



## Review Article

## A description of the proofs of formulas Langmuir, BET and Anderson related to adsorption isotherms-A Review

Yadollah Saghapoor, Rahman Alizadeh

Department of Chemistry, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran

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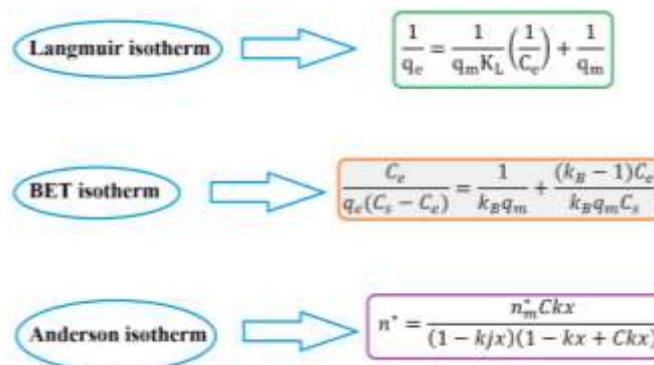
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## ABSTRACT

Adsorption isotherms have the ability to describe the mechanisms between adsorbent and adsorbed at constant temperature. In this paper, we have extracted the equations of different isotherms with new and simple methods. In this regard, we have proved the isotherms of Langmuir, Brunauer, Emmett and Teller (BET) and Anderson

## GRAPHICAL ABSTRACT



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\* Corresponding author: Yadollah Saghapoor

✉ E-mail: [y.saghapoor@gmail.com](mailto:y.saghapoor@gmail.com)

☎ Tel number: 09166728460

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## Introduction

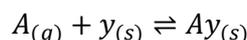
One of the most important issues is the issue of environmental pollution. Avoidance of hazardous chemicals and heavy metals is not avoided in industrial societies. Elimination of chemical elements or compounds is mandatory for health. Adsorption is one of the least expensive methods of removing contaminants. Absorbents tend to absorb one or more components of the fluid medium. This adsorption can be physical or chemical. Isotherms represent a kind of equilibrium relationship between the concentration of adsorbent in the liquid phase and the solid phase. In this article, Langmuir, BET and Anderson isotherms are examined.

### Langmuir isotherm

We examine this isotherm for two types of systems. These two types include single gas and Mixtures of gases absorbed [1-4].

#### I. single gas

For this type of system, the following balance is established:



Gas A is an inseparable substance and y is an adsorbent. The equilibrium constant of this absorption is:

$$K = \frac{\Gamma_{Ay}}{[A]\Gamma_y} \quad (1)$$

In this equation,  $\Gamma_{Ay}$  and  $\Gamma_y$  are the number of occupied and unoccupied places per unit area, respectively. If the fraction of occupied space is equal to  $\theta$ , So the fraction of unoccupied space is equal to  $(1 - \theta)$  And S is the number of sites on the surface. So the equilibrium constant can be written as follows:

$$K_c = \frac{\Gamma_{Ay}}{[A]\Gamma_y} = \frac{\theta S/cm^2}{[A](1-\theta)S/cm^2} = \frac{\theta}{[A](1-\theta)} \quad (2)$$

We have a rearrangement:

$$\theta = \frac{K_c[A]}{1 + K_c[A]} \quad \text{or} \quad \theta = \frac{P_A K_p}{1 + P_A K_p} \quad (3)$$

On the other hand, we can have:  $\theta = V/V_m$

V is the volume of the absorbed that covers a fraction of the adsorbent surface and  $V_m$  is the volume of the absorbed that covers the entire surface of the adsorbent. By equating them, it is obtained:

$$V = \frac{V_m P_A K_L}{1 + P_A K_L} \quad (4)$$

Or:

$$\frac{1}{V} = \frac{1}{V_m K_L} \left(\frac{1}{P_e}\right) + \frac{1}{V_m} \quad (5)$$

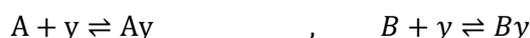
$P_e$ , Equilibrium pressure and  $K_L$  is the Langmuir equilibrium constant and is equivalent to  $K_p$ . For the liquid phase:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \left(\frac{1}{C_e}\right) + \frac{1}{q_m} \quad (6)$$

$q_e$  is the amount of material adsorbed on the adsorbent.  $q_m$  is the maximum amount of substance that can be absorbed.

