SURFACE PHENOMENA

Adsorption on Solids

When a finely divided solid is stirred into a dilute solution of a dye, the depth of colour in the solution is much decreased. If a finely divided solid is exposed to a gas at low pressure, the pressure decreases noticeably. In these situations the dye or gas is adsorbed on the surface.

Adsorption is the process in which the molecules, atoms (or) ionic species of a substance get attached to the surface of another. Example: Ammonia is adsorbed on charcoal. Here, ammonia is known as the adsorbate and charcoal as absorbent. The phenomenon of adsorption is known as surface phenomena.

Adsorption and Free Energy Relation

As a result of adsorption there is a decrease in the residual force acting along the surface of the adsorbate. Consequently, there is a decrease of surface energy which appears as a heat. The adsorption is accompanied by the evaluation of heat. The amount of heat evolved when one mole of a gas (or) a vapour is adsorbed on a solid is known as *molar heat of adsorption*.

The ΔH for this process is negative since the state of adsorbate gets changed from more random gaseous state to less random adsorbed state on the surface of the solid. The adsorption is also accompanied by decrease of entropy of the system. We know that

$$\Delta G = \Delta H - T\Delta S$$

Since ΔH and ΔS are both negative, ΔG should also be negative. The heat of adsorption per molecule of the adsorbate goes on decreasing and ΔH becomes equal to $T\Delta S$.

$\Delta H = T\Delta S$ i.e. $\Delta G = 0$

This is the state at which the equilibrium is established.

Types of Adsorption

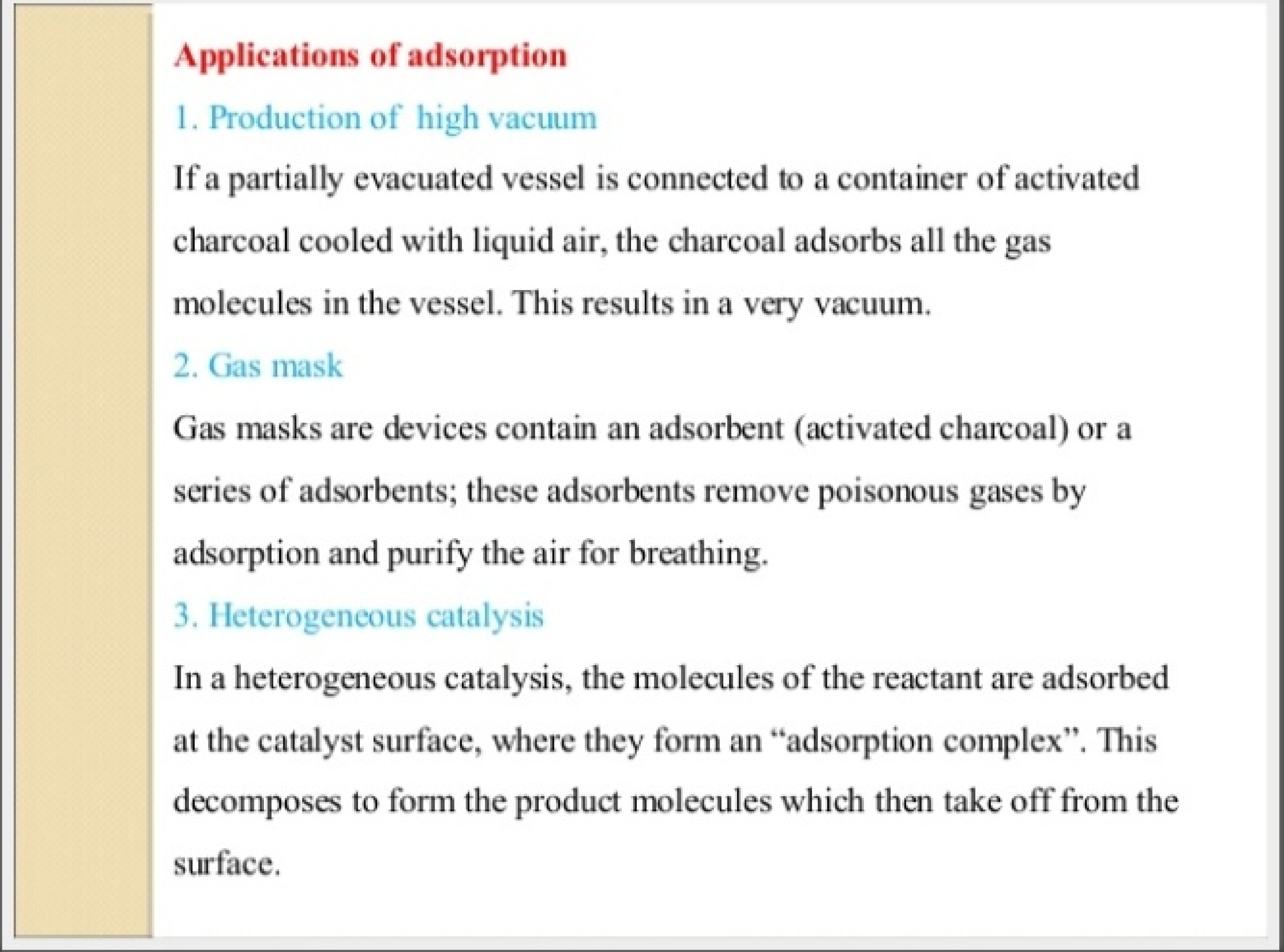
There are two types of adsorption, viz., i) Physical adsorption (or) physisorption and (ii) Chemical adsorption (or) chemisorption.

The two types of adsorption differ upon the interaction between adsorbate and the adsorbent. If the adsorbate and the adsorbent are held together by means of van der Walls' forces, then this type o adsorption is known as *Physisorption*.

If the adsorption is by a chemical process (chemical interaction) between the surface of the atom c the adsorbent and the atom of the adsorbate, then this type of adsorption is known as *Chemisorption*

Difference between Physisorption and Chemisorption

Characteristics	Physisorption	Chemisorption
Nature of the operating force	Weak van der Walls forces	Strong van der Walls forces
Occurrence	At ordinary temperature	At high temperature
Heat of adsorption	Low	High
Specificity	Non-specific	Highly specific
Reversibility	Almost completely reversible	Irreversible
Structure of the adsorbed layer	Multi-layers	Monolayer
When temperature increases	Adsorption decreases	Adsorption increases and then decreases



Applications of adsorption

1. Production of high vacuum

If a partially evacuated vessel is connected to a container of activated charcoal cooled with liquid air, the charcoal adsorbs all the gas molecules in the vessel. This results in a very vacuum.

