Mass Transfer Issues with Adsorption on a Surface

David Keffer
Department of Chemical and Biomolecular Engineering
University of Tennessee, Knoxville
first begun: March, 2004
Last updated: November 18, 2011

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, θ_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.

ε	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]
ρ_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, ε, and fractional occupancy, θ_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 Δz 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 Δz 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, $k_{ads,A}$, $k_{des,A}$, ε, ρ_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).

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

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 θ_A and $\rho_{b,A}$. Once you have θ_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,

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

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,

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

For the total density in the bulk phase,

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

For the total density in the adsorbed phase,

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

For the total density of component i in all phases,

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

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,

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

For the total density in the adsorbed phase,

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

III.E. Thermodynamic Equilibrium (multicomponent)

If we want the time dependence of the bulk concentrations and surface converages without knowing the rate laws, then we must differentiate our constraints representing thermodynamic equilibrium and conservation of mass.

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

$$\rho_{t,i} = \theta_i \rho_R m_i + \rho_{b,i}\varepsilon \quad \text{(III.2)}$$

Differentiation of the mass balance yields

$$\frac{\partial \rho_{t,i}}{\partial t} = \rho_R m_i \frac{\partial \theta_i}{\partial t} + \varepsilon \frac{\partial \rho_{b,i}}{\partial t}$$

Differentiation of the adsorption isotherm yields

$$\frac{\partial \theta_i}{\partial t} = \frac{K_i}{1+\sum_{j=1}^{N_c} K_i \rho_{b,i}} \frac{\partial \rho_{b,i}}{\partial t} - \frac{K_i \rho_{b,i}}{\left(1+\sum_{j=1}^{N_c} K_i \rho_{b,i}\right)^2} \sum_{j=1}^{N_c} K_i \frac{\partial \rho_{b,i}}{\partial t}$$

In the working of the problem, we will know the $\frac{\partial \rho_{t,i}}{\partial t}$, so we manipulate the mass balance to solve for $\frac{\partial \rho_{b,i}}{\partial t}$

$$\frac{\partial \rho_{b,i}}{\partial t} = \left(\frac{\partial \rho_{t,i}}{\partial t} - \rho_R m_i \frac{\partial \theta_i}{\partial t} \right) \frac{1}{\varepsilon}$$

Substitution of this expression into the differentiated adsorption isotherm yields

$$\frac{\partial \theta_i}{\partial t} = \frac{K_i}{1+\sum_{j=1}^{N_c} K_i \rho_{b,i}} \left(\frac{\partial \rho_{t,i}}{\partial t} - \rho_R m_i \frac{\partial \theta_i}{\partial t} \right) \frac{1}{\varepsilon} - \frac{K_i \rho_{b,i}}{\left(1+\sum_{j=1}^{N_c} K_i \rho_{b,i}\right)^2} \sum_{j=1}^{N_c} K_i \left(\frac{\partial \rho_{t,i}}{\partial t} - \rho_R m_i \frac{\partial \theta_i}{\partial t} \right) \frac{1}{\varepsilon}$$

This is a system of linear algebraic equations that can be solved for the time dependence of the fractional occupancy.

Clearly, it may be simpler to just solve for the evolution of the total densities of each component using an ODE solver and use the Newton-Raphson method at each step to solve the thermodynamic and mass balance constraints. The alternative, generating the ODEs for solution of the bulk concentration and fractional occupancies may be more trouble than it is worth.

III. Reactive Systems

III.A. Adsorption rate constants known (unlikely)

Consider a batch reactor with a heterogeneous reactive system in which A and B adsorb reversibly and A is irreversibly converted to B in a surface reaction. Five reactions and five elementary rate laws can be written.

adsorption of A:	$A_b + S \rightarrow A_a$	$r_1 = k_1 C_A \theta_S$
desorption of A:	$A_a \rightarrow A_b + S$	$r_2 = k_2 \theta_A$
surface rxn of A:	$A_a \rightarrow B_a$	$r_3 = k_3 \theta_A$
adsorption of B:	$B_b + S \rightarrow B_a$	$r_4 = k_4 C_B \theta_S$
desorption of B:	$B_a \rightarrow B_b + S$	$r_5 = k_5 \theta_B$

As noted above, it is unlikely that we will know the four rate constants associated with adsorption. However, in the case that we did know them, we could simply generalize our balances for each component. We ignore all flow terms since we are in a batch reactor.

$$\frac{\partial C_{b,i}}{\partial t} = \frac{1}{\varepsilon}\left(\sum_{j=1}^{n_r} \nu_{j,i} r_j\right) \qquad \text{bulk components}$$

$$\frac{\partial \theta_i}{\partial t} = \frac{1}{\rho_R}\left(\sum_{j=1}^{n_r} \nu_{j,i} r_j\right) \qquad \text{adsorbed components}$$

These reactions include the adsorption and desorption reactions.
These equations can be straightforwardly solved using a numerical technique.
Examples 1 and 2 in the following lecture module solve this problem.

III.B. Adsorption rate constants unknown (much more likely)

If the rate constants for adsorption are unknown, we rely on thermodynamic constraints and the conversation of mass to determine all of the bulk concentrations and the fractional occupancies. We write balances only on the total (bulk + adsorbed) amount of each component. Adsorption and desorption do not change the total amount of a component and are not included. Only reactions which convert one component to another are included (thus the asterisk on the summation).

$$\frac{\partial C_{t,i}}{\partial t} = \sum_{j=1}^{n_r} {}^{*}\nu_{j,i} r_j \qquad \text{total amount of components}$$

In order to solve this numerically, the system of algebraic equations represented by the hermodynamic constraints and the conversation of mass must be sovled at each time step to yield the current bulk concentrations and the fractional occupancies. From this we know all the interesting system properties as a function of time.

Example 3 in the following lecture module solves this problem.