{(Kp)^{1/2}}{1 + (Kp)^{1/2}}$$

Isosteric enthalpy of adsorption $\Delta_{ad}H^\phi$

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

$$Kp = \frac{\theta}{1-\theta}$$

$$\ln K + \ln p = \text{const.}$$

21

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Isosteric enthalpy of adsorption

$$\left(\frac{\partial \ln p}{\partial T} \right)_\theta = - \left(\frac{\partial \ln K}{\partial T} \right)_\theta$$

$$\therefore \left(\frac{\partial \ln p}{\partial T} \right)_\theta = - \left(\frac{\partial \ln K}{\partial T} \right)_\theta = - \frac{\Delta_{ad}H^\phi}{RT^2} = \frac{d(1/T)}{dT} \cdot \frac{\Delta_{ad}H^\phi}{R}$$

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

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Isosteric enthalpy of adsorption

Example :

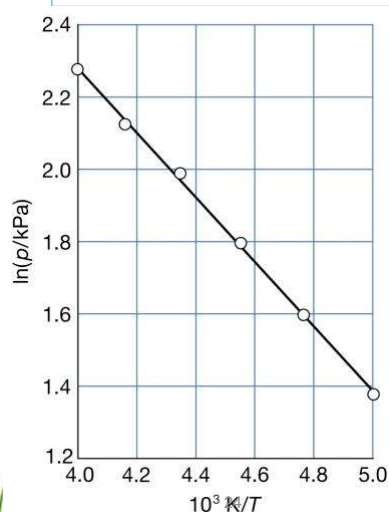
T/K	200	210	220	23	240	250
p/kPa	4.00	4.95	6.03	7.20	8.47	9.85

$10^3/(T/K)$	5.00	4.76	4.55	4.35	4.17	4.00
Ln (p/kPa)	1.39	1.60	1.80	1.97	2.14	2.29

23

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Isosteric enthalpy of adsorption



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

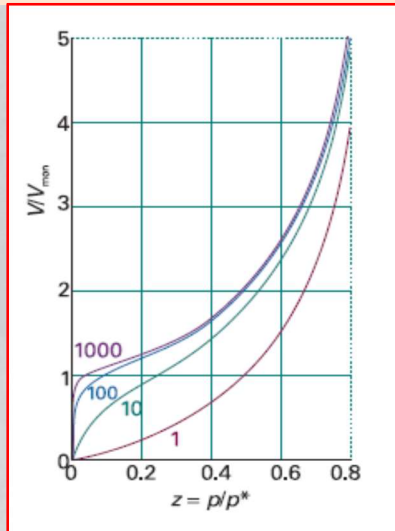
Slope = -0.904

$$\Delta_{ad} H^\phi = -(0.904 \times 10^3 K) \times R$$

$$= 7.52 \text{ kJ mol}^{-1}$$

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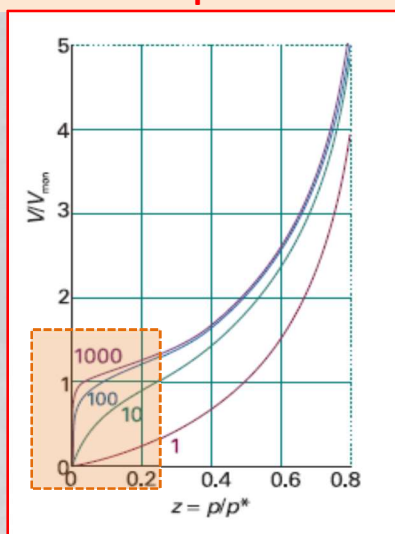
2.3 Adsorption isotherms: The BET adsorption isotherm



