Adsorption Fundamentals and Processes
Lectures 7-10

1. Introduction and Equilibrium
2. Mass Transfer parameters and Column Dynamics
3. Adsorption Separation Processes
Adsorption Separation

- Affinity of solids for gases and vapours
- Separation results from difference in affinity

Packed bed of granular solid which retains A (until capacity for A is exhausted)

- Adsorbent (or sorbent): the one that adsorbs i.e., the solid.
- Adsorbate (or sorbate): component(s) of the fluid stream that is/are adsorbed

<table>
<thead>
<tr>
<th>Physical</th>
<th>Chemical</th>
</tr>
</thead>
</table>
| 1. Reversible  
2. Intermolecular forces of attraction  
3. Exothermic, low heat of adsorption | 1. Irreversible  
2. Electron transfer – chemical bond  
3. Exothermic, high heat of adsorption |
**Adsorbents**

- Normally used in granular form. Size range: 50µm – 12 mm
- Should not give large pressure drop
- Should have adequate strength and hardness
- Highly porous with large internal surface area per unit weight. Surface area inside the pore structure is important for adsorption
  
  * Typical carbon: 1,000 – 1,500 m²/gm  
  * Gas mask charcoal: 10,000 m²/gm

- The pores are normally very small and allows only diffusive transport of adsorbates

<table>
<thead>
<tr>
<th>Pore Type</th>
<th>Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropores</td>
<td>&lt;20</td>
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<tr>
<td>Mesopores</td>
<td>20-50</td>
</tr>
<tr>
<td>Macropores</td>
<td>&gt;50</td>
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</tbody>
</table>

IUPAC Classification (pore diameter)
Common Industrial Adsorbents and Pore Size Distribution

- Common industrial adsorbents:
  - Silica gel (250-900 m²/gm)
  - Activated alumina (200-300 m²/gm)
  - Activated carbon
  - Carbon molecular sieve (CMS)
  - Zeolites – A, X, Y

- Silica gel & Alumina have unimodal distribution
- Zeolite and MSC have bimodal distribution
- (MSC: mean of macropore size distribution is around 1000 Å)
- Activated carbon has trimodal distribution
- Zeolites have fixed micropore size
- All others show micropore size distribution
Important Adsorption Separation Processes

- Dehumidifying air for dry room – alumina
- Drying of reactive/nonreactive gases – 3A zeolite, silica gel, alumina
- Odours from air – activated carbon
- Removal of pollutants from industrial gases (CO₂, SO₂, H₂S etc) – zeolite, activated carbon
- Removal of VOCs from air – activated carbon
- Recovery of valuable solvent from dilute mixtures with air and other gases in paint industry – activated carbon
- Recovery of hydrogen from refinery fuel gas – silica gel, activated carbon
- Recovery of hydrogen from cracked gas – zeolite, activated carbon
• Decolourization of petroleum products and aqueous sugar solution – activated carbon
• Separation of normal and iso-paraffins for upgrading of gasoline – 5A zeolite
• Separation of xylene isomers – X or Y zeolites
• Air separation – 5A zeolite, 13X zeolite (oxygen), CMS (nitrogen)
• Water treatment – activated carbon

Scale of operation: Few grams in laboratory to over 13,000 kg in large industrial operations

Basis of Separation

♦ Steric – size exclusion
♦ Equilibrium – difference in affinity
♦ Kinetic – difference in rate of diffusion
Modelling and Design of an Adsorption Process

Model and Parameters

Phase Equilibrium

Feed composition
Pressure
Temperature
Bed length
Adsorbent size

Dispersion Coefficient

Convection

Purity
Recovery
Productivity
Cycle time
Number of beds
v vs. t at exit
v vs. t at exit

Pore diffusion model

Lumped resistance model

Determination of parameters
Phase Equilibrium: Isotherm Models

The great majority of the isotherms observed to-date can be classified into the following 5 types:

Many theories and models have been developed to interpret different types of isotherms. The resulting isotherm equations are calibrated with experimental data and then used for prediction purposes.
Different Modelling Approaches:

