# Mass Transfer Issues with Adsorption on a Surface

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## I. Adsorption Isotherms

### *I.A. Single-Component Langmuir Isotherm (simplest model):*

Consider adsorption as a kind of elementary reaction: A + S ←→AS

Adsorption is the forward reaction. The rate of adsorption per unit volume of reactor is given by

$$r_a = k_a \rho_A \theta_S = k_a \rho_A (1-\theta)$$

$$r_d = k_d \theta$$

where θ is the fractional occupancy of adsorption sites by component A, $\theta_S$ is the fraction of empty sites and $\theta + \theta_S = 1$.

At equilibrium $r_a = r_d$

$$k_d \theta = k_a \rho_A (1-\theta)$$

$$\theta = K \rho_A (1-\theta)$$

where the equilibrium coefficient, $K = \frac{k_a}{k_d}$. Solving for θ, you arrive at the Langmuir Isotherm for a single component:

$$\theta = \frac{K\rho_A}{1+K\rho_A} \tag{1}$$

### *I.B. Binary Langmuir Isotherm (simplest model):*

$$r_{A,a} = k_{A,a} \rho_A \theta_S = k_{A,a} \rho_A (1-\theta_A-\theta_B)$$

$$r_{A,d} = k_{A,d} \theta_A$$

at equilibrium $r_{A,a} = r_{A,d}$

$$k_{A,d}\theta_A = k_{A,a}\rho_A\left(1-\theta_A-\theta_B\right)$$

We can write this as

$$\theta_A = K_A\rho_A\left(1-\theta_A-\theta_B\right) \qquad \text{for A} \tag{2.A}$$

where $K_A = \dfrac{k_{a,A}}{k_{d,A}}$.

We can repeat the analogous derivation for component B

$$\theta_B = K_B\rho_B\left(1-\theta_A-\theta_B\right) \qquad \text{for B} \tag{2.B}$$

where $K_B = \dfrac{k_{a,B}}{k_{d,B}}$.

We have two equations in (1.A) and (1.B) and we have two unknowns. Solving simultaneously, yields

$$\theta_B = \frac{K_B\rho_B\left(1-\theta_A\right)}{1+K_B\rho_B}$$

$$\theta_A = K_A\rho_A\left(1-\theta_A-\frac{K_B\rho_B\left(1-\theta_A\right)}{1+K_B\rho_B}\right)$$

$$\theta_A = K_A\rho_A - K_A\rho_A\theta_A - K_A\rho_A\frac{K_B\rho_B}{1+K_B\rho_B} + \frac{K_B\rho_B}{1+K_B\rho_B}K_A\rho_A\theta_A$$

$$\theta_A = \frac{K_A\rho_A - K_A\rho_A\dfrac{K_B\rho_B}{1+K_B\rho_B}}{1+K_A\rho_A-\dfrac{K_B\rho_B}{1+K_B\rho_B}K_A\rho_A} = \frac{K_A\rho_A}{1+K_B\rho_B+K_A\rho_A} \tag{3.A}$$

$$\theta_B = \frac{K_B\rho_B}{1+K_B\rho_B+K_A\rho_A} \tag{3.B}$$

*I.C. For n-component Langmuir isotherm:*

Based on the pattern of the adsorption isotherm in the single-component and two-component case, we can use inductive reasoning to arrive at the expression for the n-component system:

$$\theta_i = \frac{K_i \rho_i}{1 + \sum_{j=1}^{N_c} K_i \rho_i} \tag{4}$$

*I.D. assumptions of Langmuir isotherm*

1. energetically homogeneous surface
2. no adsorbate-adsorbate (lateral) interactions – no phase transitions
3. only one adsorbate per adsorption site

## II. Material Balances

### *II.A. Parameter Definitions*

We have a packed bed. The void fraction is the volume fraction of the reactor that is not occupied by the solid particles.

| | | |
|---|---|---|
| $\varepsilon$ | void fraction | [dimensionless] |

These particles are defined by several parameters. Let us for the time being assume spherical particles. Then the following parameters are relevant.

| | | |
|---|---|---|
| $D_P$ | pellet diameter | [length] |
| $\rho_S$ | site density on surface of pellet | [sites/area] |

These parameters must be known.