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25

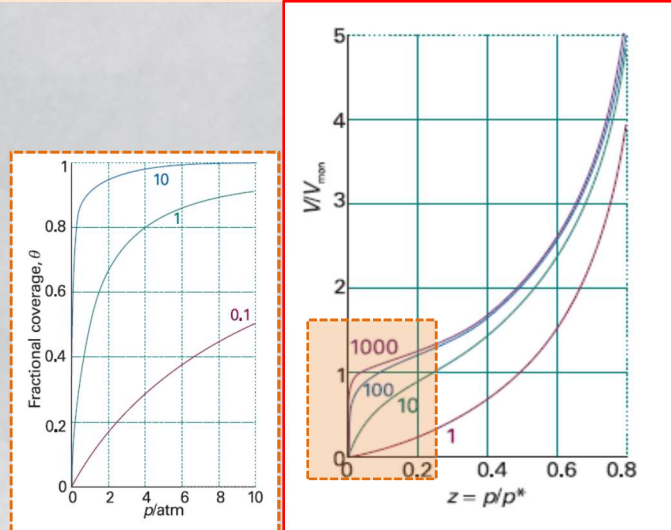
2.3 Adsorption isotherms: The BET adsorption isotherm



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26

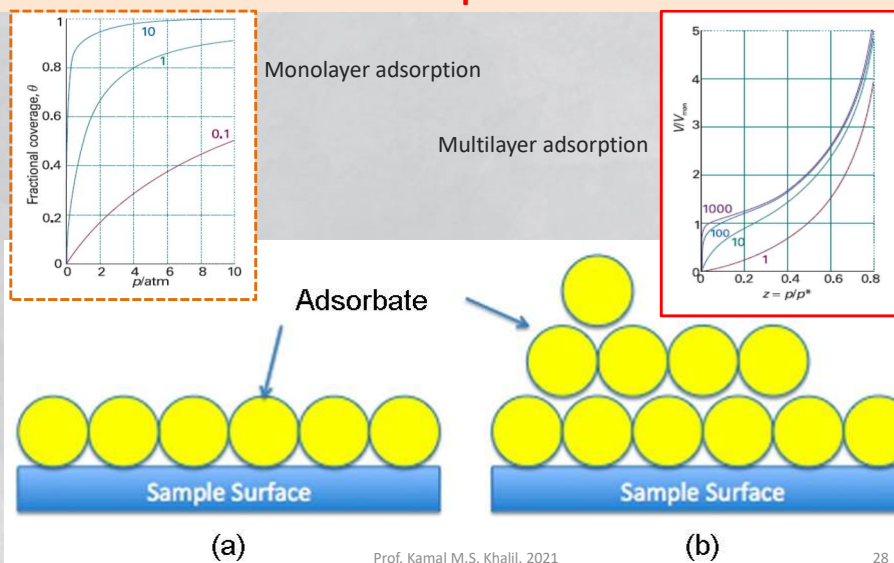
2.3 Adsorption isotherms: The BET adsorption isotherm



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27

2.3 Adsorption isotherms: The BET adsorption isotherm



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28

2.3 Adsorption isotherms: The BET adsorption isotherm

- Here we deal with the case of **multilayer adsorption**.
- In this case the adsorbed layer can act as a substrate for further (physical) adsorption, so the isotherm can be expected to rise **indefinitely**.
- The most widely used isotherm for dealing with this type of adsorption is the **Brunauer, Emmett, and Teller isotherm**, which called the **BET isotherm**.

$$\frac{V}{V_{mon}} = \frac{c}{(1-z)\{1-(1-C)z\}} \quad \text{with } z = \frac{P}{P^*} \quad Eq(8)$$

$$c = e^{(\Delta_{des}H^0 - \Delta_{vap}H^0)/RT}$$

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29

2.3 Adsorption isotherms: The BET adsorption isotherm

$$\frac{V}{V_{mon}} = \frac{c}{(1-z)\{1-(1-C)z\}} \quad \text{with } z = \frac{P}{P^*} \quad Eq(8)$$

$$c = e^{(\Delta_{des}H^0 - \Delta_{vap}H^0)/RT}$$

where:

p^* = vapour pressure above the multiplayer adsorbate,
which resembles a pure liquid,