2. Gas mask

Gas masks are devices contain an adsorbent (activated charcoal) or a series of adsorbents; these adsorbents remove poisonous gases by adsorption and purify the air for breathing.

3. Heterogeneous catalysis

In a heterogeneous catalysis, the molecules of the reactant are adsorbed at the catalyst surface, where they form an "adsorption complex". This decomposes to form the product molecules which then take off from the surface.

4. Removal of coloring matter from solutions

Animal charcoal removes colours of solution by adsorbing coloured impurities thus in the manufacture of cane-sugar, the coloured solution is clarified by treating with animal charcoal or activated charcoal.

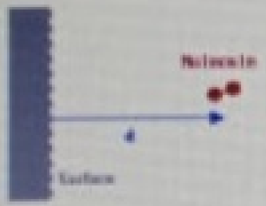
5. Chromatographic analysis

Mixtures of small quantities of organic substances can be separated with the help of chromatography which involves the principles of selective adsorption.

Potential energy curves and energetics of adsorption

A single molecule approaching a clean surface

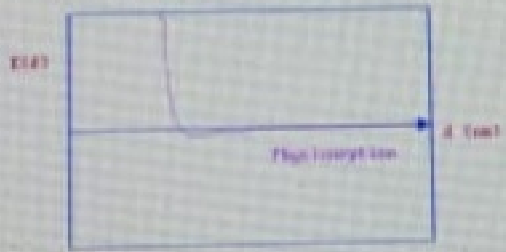
Simple model: The energy of the system **E** is a function only of of the distance **d** of an adsorbate from a surface i.e. **E = E(d)**



We neglect

- the angular orientation of the molecule
- changes in the internal bond angles and bond lengths of the molecule
- the position of the molecule parallel to the surface plane

Physisorption (e.g. Ar / metals)
In the case of pure physisorption , the only attraction between the adsorbing species and the surface arises from weak, van der Waals forces.



There is no barrier to prevent the molecule from approaching the surface, i.e. the process is not activated and the kinetics of physisorption are very fast.

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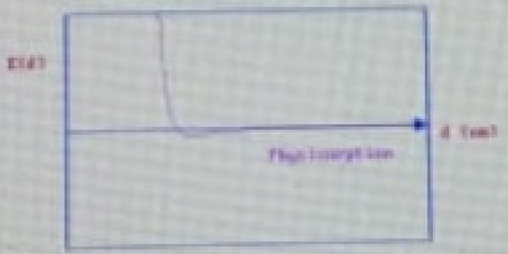

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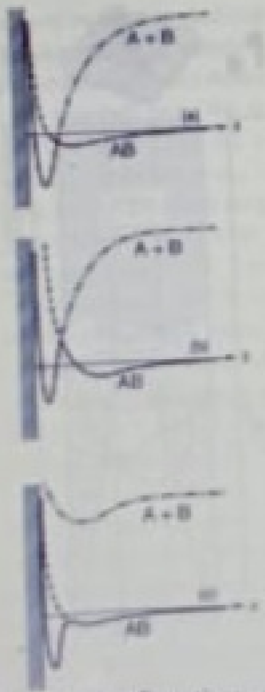
Molecular chemisorption



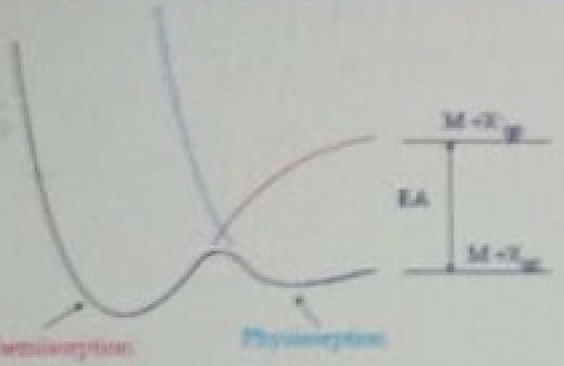
Three different state configurations: a) dissociative chemisorption, b) dissociative chemisorption with a physisorbed precursor, c) molecular chemisorption. From Lennard-Jones, 1932

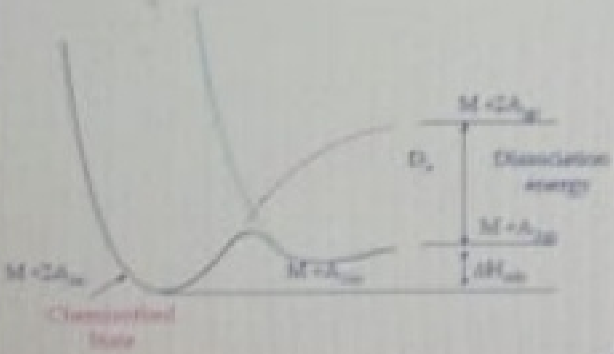
If chemical bond formation between the adsorbate and substrate can also occur, the **E(d)** curve is dominated by a much deeper chemisorption minimum at shorter values of **d**.

The depth of the chemisorption well is a measure of the strength of binding to the surface.

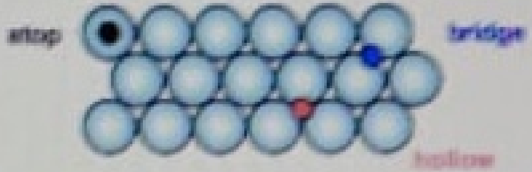
Molecule - initially being completely isolated from the surface (very large **d**) - can also be dissociated in isolated atoms.