- Kinetic Approach
- Thermodynamic Approach
- Potential Approach

**Kinetic Approach: Langmuir Isotherm**

- This is the simplest and by far the most widely used isotherm model. The development is based on monolayer absorption on **homogeneous surfaces** with the following assumptions:
  - Adsorption of absorbate molecules takes place at **well-defined localized sites**.
  - All the adsorption sites are energetically identical, and **each site accommodates one absorbate molecule only**.
  - There are no lateral interactions between neighbouring adsorbed molecules.
Rate of adsorption = $k_a p (1 - \theta)$
Rate of desorption = $k_d \theta$

$\theta$ is fraction of surfaces occupied = $\frac{q}{q_s}$

$q_s$ is monolayer saturation capacity

At equilibrium, $k_a p (1 - \theta) = k_d \theta$

or, $\theta = \frac{q}{q_s} = \frac{b' p}{1 + b' p}$

$b' = f(T) = b_0 \exp\left(-\frac{\Delta H}{R g T}\right)$

$q_s \neq f(T)$

\[
\frac{q}{q_s} = b' p
\]

or, $q = (b' q_s) p = K'$

$K' = K_0 \exp\left(-\frac{\Delta H}{R g T}\right)$

which shows that Langmuir isotherm reduces to Henry’s Law at low concentration and is therefore thermodynamically consistent.
Rearranging the Langmuir expression:

\[
\frac{1}{q} = \frac{1}{q_s} + \frac{1}{b \cdot q_s p} = \frac{1}{q_s} + \frac{1}{K' \cdot p}
\]

Gas phase in concentration unit

\[
\frac{q}{q_s} = \frac{bc}{1 + bc}
\]

or, \[
\frac{1}{q} = \frac{1}{q_s} + \frac{1}{Kc}
\]

plot of \(\frac{1}{q}\) vs \(\frac{1}{p}\) will give \(K\) and \(q_s\)

\[
b' R_g T = b
\]

\[
bq_s = K \text{ (dimensionless)}
\]

\[
K = K_o e^{-\Delta U / R_g T}; K' = K'_o e^{-\Delta H / R_g T}
\]

\[
\Delta U = \Delta H + R_g T
\]

Use average \(T\) for calculating \(\Delta H\) from \(\Delta U\)

* What are the values of \(K'\) and \(q_s\)?
One may also plot $\frac{c}{q} vs. c$ to get $q_s$ from slope and $K$ from intercept. For an ideal Langmuir system such plots at different temperatures should be parallel.

Langmuir parameters will have physical significance if

- The assumptions are valid
- Extensive data are used

Figure: Regression of O$_2$ adsorption data on CMS for linearized Langmuir model.
IMPORTANT POINTS TO REMEMBER

♦ Best fit of $\frac{1}{q}$ vs $\frac{1}{c}$ or $\frac{c}{q}$ vs $c$ is not equivalent to best-fit of $q$ vs $c$. The linear form is easier for manually extracting $q_s$ and $b$ and is commonly used. Standard nonlinear parameter search methods are widely available now and should be preferred.

♦ Systems not conforming to Langmuir assumptions but the experimental isotherm data showing the Langmuir shape are commonly modelled as Langmuir isotherm for simplicity (specially with regard to numerical simulation of column dynamics). In those cases the parameters should be treated as EMPIRICAL CONSTANTS.

♦ For example, $K$ and $\Delta H$ obtained from parameter search over a wide data range will differ from $K$ and $\Delta H$ obtained by pulse chromatographic study in the linear range.
Multi-site Langmuir Isotherm (Nitta)

- Langmuir isotherm model does not recognize the difference in size of different gas molecules.
- Assumes fixed number of sites ($q_s$), but recognizes that depending on the size of the gas molecule relative to the size of the site ($a_i$) a molecule may take a fraction of or more than one site.
- The following rate equations apply for component $i$:

  \[
  \text{Rate of adsorption} = (k_a)_i p_i (1 - \theta_i)^{a_i} = (k'_a)_i c_i (1 - \theta_i)^{a_i}
  \]

  \[
  \text{Rate of desorption} = (k_d)_i \theta_i
  \]

At equilibrium, the two rates are equal and that gives

\[
b_i c_i = \frac{q_i}{q_{si}} a_i \left(\frac{1 - q_i}{q_{si}}\right)^{a_i}
\]

where $a_i q_{si} = q_s$
Figure: Equilibrium isotherm data for oxygen (closed symbols) and nitrogen (open symbols) in a carbon molecular sieve and their fits to (a) Langmuir model and (b) multisite Langmuir model.