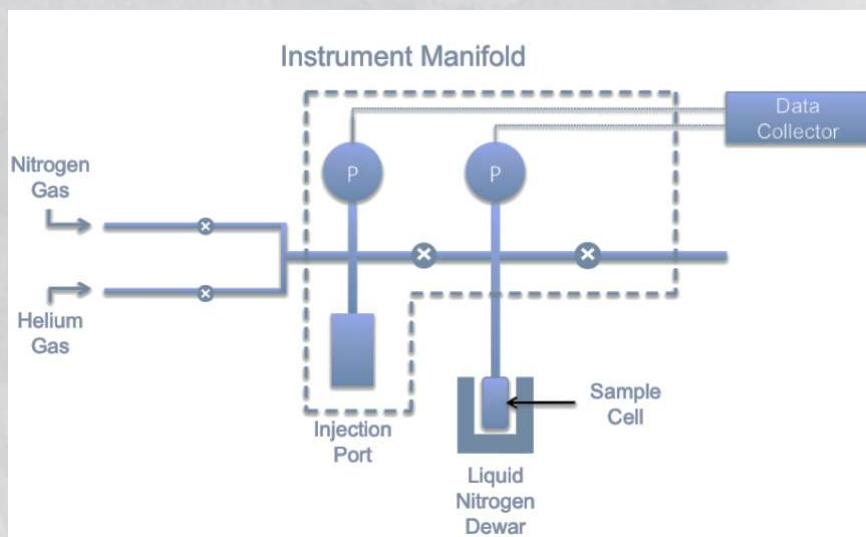
V_{mon} = the volume corresponding to the monolayer coverage,

c = constant large when $\Delta_{des}H^0$ from the mono layer is
large compared with the $\Delta_{vap}H^0$ of the liquid
adsorbate.

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30

Schematic representation of the BET instrument



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31

Schematic representation of the BET instrument



ASAP 2020 Accelerated Surface Area and Porosity Analyzer

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32

2.4 The rates of surface processes

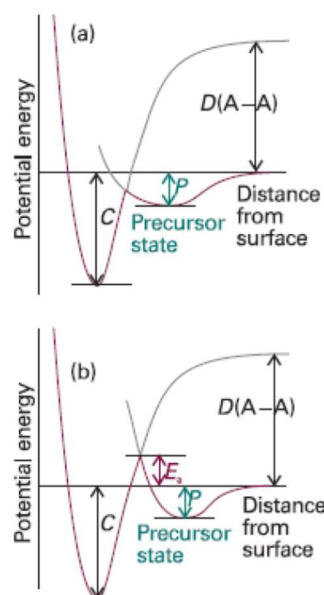
- Fig. 21 shows how the potential energy of a molecule varies with its distance from the substrate surface.
- As the molecule approaches the surface its energy falls as it becomes physisorbed into the **precursor state** for chemisorption.
- Dissociation into fragments often takes place as a molecule moves into its chemisorbed state.
- In most cases, therefore, we can expect there to be a potential energy barrier separating the precursor and chemisorbed states.

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33

2.4 The rates of surface processes

- Fig. 15: The potential energy profiles for the dissociative chemisorption of an A_2 molecule.
- In each case, P is the enthalpy of (non-dissociative) physisorption and C that for chemisorption (at $T = 0$).
- The relative locations of the curves determines whether the chemisorption is
- (a) not activated or
- (b) activated chemisorbed states.



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34

(a) The rate of adsorption

- (a) The rate of adsorption
- The rate at which a surface is covered by adsorbate depends on the ability of the substrate to dissipate the energy of the incoming particle as thermal motion as it crashes on to the surface.
- The proportion of collisions with the surface that successfully lead to adsorption is called **the sticking probability, s** :

$$s = \frac{\text{rate of adsorption of particles by surface}}{\text{rate of collision of particles by surface}} \quad \text{Eq (13)}$$

Values of s vary widely. For example, at room temperature CO has s in the range 0.1–1.0 for several d-metal surfaces, but for N_2 on rhenium $s < 10^{-2}$ indicating that more than a hundred collisions are needed before one molecule sticks successfully.