6.4 Nondissociative Chemisorption





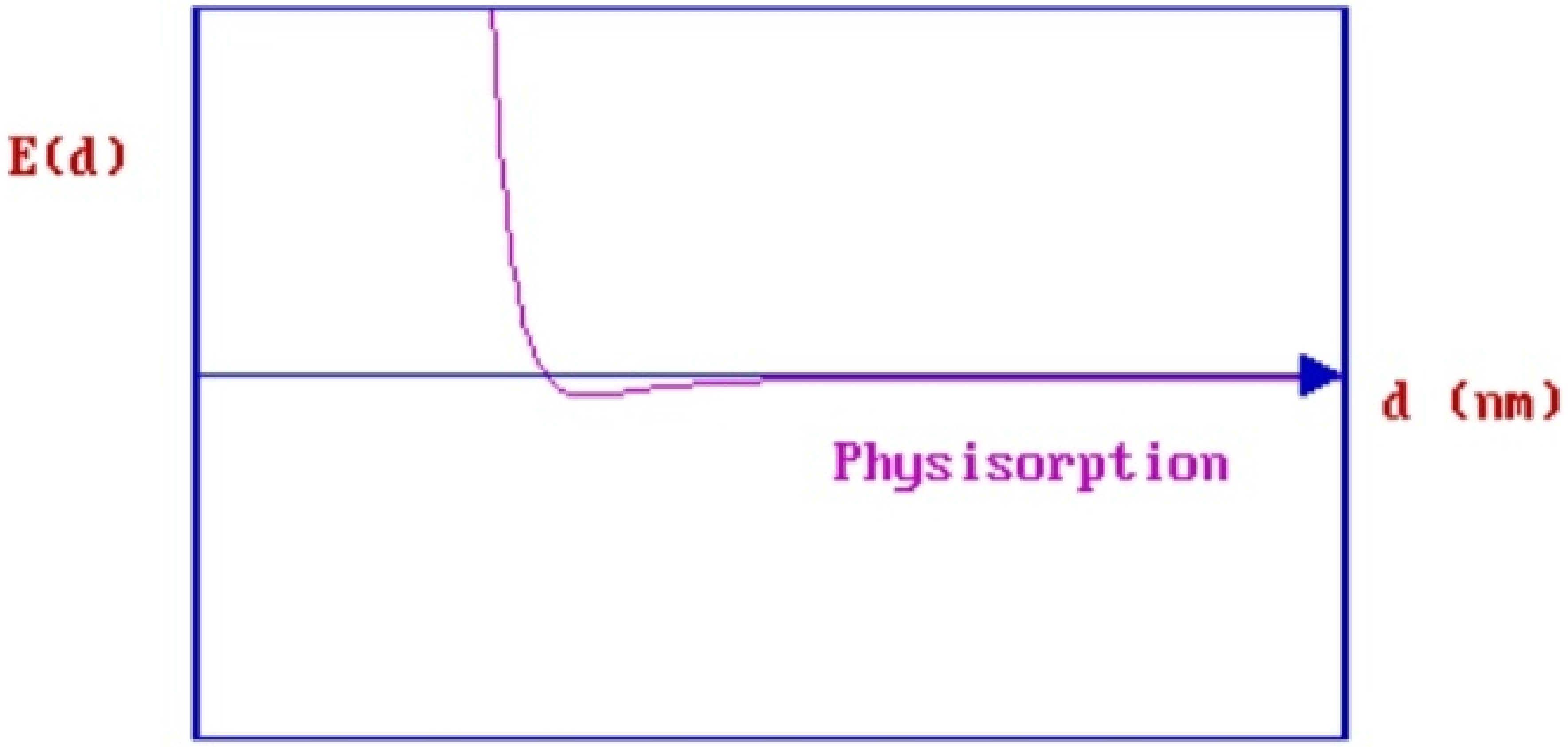
- Sequential filling of binding sites



- Binding energies depend on crystal face
- Steps, defects affect adsoprtion energies
- 2D alloyed layers, compound layers can exist when no such bulk phase is known
- Adsorption chemistry is analogous to cluster inorganic chemistry