<table>
<thead>
<tr>
<th>Adsorbate (Data Points)</th>
<th>Langmuir Isotherm</th>
<th>Multisite Langmuir Isotherm</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b_0 \times 10^3$ (cc/mmol)</td>
<td>$(-\Delta U)$ (kcal/mol)</td>
<td>$q_{si}$ (mmol/cc)</td>
</tr>
<tr>
<td>O$_2$ (92)</td>
<td>3.86</td>
<td>3.90</td>
<td>3.80</td>
</tr>
<tr>
<td>N$_2$ (82)</td>
<td>2.80</td>
<td>4.26</td>
<td>2.87</td>
</tr>
</tbody>
</table>

- Do you see the improvement in fit?
- Which component shows more improvement?
- What is the quantitative measure of improvement?
- Any striking difference in the parameters?
The following experimental results were obtained to examine if the $q_s$ values from the multisite Langmuir model are physically realistic. What is your conclusion? Why?

**Figure:** Measured equilibrium adsorbed amount of oxygen and nitrogen in a CMS at $-35 \, ^\circ C$ are compared with predictions of multisite Langmuir model and Langmuir model using parameters in the table on the previous page. Solid and dotted lines are predictions of multisite Langmuir and Langmuir models, respectively.
Isosteric Heat of Adsorption

- The following relationship holds at equilibrium:
  \[ \mu_s = \mu_g \]
  \( \mu_s \): chemical potential of adsorbed gas
  \( \mu_g \): chemical potential of unadsorbed gas

- The relationship will also be true for liquid adsorption, in this case the chemical potential of the adsorbed species in all three phases must be equal.

- Assuming ideal vapour phase we have
  \[ \mu_s = \mu_g = \mu^\circ_g + RT \ln \left( \frac{p}{p^\circ} \right) \]
  where superscript \((\circ)\) denotes reference state.

\[ \left( \frac{\partial (\mu_s / T)}{\partial T} \right)_q = \left( \frac{\partial (\mu^\circ_g / T)}{\partial T} \right)_q + R \left( \frac{\partial \ln p}{\partial T} \right)_q \]
- Applying Gibbs-Helmholtz relation: \( \left( \frac{\partial (\mu / T)}{\partial T} \right) = - \frac{\overline{H}}{T^2} \)

\[- \frac{\overline{H}_S}{T^2} = - \frac{\overline{H}_g}{T^2} + R \left( \frac{\partial \ln p}{\partial T} \right)_q \]

or, \( \left( \frac{\partial \ln p}{\partial T} \right)_q = \frac{\overline{H}_g - \overline{H}_S}{RT^2} = \frac{H_g - H_s}{RT^2} = - \Delta H_s \)

\( \overline{H} \) is the partial molar enthalpy. \( H \) is molar enthalpy.

For ideal vapour \( \overline{H}_g = H_g \).

- \( - \Delta H_s = (H_g - H_g) \) is enthalpy change due to adsorption. This is commonly called ISOSTERIC HEAT OF ADSORPTION.

- \( \overline{H}_S \) and therefore \( \Delta H_s \) are in general functions of \( q \)

- If the heat capacity of the sorbate in adsorbed and vapour phases can be neglected, \( \Delta H_s \) is independent of temperature. Hence
\[
\int \partial \ln p = -\frac{\Delta H_s}{R} \int \frac{\partial T}{T^2} + \text{constant}
\]

or,
\[
\ln p = +\frac{\Delta H_s}{RT} + \text{constant}
\]

* \( \ln p \ vs \ \frac{1}{T} \) should yield linear isostere of slope \( \frac{\Delta H_s}{R} \) for a given value of \( q \)
Information concerning the variations of $\Delta H_s$ with adsorbent loading ($q$) can provide useful information concerning the nature of the adsorption surface and the adsorbed phase.