Given these parameters, the surface area per particle and the volume per particle are

$$A_p = \pi D_P^2$$

$$V_p = \frac{\pi}{6} D_P^3$$

and the ratio of surface area to volume is

$$\frac{A_p}{V_p} = \frac{6}{D_P}$$

The number of adsorption sites per particle is

$$N_s = A_p \rho_s$$

The number of particles per volume of reactor is

$$\rho_P = \frac{(1-\varepsilon)}{V_P}$$

The density of sites per volume of reactor is thus

$$\rho_R = N_S \rho_P = \rho_s \frac{A_p}{V_P}(1-\varepsilon) = 6\rho_s \frac{(1-\varepsilon)}{D_P}$$

*II.B. "Lever-Rule" Material Balance between adsorbed and bulk phases (1 component)*

Consider a given differential volume element of the reactor containing a single component. Within this volume, we have void fraction, $\varepsilon$, and fractional occupancy, $\theta_A$, and bulk density, $\rho_{b,A}$. The lowercase b stands for bulk and the uppercase A stands for component A. The volume of the element is $V_t$, where the t stands for total. The total mass of A in the differential volume element is

$$M_{t,A} = M_{a,A} + M_{b,A} \tag{5}$$

We can define the total density of component A in the system to be

$$\rho_{t,A} \equiv \frac{M_{t,A}}{V_t} \tag{6}$$

Let's make it clear that this is the total mass of A per total volume.
We can define the bulk density of component A to be

$$\rho_{b,A} \equiv \frac{M_{b,A}}{V_b} \tag{7}$$

Let's make this clear that this is the mass of A in the bulk phase per bulk volume. We see that the bulk volume is related to the total volume through the void fraction

$$\varepsilon \equiv \frac{V_b}{V_t} \tag{8}$$

We can define the adsorbed density of A as being the mass of A per total volume.

$$\rho_{a,A} = \frac{M_{a,A}}{V_t} = \theta_A \rho_R m_A \tag{9}$$

where $m_A$ is the molecular weight of component A.

We divide equation (5) by the total volume, $V_t$.

$$\frac{M_{t,A}}{V_t} = \frac{M_{a,A}}{V_t} + \frac{M_{b,A}}{V_t}$$

We substitute the densities in equations (6), (7) and (9) to obtain

$$\rho_{t,A} = \rho_{a,A} + \rho_{b,A}\varepsilon \tag{10}$$

This equation can also be written as

$$\rho_{t,A} = \theta_A \rho_R m_A + \rho_{b,A}\varepsilon = \theta_A 6\rho_s \frac{(1-\varepsilon)}{D_P} m_A + \rho_{b,A}\varepsilon$$

This is a "lever-rule" type of mass balance that relates the fractional occupancy of A in the adsorbed phase to the bulk density of A through the total density of A in the system.

*II.C. Differential Material Balances (1 component)*

We perform a differential balance on the total mass of A.

$$accumulation = in - out + generation$$

The accumulation term is given by

$$accumulation = \frac{\partial M_{t,A}}{\partial t} = V_t \frac{\partial \rho_{t,A}}{\partial t}$$

where we used equation (6) and assumed the volume was constant in time.
The total volume of the differential element is the differential width of the element multiplied by the cross-sectional area, $V_t = \Delta z A_x$.
A can only enter and leave the differential volume element via convection. (There is no diffusion since it is single component.) Adsorption and desorption moves the material from the bulk phase to the adsorbed phase, but it does not move it out of the differential volume element. The convective terms accounts for fluid flowing in the bulk phase. There is no convection of the particles; they are assumed to be fixed. As a result the density that appears in the convection term must be the bulk density. Moreover, the convection occurs not through the entire cross-sectional area, but only through that portion of the cross-sectional area that is open to flow, $A_{x,f}$, where $A_{x,f} = \varepsilon A_x$

$$in - out = \left[\rho_{b,A} A_{x,f} v_z\right]_z - \left[\rho_{b,A} A_{x,f} v_z\right]_{z+\Delta z}$$

There is no generation of the total mass of A. If we put all the terms into the balance, we have

$$V_t \frac{\partial \rho_{t,A}}{\partial t} = \left[\rho_{b,A} A_{x,f} v_z\right]_z - \left[\rho_{b,A} A_{x,f} v_z\right]_{z+\Delta z}$$

This can also be written as

$$\Delta z A_x \frac{\partial \rho_{t,A}}{\partial t} = \left[\rho_{b,A} \varepsilon A_x v_z\right]_z - \left[\rho_{b,A} \varepsilon A_x v_z\right]_{z+\Delta z}$$

For constant cross-sectional area, we can divide by the volume and take the limit as $\Delta z$ goes to zero, obtaining,

$$\frac{\partial \rho_{t,A}}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_{b,A}\varepsilon v_z\right] \tag{11}$$

This total mass balance on A is a little curious because in the accumulation term we have the total density and in the convection term, we have the bulk density. Additionally, the convection term has the void fraction in it.