#### II. Mixtures of gases

If the system contains two different gases:



$$K_A = \frac{\Gamma_{Ay}}{[A]\Gamma_y} = \frac{\theta_A}{[A](1 - \theta_A - \theta_B)} \quad (7)$$

And:

$$K_B = \frac{\Gamma_{By}}{[B]\Gamma_y} = \frac{\theta_B}{[B](1 - \theta_A - \theta_B)} \quad (8)$$

Assuming the gases are ideal:

$$K_{p,A} = \frac{\theta_A}{P_A(1 - \theta_A - \theta_B)}, \quad K_{p,B} = \frac{\theta_B}{P_B(1 - \theta_A - \theta_B)} \quad (9)$$

Therefore:

$$\theta_A = K_{p,A}P_A(1 - \theta_A - \theta_B), \quad \theta_B = K_{p,B}P_B(1 - \theta_A - \theta_B) \quad (10)$$

Also:

$$\frac{\theta_A}{\theta_B} = \frac{K_{p,A}P_A}{K_{p,B}P_B} \Rightarrow \theta_B = \theta_A \frac{K_{p,B}P_B}{K_{p,A}P_A} \quad (11)$$

$\theta_B$  in  $\theta_A = K_{p,A}P_A(1 - \theta_A - \theta_B)$ :

y placement

$$\theta_A = K_{p,A}P_A \left( 1 - \theta_A - \theta_A \frac{K_{p,B}P_B}{K_{p,A}P_A} \right) \quad (12)$$

Or:

$$\theta_A = \frac{K_{p,A}P_A}{1 + K_{p,A}P_A + K_{p,B}P_B} \quad (13)$$

Such:

$$\theta_B = \frac{K_{p,B}P_B}{1 + K_{p,A}P_A + K_{p,B}P_B} \quad (14)$$

Given that:  $\theta_A + \theta_B = \frac{V}{V_m}$

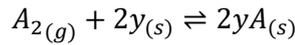
$$\frac{V}{V_m} = \frac{K_{p,A}P_A + K_{p,B}P_B}{1 + K_{p,A}P_A + K_{p,B}P_B} \quad (15)$$

$$V = V_m \frac{K_{p,A}P_A + K_{p,B}P_B}{1 + K_{p,A}P_A + K_{p,B}P_B} \quad (16)$$

For the liquid phase:

$$q_e = \frac{q_m \sum_i K_{l,i} C_{e,i}}{1 + \sum_i K_{l,i} C_{e,i}} \quad (17)$$

If we have a separable diatomic gas:



$$K_c = \frac{(\Gamma_{Ay})^2}{[A_2](\Gamma_y)^2} = \frac{\theta^2}{[A_2](1 - \theta)^2} \quad (18)$$

Or:

$$K_p = \frac{\theta^2}{P_{A_2}(1 - \theta)^2} \quad (19)$$

Accordingly:

$$\theta = \frac{(PK_p)^{0.5}}{1 + (PK_p)^{0.5}} \quad (20)$$

### BET isotherm

According to the kinetic theory of gases, the rate of gas adsorption on the uncovered surface is equal to [5-10]:

$$\vec{v}_{ads} = \alpha_o v_{dif} \theta_o \quad (21)$$

$\alpha_o$  is the probability of adsorption and  $v_{dif}$  indicates the speed of diffusion of gas molecules on the surface.  $\theta_n$  is basically defined as follows:

$$\theta_n = \frac{\text{Number of places with n particles absorbed}}{\text{Total number of places}}$$

For further explanation, consider the following level, which has eight absorption sites:

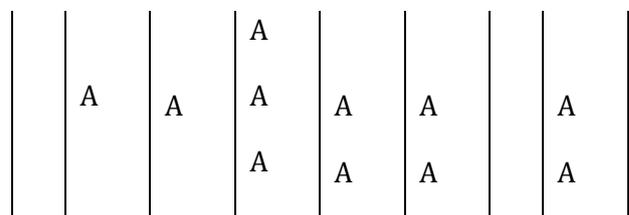


Fig.1 Particles adsorbed at different surface sites

In the first and seventh places no particle is absorbed so we can have:

$$2/8, \theta_1 = 2/8, \theta_2 = 3/8, \theta_3 = 1/8 = \theta_0$$

So  $\theta_0$  represents the number of vacancies relative to the total number of vacancies. The rate of desorption is also equal to:

$$\vec{v}_{des} = k_1 n_m^* \theta_1 \quad (22)$$

$n_m^*$  represents the number of particles adsorbed per unit area of the adsorbent to form a monolayer.  $k_1$  is also a constant velocity and surface desorption constant. In equilibrium, the rate of adsorption is equal to the rate desorption, so:

$$\alpha_0 v_{dif} \theta_0 = k_1 n_m^* \theta_1 \quad (23)$$

Or:

$$\alpha_1 v_{dif} \theta_1 = k_2 n_m^* \theta_2 \quad (24)$$

So, we have the system for the covered mode:

$$\alpha_{s-1} v_{dif} \theta_{s-1} = k_s n_m^* \theta_s \quad (25)$$

Suppose:

$$\theta_s \cong \theta_{s-1} = 1, \quad \alpha = \alpha_1 = \alpha_2 = \dots \alpha_s \neq \alpha_0, \\ k = k_2 = \dots k_s \neq k_1$$