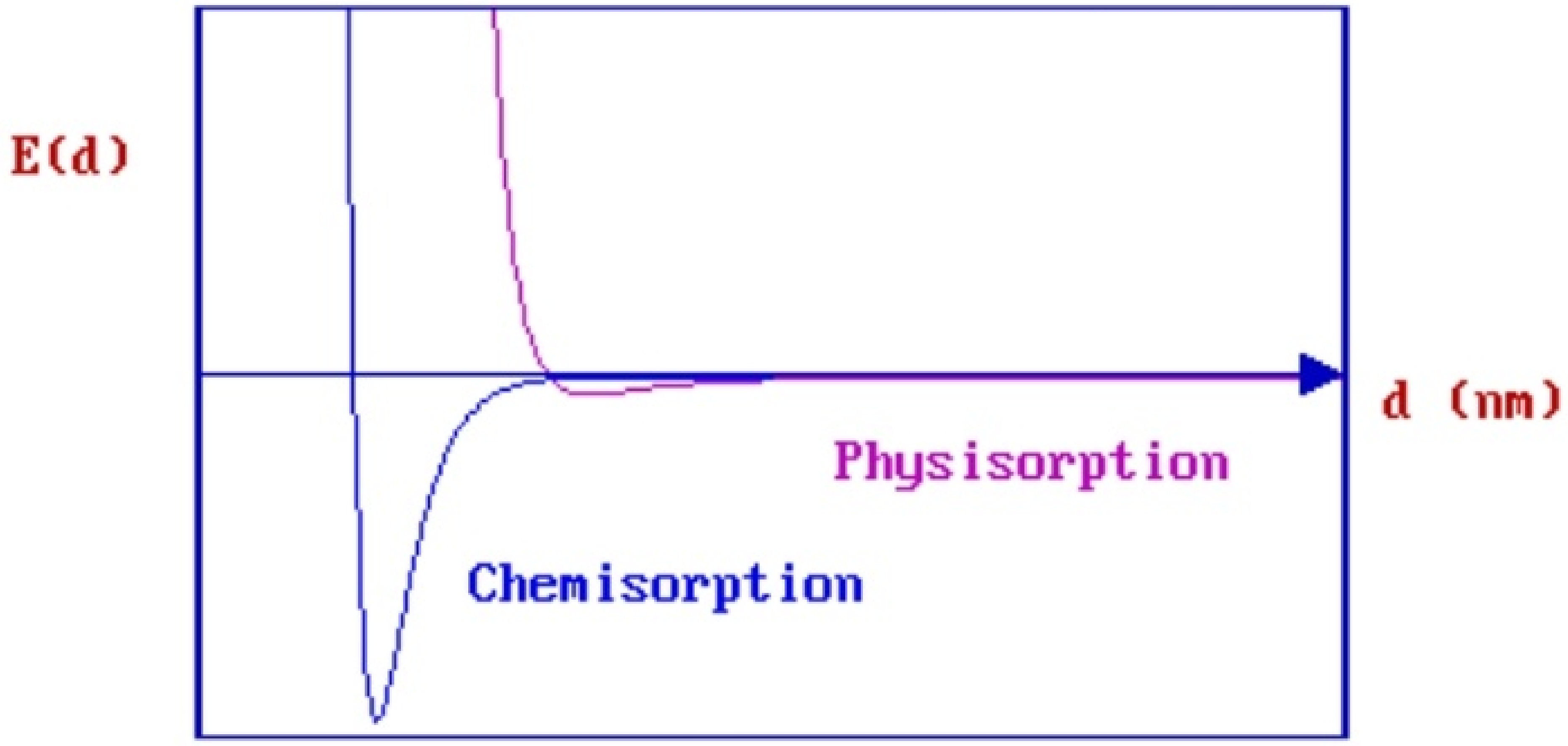
CASE I - Physisorption

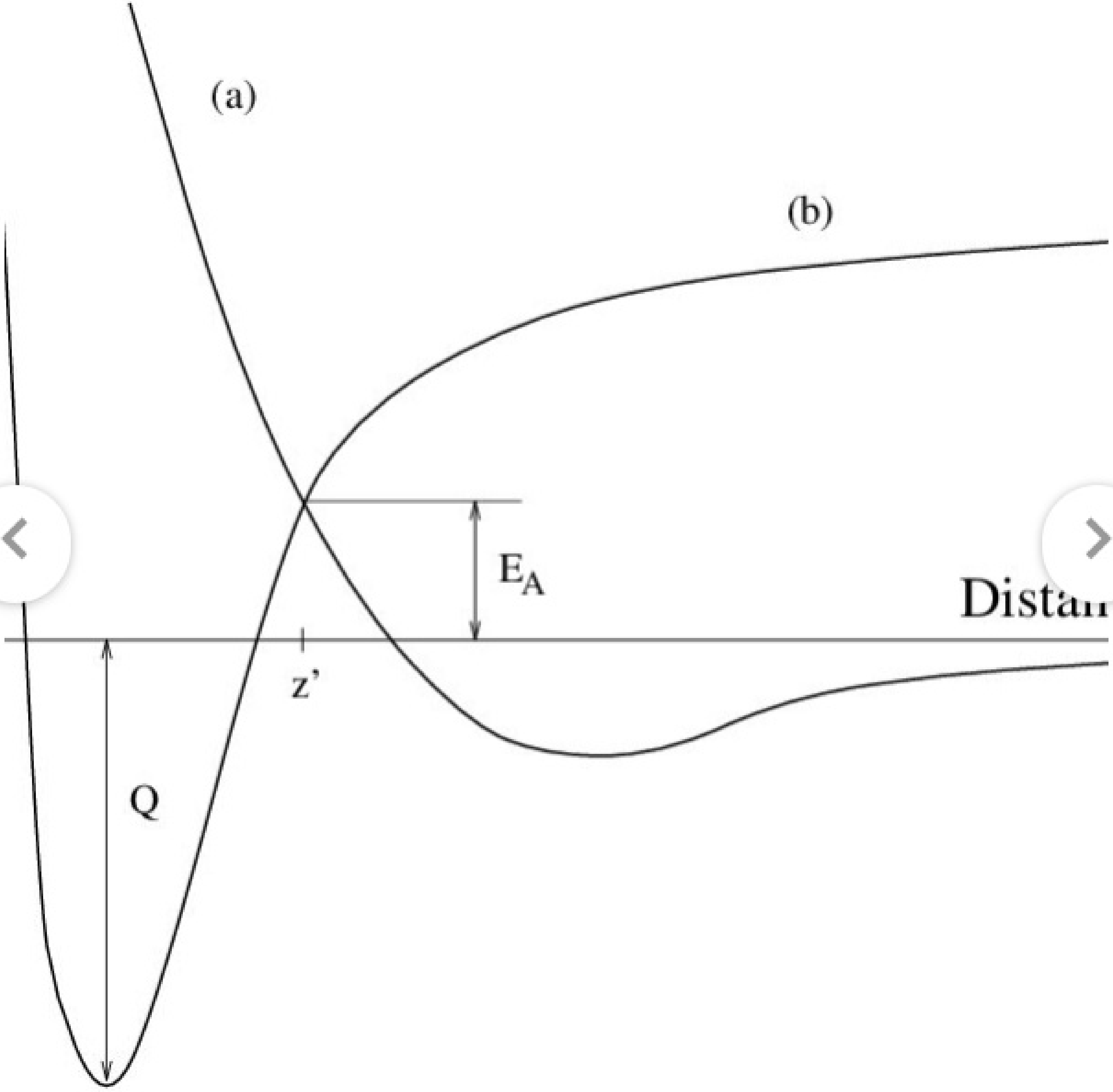
In the case of pure physisorption, e.g., Ar/metals, the only attraction between the adsorbing species and the surface arises from weak, van der Waals forces. As illustrated below, these forces give rise to a shallow minimum in the PE curve at a relatively large distance from the surface (typically $d > 0.3\,nm$) before the strong repulsive forces arising from electron density overlap cause a rapid increase in the total energy.