- $\Delta H_s$ may increase with $q$: sorbate-sorbate interaction.
- $\Delta H_s$ may decrease with $q$: energetic heterogeneity of adsorption sites.
- $\Delta H_s$ independent of $q$: adsorbent is energetically homogeneous and there is no sorbate-sorbate interaction.

Water adsorption on 4A zeolite.

$\Delta H_s$ is fairly constant up to 18% surface saturation.
Modified Langmuir Equations

- Several modifications have been proposed to improve data-fit.

- **Langmuir-Freundlich Isotherm**
  \[
  \frac{q}{q_s} = \frac{b' p^{1/n}}{1 + b' p^{1/n}} = \frac{b' p^n}{1 + b' p^n}
  \]
  For hydrocarbon adsorption on AC, this isotherm gives better fit.

- **Toth Isotherm**
  \[
  \frac{q}{q_s} = \frac{p}{(b' + p^n)^{1/n}}
  \]
  - Initially they were considered as empirical.
  - More recently, it has been shown that modifications can also be derived from Langmuir isotherm for different probability density functions to represent the distribution of heterogeneity.

Figure: solid line: Langmuir equation; dashed line: Langmuir-Freundlich equation.
**Dual-site Langmuir Isotherm**

\[
q = \frac{q_{s1}b_1c}{1+b_1c} + \frac{q_{s2}b_2c}{1+b_2c}
\]

CO₂ adsorption in 13X zeolite fits dual site Langmuir isotherm

→ All the isotherms discussed also apply to liquids. In that case, adsorbate concentration can be expressed only as C. For liquid systems, single component isotherm means adsorption of a single sorbate from liquid solutions in which the activity of the solvent is constant.
Multi-component Equilibrium

♦ Models or correlations are crucial to the design of adsorptive separation processes. They should be capable of predicting the equilibrium amount from pure gas isotherms for each constituent in the mixture, within given ranges of operating temperature and total pressure.

♦ All the pure component equilibrium models discussed can be extended to multicomponent systems of corresponding nature. Models and correlations more commonly used are discussed here.

⇒ Extended Langmuir Model

\[
\frac{q_i}{q_s} = \frac{b_i c_i}{1 + \sum_{i=1}^{n} b_i c_i}
\]

Thermodynamic consistency requires \( q_{s1} = q_{s2} = \ldots = q_s \)

♦ This means that single component data for various components should be fitted by forcing equal \( q_s \).
For correlating experimental data, forcing same $q_s$ will give reasonable multicomponent prediction when the actual values are quite close. In other cases, the error may be large and should be applied with caution.

This model is very convenient for incorporating in process simulation. Hence, very popular.
**Multi-site Langmuir**

\[ b_i c_i = \frac{q_i}{q_{si}} a_i \left(1 - \sum_{i=1}^{n} \frac{q_i}{q_{si}}\right) \]

where \( a_i q_{si} = q_s \)

### Langmuir Isotherm (forcing equal \( q_s \))

<table>
<thead>
<tr>
<th>Adsorbate (Data Points)</th>
<th>( b_0 \times 10^3 ) (cc/mmol)</th>
<th>( -\Delta U ) (kcal/mol)</th>
<th>( q_{si} ) (mmol/cc)</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2) (92)</td>
<td>1.81</td>
<td>4.35</td>
<td>3.5</td>
<td>0.196</td>
</tr>
<tr>
<td>N(_2) (82)</td>
<td>4.08</td>
<td>3.83</td>
<td></td>
<td>0.301</td>
</tr>
</tbody>
</table>

### Multisite Langmuir Isotherm

<table>
<thead>
<tr>
<th>Adsorbate (Data Points)</th>
<th>( b_0 \times 10^3 ) (cc/mmol)</th>
<th>( -\Delta U ) (kcal/mol)</th>
<th>( a_i )</th>
<th>( q_{si} ) (mmol/cc)</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2) (92)</td>
<td>1.13</td>
<td>4.26</td>
<td>2.89</td>
<td>7.20</td>
<td>0.030</td>
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<tr>
<td>N(_2) (82)</td>
<td>0.804</td>
<td>4.61</td>
<td>3.36</td>
<td>6.20</td>
<td>0.045</td>
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</tbody>
</table>

Figure: Binary isotherms for oxygen and nitrogen in a CMS at 1.5 °C.
Test your understanding: 1

Experimental equilibrium data for the adsorption of nitrogen on a sample of carbon molecular sieve have been compiled in the Table below.