So, equations(24) and (25) are:

$$\alpha v_{dif} \theta_1 = k n_m^* \theta_2 \quad (26)$$

and:

$$\alpha v_{dif} = k n_m^* \quad (27)$$

On the other hand, according to the theory of kinetic gas:

$$v_{dif} = \frac{1}{4} \bar{v} \rho \quad (28)$$

$\bar{v}$  and  $\rho$ , respectively, represent the average transfer velocity of gas molecules and the number of gas molecules per unit volume. Now, by placing the relation (28) in the equations(26) and (27) and then dividing them into two, taking into account that  $\rho$  is proportional to the pressure, we obtain:

$$\frac{\rho}{\rho_s} = \frac{\theta_2}{\theta_1} = \frac{P}{P_s} = x \quad (29)$$

Therefore, it can be written:

$$\theta_2 = x \theta_1; \theta_3 = x^2 \theta_1 \text{ or } \theta_i = x^{i-1} \theta_1$$

To obtain the relationship between  $\theta_1$  and  $\theta_0$ , we first substitute Equation (28) for (23) and (26), and then divide them by:

$$\theta_1 = \theta_0 \frac{\alpha_0 \rho k}{\alpha \rho_s k_1} \quad (30)$$

Generally:

$$\theta_i = C X^i \theta_0, \quad i = 1, 2, 3, \dots \quad (31)$$

$$\text{So: } C = \alpha_0 k / \alpha k_1, X = \frac{\rho}{\rho_s}$$

On the other hand, the numerical density of surface adsorbed molecules in all layers is equal to:

$$n^* = n_m^* \sum_{i=1}^{\infty} i \theta_i \quad (32)$$

The complete surface coverage must also be consistent with the following equation:

$$1 = \theta_0 + \sum_{i=1}^{\infty} \theta_i \quad (33)$$

Now if we replace Equation (31) by (32) and (33), we get:

$$n^* = n_m^* C \theta_o \sum_{i=1}^{\infty} i x^i \quad (34)$$

And:

$$1 = \theta_o \left( 1 + C \sum_{i=1}^{\infty} x^i \right) \quad (35)$$

Extract  $\theta_o$  from Equation(35) and place it in Equation(34):

$$n^* = \frac{n_m^* C \sum_{i=1}^{\infty} i x^i}{1 + C \sum_{i=1}^{\infty} x^i} \quad (36)$$

On the other hand, for  $X < 1$  we have mathematics:

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \quad (37)$$

And:

$$\sum_{i=1}^{\infty} i x^i = \frac{x}{(1-x)^2} \quad (38)$$

So the general form of Equation BET is as follows:

$$n^* = \frac{n_m^* C x}{(1-x)(1-x+Cx)} \quad (39)$$

And its linear shape is as follows:

$$\frac{x}{n^*(1-x)} = \frac{1}{C n_m^*} + x \frac{C-1}{C n_m^*} \quad (40)$$

By placing  $X = P/P_s$ ,  $n^*/n_m^* = V_{ads}/V_m$  is obtained:

$$\frac{P}{V_{ads}(P_s - P)} = \frac{1}{C V_m} + \frac{(C-1)P}{C V_m P_s} \quad (41)$$

$V_{ads}$  and  $V_m$  are the volume of gas absorbed in equilibrium and the volume of gas required to form a complete absorption layer, respectively. Approximately, we can also know for the liquid state:

$$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{k_B q_m} + \frac{(k_B - 1)C_e}{k_B q_m C_s} \quad (42)$$

In addition:  $C_s = C_0 - C_e$

$C_s$  is the concentration of the absorbed in the saturated state and  $q_m$  is the mass of the absorbed to form a complete layer. The isotherm constant BET is also denoted by  $K_B$ .

### Anderson isotherm

This theory in order to complete the theory BET, Expressed by Anderson. For this purpose, two adjustable parameters  $k$  and  $j$  were used, both of which are without units. Therefore:

$$n^* = \frac{n_m^* C k x}{(1 - k j x)(1 - k x + C k x)} \quad (43)$$

$k$  corrects the heat of absorption and is equal to:

$$k = \exp\left(\frac{h}{RT}\right) \quad (44)$$

$h$  is characterized by excess condensing heat.  $j$  also indicates the available fraction for layers higher than the first layer. At  $j = 1$  we have infinitely absorbed layers.

### Conclusion

By knowing the mechanism of scientific equations, the way to discover other equations is paved. Some of the intermediate formulas that appear in the study of the mechanism can be very useful for researchers

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