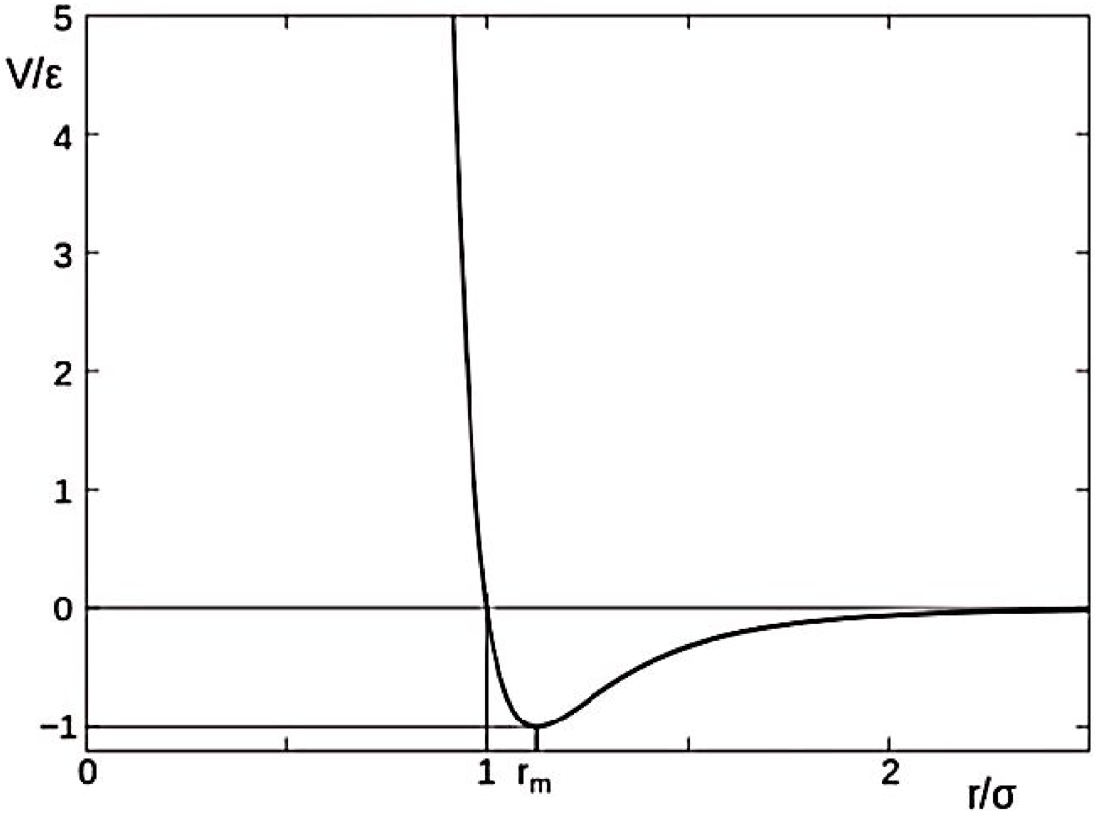
CASE II - Physisorption + Molecular Chemisorption

The weak physical adsorption forces and associated long-range attraction will be present to varying degrees in all adsorbate / substrate systems. However, in cases where chemical bond formation between the adsorbate and substrate can also occur, the PE curve is dominated by a much deeper chemisorption minimum at shorter values of *d* .





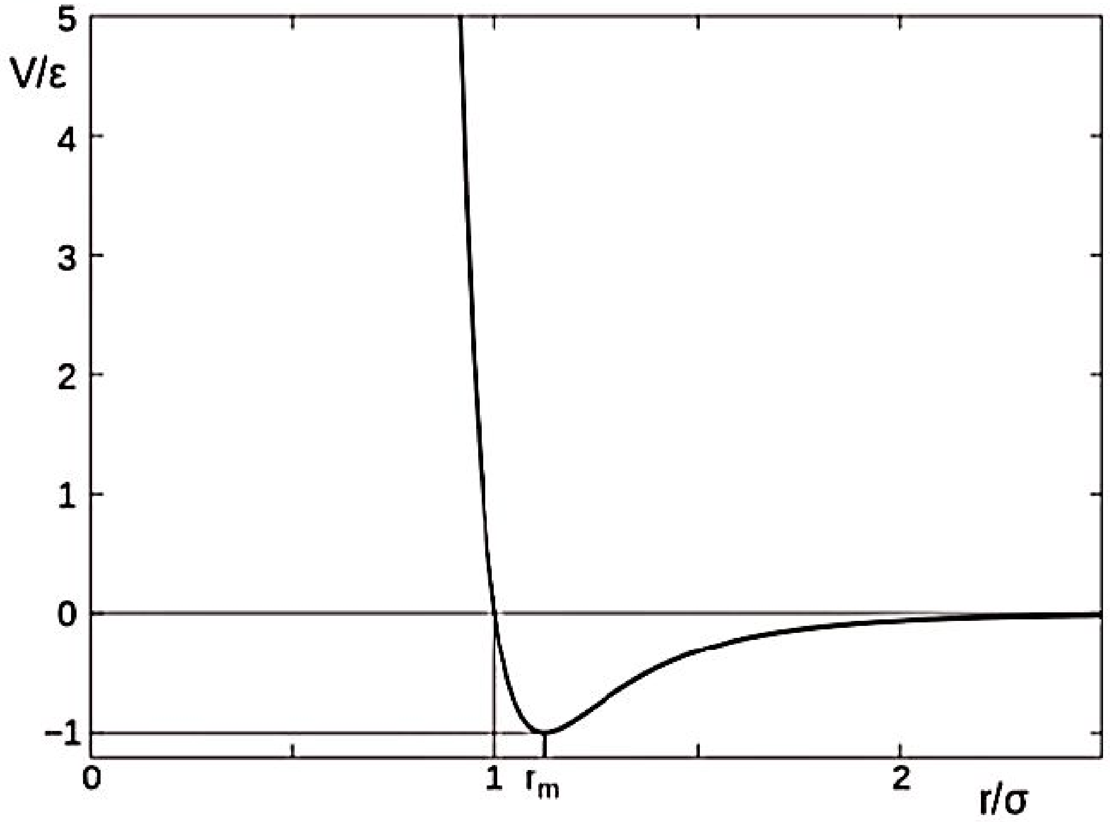
Potential energy curves for adsorption: (a) physisorption of a molecule; (b) chemisorption of two atoms.



A graph of strength versus distance for the 12-6 Lennard-Jones potential

The **Lennard-Jones potential** (also termed the **LJ potential**, **6-12 potential**, or **12-6 potential**) is a mathematically simple model that approximates the intermolecular potential energy between a pair of neutral atoms or molecules as metals or cyclic alkanes.[1][2] This interatomic potential emerged from Max Born's treatise on lattice enthalpies[3] and was elaborated in 1924 by John Lennard-Jones.[4] A common expression of the LJ potential is

$$V_{\mathrm{LJ}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] = \varepsilon\Bigg[\Bigg(\frac{r_{\mathrm{m}}}{r}$$