We now proceed to derive the balance on the mass of A in the bulk phase.

$$accumulation = in - out + generation$$

The accumulation term is given by

$$accumulation = \frac{\partial M_{b,A}}{\partial t} = V_b \frac{\partial \rho_{b,A}}{\partial t}$$

where we used equation (7) and assumed the volume was constant in time. Note that this time in the accumulation term, we have had to use the bulk volume. Again, A can only enter and leave the differential volume element via convection. The in and out terms are therefore unchanged.

$$in - out = \left[\rho_{b,A} A_{x,f} v_z\right]_z - \left[\rho_{b,A} A_{x,f} v_z\right]_{z+\Delta z}$$

A in the bulk phase is generated by desorption and consumed by adsorption. In Section I, we have assumed that the reaction rates are given per volume of the reactor, so the generation term is

$$generation = \left(-r_{ads,A} + r_{des,A}\right) V_t$$

If we put all the terms into the balance, we have

$$V_b \frac{\partial \rho_{b,A}}{\partial t} = \left[\rho_{b,A} A_{x,f} v_z\right]_z - \left[\rho_{b,A} A_{x,f} v_z\right]_{z+\Delta z} + \left(-r_{ads,A} + r_{des,A}\right) V_t$$

This can also be written as

$$\varepsilon V_t \frac{\partial \rho_{b,A}}{\partial t} = \left[\rho_{b,A} \varepsilon A_x v_z\right]_z - \left[\rho_{b,A} \varepsilon A_x v_z\right]_{z+\Delta z} + \left(-r_{ads,A} + r_{des,A}\right) V_t$$

For constant cross-sectional area, we can divide by the volume and take the limit as $\Delta z$ goes to zero, obtaining,

$$\frac{\partial \rho_{b,A}}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_{b,A} v_z\right] + \frac{1}{\varepsilon}\left(-r_{ads,A} + r_{des,A}\right) \tag{12}$$

This equation provides the evolution of the bulk density of component A. It can also be written as

$$\frac{\partial \rho_{b,A}}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_{b,A} v_z\right] + \frac{1}{\varepsilon}\left(-k_{ads,A}\rho_{b,A}\left(1-\theta_A\right) + k_{des,A}\theta_A\right)$$

We now proceed to derive the balance on the mass of A in the adsorbed phase.

The accumulation term is given by

$$accumulation = \frac{\partial M_{a,A}}{\partial t} = V_t \rho_R m_A \frac{\partial \theta_A}{\partial t}$$

where we used equation (9) and assumed the volume was constant in time. There is no convection of the adsorbed phase, thus no in and out terms. A in the bulk phase is generated by desorption and consumed by adsorption. In Section I, we have assumed that the reaction rates are given per volume of the reactor, so the generation term is

$$generation = \left(r_{ads,A} - r_{des,A}\right)V_t$$

If we put all the terms into the balance, we have

$$V_t \rho_R m_A \frac{\partial \theta_A}{\partial t} = \left(r_{ads,A} - r_{des,A}\right)V_t$$

This can also be written as

$$\frac{\partial \theta_A}{\partial t} = \frac{1}{\rho_R m_A}\left(r_{ads,A} - r_{des,A}\right) \tag{13}$$

This equation provides the evolution of the adsorbed fractional occupancy of component A. It can also be written as

$$\frac{\partial \theta_A}{\partial t} = \frac{1}{\rho_R m_A}\left(k_{ads,A}\rho_{b,A}\left(1-\theta_A\right) - k_{des,A}\theta_A\right)$$

So, if we collect the relevant evolution equations we have:

$$\frac{\partial \rho_{t,A}}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_{b,A}\varepsilon v_z\right] \qquad \text{total A} \qquad (14.t)$$

$$\frac{\partial \rho_{b,A}}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_{b,A}v_z\right] + \frac{1}{\varepsilon}\left(-k_{ads,A}\rho_{b,A}\left(1-\theta_A\right) + k_{des,A}\theta_A\right) \qquad \text{bulk A} \qquad (14.b)$$

$$\frac{\partial \theta_A}{\partial t} = \frac{1}{\rho_R m_A}\left(k_{ads,A}\rho_{b,A}\left(1-\theta_A\right) - k_{des,A}\theta_A\right) \qquad \text{adsorbed A} \qquad (14.a)$$

In order to solve this system of equations, you require the parameters, $k_{ads,A}$, $k_{des,A}$, $\varepsilon$, $\rho_R$, and the molecular weight $m_A$. You also either need to be given the velocity, $v_z$, or add a momentum balance to this set of equations to solve for it.