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35

(a) The rate of adsorption

- The sticking probability decreases as the surface coverage increases (Fig. 16).
- A simple assumption is that s is proportional to $(1-\theta)$, the fraction uncovered, and it is common to write

$$s = (1 - \theta)s_0 \quad \text{Eq(14)}$$

The results in the illustration do not fit this expression, as shown in the **Fig. 16**:

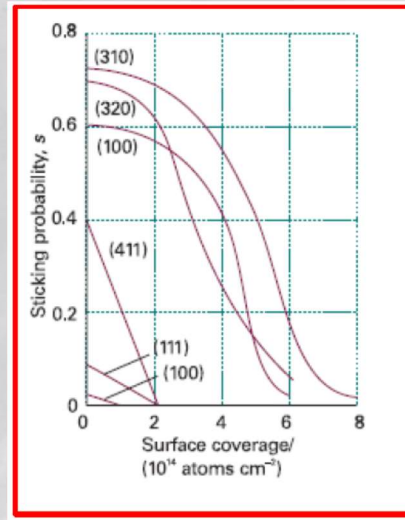
The explanation is probably that the colliding molecule does not enter the chemisorbed state at once, but moves over the surface until it encounters an empty site..

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36

(a) The rate of adsorption

- **Fig. 16:** The sticking probability of N₂ on various faces of a tungsten crystal and its dependence on surface coverage. Note the very low sticking probability for the (110) and (111) faces.
- No simple assumption is that s is proportional to $(1-\theta)$,
- The explanation is probably that the colliding molecule does not enter the chemisorbed state at once.



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37

(a) The rate of adsorption

- The sticking probability decreases as the surface coverage increases (Fig. 16).
- A simple assumption is that s is proportional to $(1-\theta)$, the fraction uncovered, and it is common to write

$$S = (1 - \theta)S_o \quad \text{Eq(14)}$$

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The explanation is probably that the colliding molecule does not enter the chemisorbed state at once, but moves over the surface until it encounters an empty site..

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38

(b) The rate of desorption

- Desorption is always activated because the particles have to be lifted from the foot of a potential well.
- A physisorbed particle vibrates in its shallow potential well, and might shake itself off the surface after a short time.
- The temperature dependence of the first-order rate of departure can be expected to be **Arrhenius-like**, with an activation energy for desorption, E_d , comparable to the enthalpy of physisorption:

$$K_d = A e^{\frac{-E_d}{RT}} \quad \text{Eq(15)}$$

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39

(b) The rate of desorption

- the half-life for remaining on the surface has a temperature dependence.

$$t \frac{1}{2} = \frac{\ln 2}{K_d} = \tau_o e^{E_d/RT} \quad \text{Eq(16)}$$

(Note the positive sign in the exponent.) If we suppose that $1/\tau_o$ is approximately the same as the vibrational frequency of the weak particle-surface bond (about 10^{12} Hz) and $E_d \sim 25 \text{ kJ mol}^{-1}$, then residence half-lives of around 10 ns are predicted at room temperature. Lifetimes close to 1 s are obtained only by lowering the temperature to about 100 K. For chemisorption, with $E_d = 100 \text{ kJ mol}^{-1}$ and guessing that $\tau_o = 10^{14}$ s.

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40

(b) The rate of desorption

- the half-life for remaining on the surface has a temperature dependence.

$$t \frac{1}{2} = \frac{\ln 2}{K_d} = \tau_o e^{E_d/RT} \quad Eq(16)$$

Because the adsorbate–substrate bond is quite stiff, we expect a residence half-life of about 3×10^3 s (about an hour) at room temperature, decreasing to 1s at about 350 K. The desorption activation energy can be measured in several ways. However, we must be guarded in its interpretation because it often depends on the fractional coverage, and so may change as desorption proceeds.

Next

3. Kinetics and activities of heterogeneous catalysis