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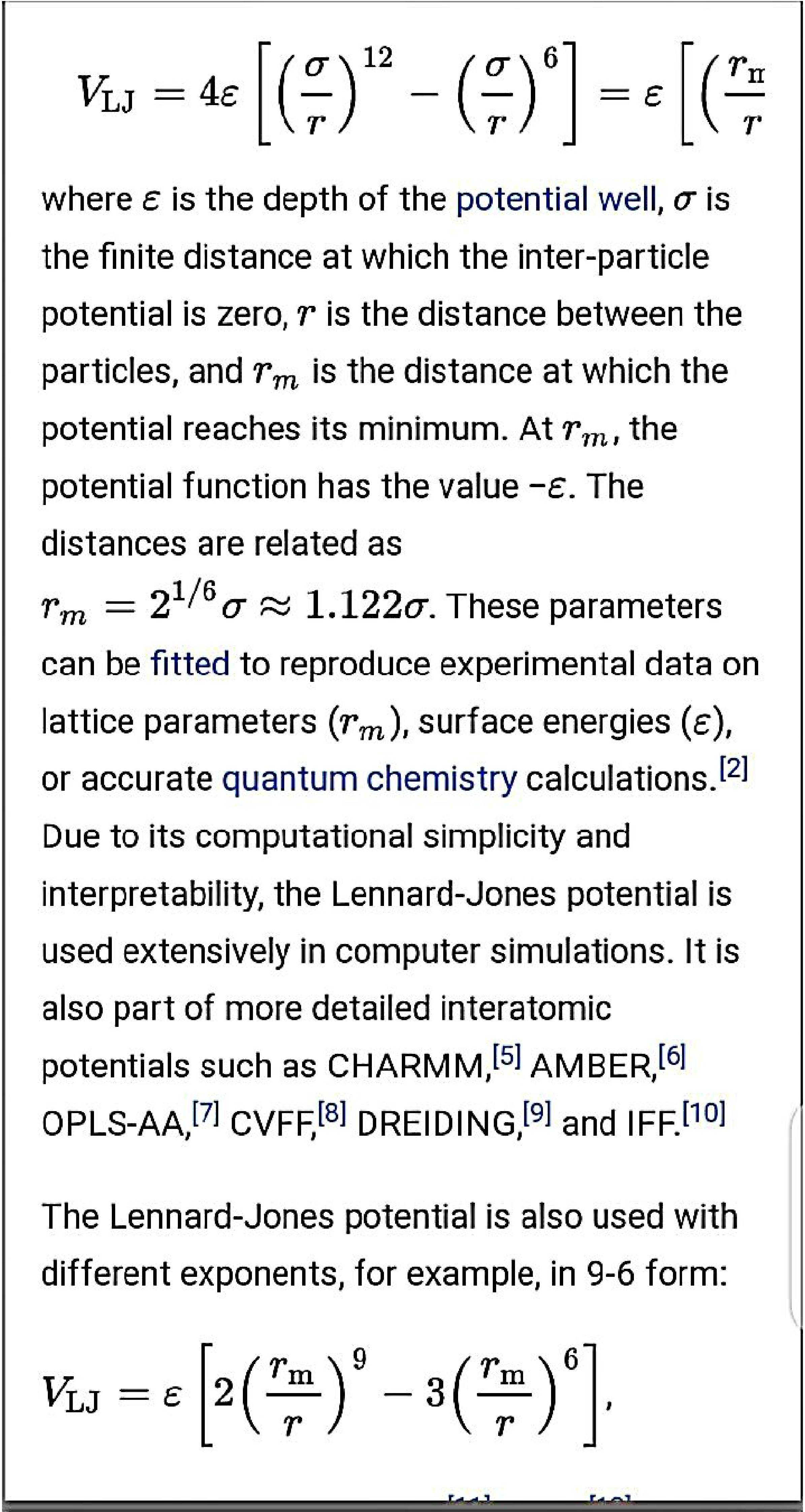

$$V_{\mathrm{LJ}} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] = \varepsilon \left[\left(\frac{r_{\mathrm{n}}}{r} \right.\right.$$

where ε is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero, r is the distance between the particles, and r_m is the distance at which the potential reaches its minimum. At r_m, the potential function has the value $-\varepsilon$. The distances are related as $r_m = 2^{1/6}\sigma \approx 1.122\sigma$. These parameters can be fitted to reproduce experimental data on lattice parameters (r_m), surface energies (ε), or accurate quantum chemistry calculations.[2] Due to its computational simplicity and interpretability, the Lennard-Jones potential is used extensively in computer simulations. It is also part of more detailed interatomic potentials such as CHARMM,[5] AMBER,[6] OPLS-AA,[7] CVFF,[8] DREIDING,[9] and IFF.[10]

The Lennard-Jones potential is also used with different exponents, for example, in 9-6 form:

$$V_{\mathrm{LJ}} = \varepsilon \left[2\left(\frac{r_{\mathrm{m}}}{r}\right)^{9} - 3\left(\frac{r_{\mathrm{m}}}{r}\right)^{6} \right],$$

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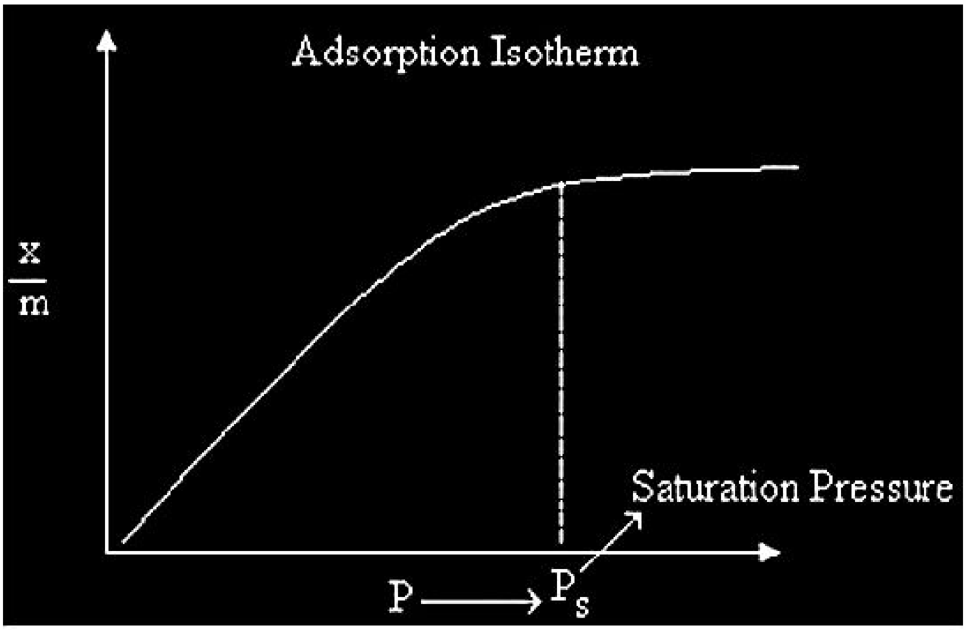
in force fields such as CFF,[11] PCFF,[12] and

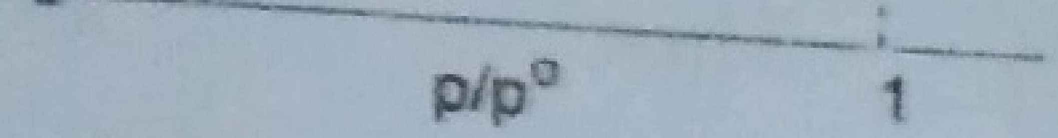
What is Adsorption Isotherm?