| | | |
|---|---|---|
| $v_s$ | superficial velocity | [length/time] |
| $v$ | true velocity | [length/time] |

$$v = \frac{v_s}{\varepsilon}$$

*II.D. Thermodynamic Equilibrium (1 component)*

What happens if we don't know the adsorption rate constants? We can assume adsorption is fast and that the system is at thermodynamic equilibrium. In this case, we can use the adsorption isotherm to relate the fractional occupancy to the bulk density. For example, we can use the Langmuir isotherm.

$$\theta_A = \frac{K\rho_{b,A}}{1+K\rho_{b,A}} \qquad (1)$$

This requires that we know the equilibrium coefficient, which is much easier to estimate than the adsorption rate constants, because it can be estimated from physical chemistry. We also have the lever rule mass balance from equation (10).

$$\rho_{t,A} = \theta_A\rho_R m_A + \rho_{b,A}\varepsilon = \theta_A 6\rho_s \frac{(1-\varepsilon)}{D_P} m_A + \rho_{b,A}\varepsilon$$

If we differentiate both of these equations we have,

$$\frac{\partial \theta_A}{\partial t} = \left[\frac{K}{1+K\rho_{b,A}} - \frac{K^2\rho_{b,A}}{\left(1+K\rho_{b,A}\right)^2}\right]\frac{\partial \rho_{b,A}}{\partial t}$$

$$\frac{\partial \rho_{t,A}}{\partial t} = \rho_R m_A \frac{\partial \theta_A}{\partial t} + \varepsilon \frac{\partial \rho_{b,A}}{\partial t}$$

We can rearrange these equations as

$$\frac{\partial \rho_{b,A}}{\partial t} = \frac{1}{\rho_R m_A \left[ \frac{K}{1+K\rho_{b,A}} - \frac{K^2 \rho_{b,A}}{\left(1+K\rho_{b,A}\right)^2} \right] + \varepsilon} \frac{\partial \rho_{t,A}}{\partial t}$$

$$\frac{\partial \theta_A}{\partial t} = \left[ \frac{K}{1+K\rho_{b,A}} - \frac{K^2 \rho_{b,A}}{\left(1+K\rho_{b,A}\right)^2} \right] \frac{\partial \rho_{b,A}}{\partial t}$$

Analogous equations can be written for spatial derivatives.

$$\frac{\partial \rho_{b,A}}{\partial z} = \frac{1}{\rho_R m_A \left[ \frac{K}{1+K\rho_{b,A}} - \frac{K^2 \rho_{b,A}}{\left(1+K\rho_{b,A}\right)^2} \right] + \varepsilon} \frac{\partial \rho_{t,A}}{\partial z}$$

$$\frac{\partial \theta_A}{\partial z} = \left[ \frac{K}{1+K\rho_{b,A}} - \frac{K^2 \rho_{b,A}}{\left(1+K\rho_{b,A}\right)^2} \right] \frac{\partial \rho_{b,A}}{\partial z}$$

So that, when we couple these equations to equation (11), the total mass balance, we have

$$\frac{\partial \rho_{t,A}}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_{b,A} \varepsilon v_z\right] \tag{15.t}$$

$$\frac{\partial \rho_{b,A}}{\partial t} = \frac{1}{\rho_R m_A \left[ \frac{K}{1+K\rho_{b,A}} - \frac{K^2 \rho_{b,A}}{\left(1+K\rho_{b,A}\right)^2} \right] + \varepsilon} \frac{\partial \rho_{t,A}}{\partial t} \tag{15.b}$$

$$\frac{\partial \theta_A}{\partial t} = \left[ \frac{K}{1+K\rho_{b,A}} - \frac{K^2 \rho_{b,A}}{\left(1+K\rho_{b,A}\right)^2} \right] \frac{\partial \rho_{b,A}}{\partial t} \tag{15.a}$$

So the solution procedure is as follows. Given $\rho_{t,A}$, solve the following set of 2 coupled algebraic equations (the isotherm and lever rule)

$$\theta_A = \frac{K\rho_{b,A}}{1+K\rho_{b,A}} \tag{1}$$

$$\rho_{t,A} = \theta_A \rho_R m_A + \rho_{b,A}\varepsilon$$

for $\theta_A$ and $\rho_{b,A}$. Once you have $\theta_A$ and $\rho_{b,A}$, you can solve all of the spatial derivatives that appear in the evolution equations. Once you have the spatial derivatives, you can evaluate equation (15) for all of the time derivatives.

## III. Multicomponent Systems

We consider a system with $N_c$ components.

