Transport Phenomena  
(Nazaroff & Alvarez-Cohen, Chapter 4)

Types of transport of a substance in a fluid (air or water)

NATURAL PROCESSES:

1. **Advection**: Passive entrainment of substance by the carrying fluid

   **Examples**
   - Smokestack fume blown by the wind
   - Sediments flowing down a river

2. **Diffusion**: Motion with respect to the carrying fluid by random molecular collision

   **Examples**
   - Spreading of a chemical in still water
   - Spreading of a toxic gas in still air

3. **Turbulent dispersion**: Motion with respect to the carrying fluid by chaotic, turbulent swirls of the fluid motion

   **Example**: Stirring cream in coffee

4. **Gravitational settling**: Vertical motion with respect to the fluid because of a density difference; particles heavier than fluid sink to the bottom; those lighter than the fluid rise to the top.

   **Examples**
   - Soil particles settling at the bottom of a lake
   - Oil drops floating on the sea

[Images and links as described in the text]
UNNATURAL PROCESSES

designed to enhance transport when natural processes are too weak

5. **Centrifugal settling** – also called inertial drift:
   Spinning of the fluid to exert a centrifugal force that acts sideways and can be much stronger than gravity
   Example: catching flies on the windshield of a moving car, cyclone dust remover

6. **Electrostatic settling** – also called **electrostatic drift**:
   Charging particles and passage through an electric field to force them to migrate out of the fluid toward an electrode where they are collected
   Example: electrostatic ash precipitator at a power plant

http://www.ppcesp.com/ppcart.html

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**Notion of mass flux**
(Nazaroff & Alvarez-Cohen, Sections 4.A.1 and 4.A.2)

Definition: \( J = \frac{\dot{m}}{A} \Leftrightarrow \dot{m} = J A \)

The flux \( J \) of a substance is defined as the amount \( \dot{m} \) that is transported per unit area \( A \) and per unit time.

**Case of advection:**

Over a time interval \( \Delta t \), fluid moving at velocity \( U \) travels a distance \( \Delta L = U \Delta t \). For a cross-sectional area \( A \), this defines a volume of size \( V = A U \Delta t \).

The amount of substance in that parcel of fluid is
\[
V C = A U \Delta t \cdot C
\]

By definition, the flux \( J \) of the substance is the amount that passes through per area and per time:

\[
J = \frac{\text{amount of substance}}{\text{area} \times \text{time}} = \frac{V C}{A \Delta t} = \frac{A U \Delta t C}{A \Delta t} = U C = \frac{\dot{Q}}{A} C
\]

Thus, in the case of **advection**, the flux is the product of the velocity of the entraining fluid and the concentration of the substance.
Fick's law for molecular diffusion
(Nazaroff & Alvarez-Cohen, Sections 4.3.A.3)

If

\[ k = \text{probability that a molecule crosses the middle line in time period } \Delta t, \]

\[ m_L = \text{mass of molecules } X \text{ on the left}, \]

\[ m_R = \text{mass of molecules } Y \text{ on the right}, \]

then

\[ km_L \] molecules move from left to right, and

\[ km_R \] molecules move from right to left in time \( \Delta t \),

with net movement of \( (km_R - km_L) \).

Thus,

\[ \text{flux} = J = \frac{\text{mass transfer}}{\text{area} \times \text{time}} = \frac{k(m_R - m_L)}{A \Delta t}. \]

In terms of concentrations:

\[ C = \frac{\text{mass}}{\text{volume}} = \frac{m}{A \Delta x} \Rightarrow m = C A \Delta x \]

\[ J = \frac{kA \Delta x}{A \Delta t} (C_L - C_R) \]

\[ J = \frac{k \Delta x}{\Delta t} (C_L - C_R) \]

The concentration difference becomes ambiguous in the limit of smooth variations.

What matters then is the rate over which the concentration varies in space, its gradient:

\[ \frac{\Delta C}{\Delta x} = \frac{C_R - C_L}{\Delta x} \Rightarrow J = -\frac{k \Delta x^2}{\Delta x} \frac{\Delta C}{\Delta x} \]

\[ J = -D \frac{\Delta C}{\Delta x} \] (over a small interval \( \Delta x \))

\[ J = -D \frac{dC}{dx} \] (for a really, really small interval \( \Delta x \))

The minus sign indicates that the flux goes “down-gradient”, that is, from higher to lower concentrations.