Adsorption isotherms have been of immense importance to researches dealing with environmental protection and adsorption techniques. The two primary methods used for predicting the adsorption capacity of a given material are known as the ***Freundlich and Langmuir isotherms.***

An adsorption isotherm is a graph that represents the variation in the amount of adsorbate(x) adsorbed on the surface of the adsorbent with the change in pressure at a constant temperature.



Adsorption Isotherm



The Brunauer, Emmet, and Teller (BET) Isotherm

This isotherm explains the multilayer adsorption.

The first step in the adsorption process is

$$A_{(g)} + S \rightleftharpoons AS \qquad K_1 = \frac{\theta_1}{\theta_v p} \tag{1}$$

where K_1 is the equilibrium constant, θ_1 is the fraction of the surface sites covered by a single molecule, and θ_v is the fraction of vacant sites.

Additional molecules sit on the top of another to form a variety of multilayers.

$$A_{(g)} + AS \rightleftharpoons A_2S \qquad K_2 = \frac{\theta_2}{\theta_1 p}$$

$$A_{(g)} + A_2S \rightleftharpoons A_3S \qquad K_3 = \frac{\theta_3}{\theta_2 p}$$

$$A_{(g)} + A_{n-1}S \rightleftharpoons A_nS \qquad K_n = \frac{\theta_n}{\theta_{n-1} p}$$

where the symbol A_3S indicates a surface site that has a stack of three A molecules piled up on it.

The θ_i is the fraction of sites on which the stack of A molecules is *i* layers deep.

The interaction between the first A molecule and the surface site is unique, depending on the particular nature of the A molecule and the surface. However, the interaction between first A and second A and that between second A and third A are very similar to the interaction between two A molecules in the liquid. Therefore, all of these processes except the first one are regarded as equivalent to liquefaction and so they have the same equilibrium constant, K. Thus BET treatment assumes that

$$K_2 = K_3 = K_4 = \ldots = K_n = K$$

where K is the equilibrium constant for the reaction $A_{(g)} \rightleftharpoons A_{(liquid)}$. Then

$K = \frac{1}{p^o}$, where p° is the equilibrium vapour pressure of the liquid.

Applying equilibrium condition, we have

$$\theta_2 = \theta_1 Kp, \qquad \theta_3 = \theta_2 Kp, \qquad \theta_4 = \theta_3 Kp \ldots$$

Combining the first two we have, $\theta_3 = \theta_1 (Kp)^2$. Repeating the operation, we find

$$\theta_i = \theta_1 (Kp)^{i-1} \tag{2}$$

The sum of all these fractions must be equal to unity;

$$1 = \theta_v + \sum_{i=1} \theta_i = \theta_v + \sum_{i=1} \theta_1 (Kp)^{i-1}$$

Putting $Kp = x$, the equation becomes

$$1 = \theta_v + \theta_1 (1 + x + x^2 + x^3 + \ldots)$$

This series is simply an expansion of $1/_{1-x}$. Thus

$$1 = \theta_v + \frac{\theta_i}{1-x} \tag{3}$$

From equation (1) we have $\theta_v = \frac{\theta_1}{K_1 p}$ and putting $\frac{K_1}{K} = c$, then

$$\theta_v = \frac{\theta_1}{cx}$$

Equation (3) becomes

$$1 = \theta_1 \left(\frac{1}{cx} + \frac{1}{1-x} \right)$$

and therefore,

$$\theta_1 = \frac{cx(1-x)}{1+(c-x)x} \tag{4}$$

Let N be the total number of molecules adsorbed per unit mass of the adsorbent and c_s be the total number of surface sites per unit mass. Then $c_s\theta_1$ is the number of sites carrying one molecule, $c_s\theta_2$ is the number carrying two molecules, and so on. Then

$$N = c_s(1\theta_1 + 2\theta_2 + 3\theta_3 + \ldots) = c_s \sum_i i\theta_i$$

From equation (2) we have $\theta_i = \theta_1 x^{i-1}$. Therefore,

$$N = c_s \theta_1 \sum_i i x^{i-1} = c_s \theta_1 (1 + 2x + 3x^2 + \ldots)$$

we know that

$$1+2x+3x^2+\dots=\frac{d}{dx}(1+x+x^2+x^3+\dots)$$

$$=\frac{d}{dx}\left(\frac{1}{1-x}\right)=\frac{1}{(1-x)^2}$$

Therefore,

$$N=\frac{c_s\theta_1}{(1-x)^2}$$

If the entire surface were covered with monolayer, then N_m molecules would be adsorbed; $N_m = c_s$ and

$$N=\frac{N_m\theta_1}{(1-x)^2}$$

Using the value of θ_1 from equation (4), we have

$$N=\frac{N_m cx}{(1-x)[1+(c-1)x]}$$

In terms of volume of the gas adsorbed we can write

$$v=\frac{v_m cx}{(1-x)[1+(c-1)x]}$$

Recalling that $x = Kp$ and $K = 1/p^o$, we have

$$v=\frac{v_m cp}{(p^o-p)[1+(c-1)(p/p^o)]} \tag{5}$$

This equation is known as the BET isotherm. The volume, v, is measured as a function of p. When $p = p^o$, the equation shows that $v \to \infty$. This accounts for the steep rise of the multilayer isotherm as the pressure approaches p^o.