### *III.A. Thermodynamic Constraints*

As noted above, if the adsorptive system is at thermodynamic equilibrium, there is a thermodynamic constraint for each component. If we use the Langmuir isotherm, the constraint is

$$\theta_i = \frac{K_i \rho_{b,i}}{1 + \sum_{j=1}^{N_c} K_i \rho_{b,i}} \tag{III.1}$$

There are $N_c$ of these constraints.

### *III.B. "Lever-Rule" Constraints*

For each component, i, we can write

$$M_{t,i} = M_{a,i} + M_{b,i}$$

We have the following definitions

$$\rho_{t,i} \equiv \frac{M_{t,i}}{V_t} \qquad \rho_{b,i} \equiv \frac{M_{b,i}}{V_b} \qquad \rho_{a,i} = \frac{M_{a,i}}{V_t} = \theta_i \rho_R m_i$$

This leads to the following constraints.

$$\rho_{t,i} = \rho_{a,i} + \rho_{b,i} \varepsilon$$

$$\rho_{t,i} = \theta_i \rho_R m_i + \rho_{b,i} \varepsilon = \theta_i 6 \rho_s \frac{(1-\varepsilon)}{D_P} m_i + \rho_{b,i} \varepsilon \tag{III.2}$$

There are $N_c$ of these constraints.

### *III.C. "Sum of the Mass Fractions is Unity" Constraints*

$$\sum_{i=1}^{N_c} w_{\phi,i} = 1 \qquad \text{for all phases } \phi$$

If we multiply this by the phase density we have,

$$\sum_{i=1}^{N_c} \rho_{\phi,i} = \rho_\phi \qquad \text{for all phases } \phi \qquad \text{(III.3)}$$

There are 3 of these constraints for the bulk, adsorbed and total phases. For the total and bulk phases, we have respectively

$$\sum_{i=1}^{N_c} \rho_{t,i} = \rho_t$$

$$\sum_{i=1}^{N_c} \rho_{b,i} = \rho_b$$

For the adsorbed phase we have

$$\sum_{i=1}^{N_c} \rho_{a,i} = \rho_a$$

which can be shown to be equivalent to

$$\sum_{i=1}^{N_c} \theta_i = 1 - \theta_S$$

*III.D. Degree of Freedom Analysis*

For a system with $N_c$ components, we have $3(N_c+1)$ variables and $2N_c$+3 constraints. Therefore, we have $N_c$ independent unkowns.

In the binary system, we have For a system with $N_c$=2 components, we have $3(N_c+1)$=9 variables and $2N_c$+3=7 constraints. Therefore, we have $N_c$=2 independent unkowns. The 9 variables are $\rho_t, \rho_a, \rho_b, \rho_{t,A}, \rho_{a,A}, \rho_{b,A}, \rho_{t,B}, \rho_{a,B}, \rho_{b,B}$. The 7 constraints are 2 isotherms, 2 lever rules and 3 sums of the mass fractions. The 2 independent unknowns can be chosen carefully from the full set of 9 unknowns, for example: $\rho_t, \rho_{t,A}$.

*III.D. Differential Material Balances*

For the total density in all phases,

$$\frac{\partial \rho_t}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_b \varepsilon v_z\right] \qquad \text{(III.4)}$$

For the total density in the bulk phase,

$$\frac{\partial \rho_b}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_b v_z\right] + \frac{1}{\varepsilon}\sum_{i=1}^{N_c}\left(-r_{ads,i} + r_{des,i}\right) \tag{III.5}$$

For the total density in the adsorbed phase,

$$\frac{\partial \rho_a}{\partial t} = \sum_{i=1}^{N_c}\left(r_{ads,i} - r_{des,i}\right) \tag{III.6}$$

For the total density of component i in all phases,

$$\frac{\partial \rho_{t,i}}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_{b,i}\varepsilon v_z\right] - \frac{\partial}{\partial z}\left[j_{b,i}\varepsilon\right] \qquad \text{for all i} \tag{III.7}$$

where $j_{b,i}$ is the diffusive mass flux of component i relative to the center of mass velocity.
For the total density in the bulk phase,

$$\frac{\partial \rho_{b,i}}{\partial t} = -\frac{\partial}{\partial z}\left[\rho_{b,i} v_z\right] - \frac{\partial}{\partial z}\left[j_{b,i}\right] + \frac{1}{\varepsilon}\left(-r_{ads,i} + r_{des,i}\right) \qquad \text{for all i} \tag{III.8}$$

For the total density in the adsorbed phase,

$$\frac{\partial \rho_{a,i}}{\partial t} = r_{ads,i} - r_{des,i} \qquad \text{for all i} \tag{III.9}$$

# III. Reactive Systems