(a) Find the Langmuir isotherm model parameters for this system by performing both linear and nonlinear regression of the experimental data. Use q_c values for the adsorbed phase. Isotherm parameters include heat of adsorption.

(b) In how many ways can you perform the non-linear regression? Discuss the difference.

Table: Equilibrium data of nitrogen on carbon molecular sieve.

<table>
<thead>
<tr>
<th>Temp. (T) K</th>
<th>Gas phase conc. (C) mmol/cc</th>
<th>Adsorbed conc. based on particle volume (q) mmol/cc</th>
<th>Adsorbed conc. based on microparticle volume (q_c) mmol/cc</th>
<th>Temp. (T) K</th>
<th>Gas phase conc. (C) mmol/cc</th>
<th>Adsorbed conc. based on particle volume (q) mmol/cc</th>
<th>Adsorbed amount based on microparticle volume (q_c) mmol/cc</th>
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</thead>
<tbody>
<tr>
<td>302.15</td>
<td>0.0220</td>
<td>0.2011</td>
<td>0.2893</td>
<td>308.15</td>
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<td>0.9618</td>
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</tbody>
</table>
(a) You should be able to handle linear regression – consult the example given, if it is not yet clear.

- q is the total equilibrium amount per unit volume of adsorbent particle corresponding to gas concentration, c.
- qc is the equilibrium amount per unit volume of microparticle.
- \( q = \varepsilon_p c_p + (1-\varepsilon_p)q_c \). This implies that there is no adsorption in the macropores.
- Similarly, \( K = \varepsilon_p + (1-\varepsilon_p)K_c \) where K is Henry’s constant based on particle volume and \( K_c \) is based on microparticle volume

Nonlinear regression:

\[
\frac{q_c}{q_s} = \frac{bc}{1 + bc}
\]

Note that \( q_s \neq f(\text{temperature}) \); \( b = f(\text{temperature}) \)

We have data at three temperatures. Hence, the objective of nonlinear regression would be to find \( q_s \) and three b values at three temperatures. Since \( q_s \) is common, data at all three temperatures should be regressed at the same time. This may be viewed as an optimization problem with the following objective function:
Minimize \[
\sum_{i=1}^{n} \left( \left( q_c^i \right)^\text{exp} - \left( q_c^i \right)^\text{theo} \right)^2
\]

\[
= \sum_{j=1}^{3} \sum_{i=1}^{n} \left( q_c^j - \frac{q_s b_j C_j^\text{exp}}{1 + b_j C_j^\text{exp}} \right)^2
\]

The parameters to be varied to minimize the objective function are \( q_s \) and \( b_j \) i.e., \( b_1, b_2 \) and \( b_3 \) corresponding to the experimental temperatures \( T_1 (=302.15 \text{ K}) \), \( T_2 (=308.15 \text{ K}) \) and \( T_3 (=323.15 \text{ K}) \).

- Use Solver (under Tools) in EXCEL spreadsheet to solve the above problem.

\[ b = b_o e^{-\frac{\Delta U}{R_g T}} \]

- Recall that

\[ \text{or, } b_j = b_o e^{-\frac{\Delta U}{R_g T_j}} \]

- What will be the slope of \( b_j \) vs \((1/T_j)\) plotted on a semi-log graph?
- Calculate \( \Delta U \) and then \( \Delta H \).

(ii) The Langmuir isotherm may also be written as

\[
\frac{q_c}{q_s} = \frac{b_o e^{-\frac{\Delta U}{R_g T C}}}{1 + b_o e^{-\frac{\Delta U}{R_g T C}}}
\]

- Set up the minimization problem using the isotherm equation in the above form.
- What are the fitting parameters in this formulation?
- What is the difference with the previous method?

Form groups to discuss and verify results