Evaluation of c and v

Determination of surface area of a solid

From the value of v_m we can calculate N_m.

$$N_m = N_A \frac{pv_m}{RT}$$

At STP $N_m = N_A \dfrac{v_m}{0.022414\ m^3/mol}$

N_A is the Avagadro number and N_m is the number of molecules required to cover a unit mass with a monolayer. If the area covered by one molecule is a, then

Area/unit mass = Surface area of the solid $S = N_m a$

Determination of enthalpy change

The equilibrium constants K and K_1 can be written as

$$K_1 = e^{-\Delta G_1^o/RT} \quad \text{and} \quad K = e^{-\Delta G_{liq}^o/RT}$$

where ΔG_1^o is the standard free energy of adsorption of the first layer and ΔG_1^o is the standard free energy change of liquefaction. Dividing the first equation by the second equation, we obtain c.

$$c = \frac{K_1}{K} = e^{-[\Delta G_1^o - \Delta G_{liq}^o]/RT}$$

We know

$$\Delta G_1^o = \Delta H_1^o - T\Delta S_1^o \qquad \text{and} \qquad \Delta G_{liq}^o = \Delta H_{liq}^o - T\Delta S_{liq}^o$$

and assuming that $\Delta S_1^o \approx \Delta S_{liq}^o$, then

$$c = e^{-[\Delta H_1^o - \Delta H_{liq}^o]/RT}$$

The heat of liquefaction is negative of the heat of vapourization. Therefore,

$$c = e^{-[\Delta H_1^o + \Delta H_{vap}^o]/RT}$$

Taking logarithms and rearranging,

$$\Delta H_1^o = -\Delta H_{vap}^o - RT \ln c$$

Since we know the value of ΔH_{vap}^o of the adsorbate, the value of ΔH_1^o can be calculated from the measured value of c. In all cases, it is found that $c > 1$, which implies that $\Delta H_1^o < \Delta H_{liq}^o$. The adsorption in the first layer is more exothermic than liquefaction.

Adsorption from Solutions

(1) The process of adsorption can take place from solutions also.

(2) In any solution, there are two (or more) components ; **solute** and **solvent.** The solute may be present in the molecular or ionic form.

(3) The extent of adsorption from solution depends upon the concentration of the solute in the solution, and can be expressed by the **Freundlich isotherm**.

(4) The Freundlich adsorption isotherm for the adsorption from solution is, $\frac{x}{m} = kc^{\frac{1}{n}}$ where, x is the mass of the solute adsorbed, m is the mass of the solid adsorbent, c is the equilibrium concentration of the solute in the solution, n is a constant having value greater than one,

k is the proportionality constant, (The value of k depends upon the nature of solid, its particle size, temperature, and the nature of solute and solvent etc.)

(5) The plot of x/m against c is similar to that Freundlich adsorption isotherm. The above equations may be written in the following form, $\log\frac{x}{m} = \log k + \frac{1}{n}\log c$ where c, is the equilibrium concentration of the solute in the solution.

it known as adsorption isotherme.

Gibb's adsorption isotherm:

J. willard Gibb's & J. J. Jamson derived a relationship between adsorption and surface tension its known as Gibb's adsorption isotherm.

It is considered γ is the interfacial tension. The free energy G is given by

$$G = \mu_1 n_1 + \mu_2 n_2 \quad \text{——} ①$$

where n_1, n_2 are no. of molecule. μ_1, μ_2 chemical potential of two species

The γs may added in calculating the free energy

thus, $G = \gamma s + \mu_1 n_1 + \mu_2 n_2$ —— ②

on differenation equation ②.

$$dG = \gamma ds + s d\gamma + \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \quad \text{———} ③$$

⑤

The value of dG obtained by the use of thermodynamic function by adding the surface entropy.

$$dG = -SdT + VdP + \gamma ds + \mu_1 dn_1 + \mu_2 dn_2 \quad \text{———} ④$$

by comparing equation ③ & ④

$$SdT - VdP + sd\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \text{———} ⑤$$

at constant temperature and pressure is 0.

$$sd\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \text{———} ⑥$$

This equation is an analogous to Gibb's-Duhem equation. This equation wholed goods for surface phase but the bulk phase is quite free from surface phase and therefore only Gibb's Duheme equation wholes good.

Let n_1, n_2 be the no. of molecule in surface phase whifin n_1^o, n_2^o be the no. of molecules in bulk-phase.

For the bulk phase the following relationship may be given.

$$n_1^o d\mu_1 + n_2^o d\mu_2 = 0 \quad \text{———} ⑦$$

The above equation does not contain γs term. Since its free from surface effect.

on equation ⑦ × $\frac{n_1}{n_1^o}$ and subracting with equation ⑥.

$$n_1 d\mu_1 + \frac{n_1 n_2^o}{n_1^o} d\mu_2 = 0 \quad \text{———} ⑧$$

⑥ − ⑧

equ⑥ - equ⑧

$$sd\gamma + n_2 d\mu_2 - \frac{n_1 n_2^o}{n_1^o} d\mu_2 = 0 \quad \text{———} ⑨$$

$$-sd\gamma = n_2 d\mu_2 - \frac{n_2^o}{n_1^o} n_1 d\mu_2 \quad \text{———} ⑩$$

$$-sd\gamma = \left(n_2 - \frac{n_1 n_2^o}{n_1^o}\right) d\mu_2 \quad \text{———} ⑪$$

$$-\frac{d\gamma}{d\mu_2} = \left[\frac{n_2 - \frac{n_1 n_2^0}{n_1^0}}{s}\right]$$ ⑫

The R.H.S of equation ⑫ is called concentration of solute and represented by S_2.

$$\therefore S_2 = -\frac{d\gamma}{d\mu_2}$$ ⑬

we know that $\mu_2 = \mu_2^0 + RT\ln a_2$ ⑭

where a_2 is activity of solute and constant temperature

differenating equ ⑭

$$d\mu_2 = RT\,d\ln a_2$$ ⑮

Substitute the values in equation ⑬ we get $\left(\because d\ln a_2 = \frac{da_2}{a_2}\right)$

$$S_2 = \frac{-d\gamma}{RT\,d\ln a_2}$$

$$S_2 = \frac{-a_2\,d\gamma}{RT\,da_2}$$

This equation known as Gibb's adsorption isotherm equation

* If the value of $\frac{d\gamma}{da_2}$ = -ve surface tension increase with increasing the concentration. (i-e) there is an excess solute present at the inter phase.

* If $\frac{d\gamma}{da^2}$ is positive S_2 is +ve it means further addition of solute decrease the surface tension of the solution.