\( D \) is called the diffusivity (units of \( \text{m}^2/\text{s} \)).
Diffusion coefficients for selected substances:

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Temperature</th>
<th>$D$ (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>0°C</td>
<td>0.207</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>25°C</td>
<td>0.096</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>20°C</td>
<td>0.151</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>40°C</td>
<td>0.147</td>
</tr>
</tbody>
</table>

Examples in **AIR**

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Temperature</th>
<th>$D$ (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH</td>
<td>20°C</td>
<td>1.19 x 10⁻⁵</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>25°C</td>
<td>1.02 x 10⁻⁵</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>25°C</td>
<td>2.00 x 10⁻⁵</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>15°C</td>
<td>1.00 x 10⁻⁵</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>C₆H₅CH₂CH₃</td>
<td>20°C</td>
<td>8.1 x 10⁻⁶</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>20°C</td>
<td>0.85 x 10⁻⁵</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>15°C</td>
<td>1.26 x 10⁻⁵</td>
</tr>
</tbody>
</table>

Examples in **WATER**

<table>
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<tr>
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<th>Temperature</th>
<th>$D$ (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>CH₃COOH</td>
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<td>15°C</td>
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(Taken from Nazaroff & Alvarez-Cohen, Tables 4.A.2-3, pages 166-167)

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**An application:**

Take benzene (C₆H₆), a volatile liquid, at 25°C.

Molecular weight: $MW = 6\times12 + 6\times1 = 78$ g/mol

Environmental Chemistry 2 – slide 2 → $P_{sat} = 12,800$ Pa = 0.126 atm

Previous slide → $D = 0.096$ cm²/s = $9.6 \times 10^{-6}$ m²/s

$$x = L$$

$$C = 0$$

$$\frac{dC}{dx} = \frac{MW \cdot P_{sat}}{RT \cdot L}$$

$$C = \frac{MW \cdot P_{sat}}{RT} \left( \frac{0.126 \text{ atm}}{(82.05 \times 10^{-5})(273.15 + 25 \text{ K})} \right) = 5.164 \text{ mol/m}^3$$

$C_{benzene} = MW \cdot [C₆H₆] = (78 \text{ g/mol})(5.164 \text{ mol/m}^3) = 402.8 \text{ g/m}^3$

$$J = -D \frac{\Delta C}{\Delta x} = -D \frac{0 - C}{L} = D \frac{C}{L} \quad L = 20 \text{ cm} = 0.20 \text{ m}$$

$$J = (9.6 \times 10^{-6} \text{ m}^2/\text{s}) \left( \frac{402.8 \text{ g/m}^3}{0.20 \text{ m}} \right) = 0.0193 \text{ g/m}^3 \cdot \text{s}$$
**Turbulent dispersion**  
(Nazaroff & Alvarez-Cohen, Section 4.A.4)

For turbulent dispersion, it is customary to use the same expression as for molecular diffusion but with a much higher value for the diffusivity coefficient $D$. Then, the $D$ value no longer depends on the substance being dispersed but rather on the turbulence level in the carrying fluid, which may vary from place to place and time to time according to flow characteristics.

In Nazaroff & Alvarez-Cohen, the turbulent diffusivity is denoted $\varepsilon$ (epsilon) and called dispersion coefficient (page 168).

**Width of plume (for both molecular diffusion and turbulent dispersion)**

$$\sigma = \sqrt{2Dt} = \sqrt{\frac{2D}{u} \frac{x}{u}} \quad \text{with} \quad t = \frac{x}{u}$$

Plume width: $4\sigma = 4\sqrt{2D \frac{x}{u}} = 5.66 \sqrt{\frac{Dx}{u}}$

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**Drag on falling (rising) particles**  
(Nazaroff & Alvarez-Cohen, Section 4.B.1)

Most often, particles in air and water are either heavier or lighter. Thus, they fall (settle) or rise with respect to the air or water.

Particles in relative motion with respect to a fluid are subject to a frictional drag force, $F_d$.

In fluid mechanics, we learn that:

$$F_d = (\text{drag coefficient})(\text{frontal area}) \left( \frac{1}{2} \rho_f V_p^2 \right)$$

$$= C_d \left( \frac{\pi}{4} d_p^2 \right) \left( \frac{1}{2} \rho_f V_p^2 \right)$$

$$= \frac{\pi}{8} C_d \rho_f \frac{d_p^2}{4} V_p^2$$

where $\rho_f = \text{density of fluid}$  
$V_p = \text{particle velocity}$
The drag coefficient is not constant, except for the very large particles that move fast with respect to the fluid.

In general, it is a function of the speed of the particle, measured in terms of the Reynolds number:

\[
\text{Re}_p = \frac{\rho_f d_p V_p}{\mu_f}
\]

where \(\rho_f\) = density of fluid
\(d_p\) = particle diameter
\(V_p\) = particle velocity
\(\mu_f\) = fluid viscosity

Three regimes:

**Stokes (slow):**
\(C_d = \frac{24}{\text{Re}_p}\) \(\text{Re}_p < 0.3\) \(F_d = 3\pi\mu_f d_p V_p\)

**Intermediate:**
\(C_d = \frac{24}{\text{Re}_p} (1 + 0.14 \text{Re}_p^{0.7})\) \(0.3 < \text{Re}_p < 1000\)

**Newton (fast):**
\(C_d = 0.445\) \(1000 < \text{Re}_p\) \(F_d = 0.175\rho_f d_p V_p^2\)

**Correction for the very small particles** (diameter < 1 \(\mu m = 10^{-6}\) m):

(Nazaroff & Alvarez-Cohen, page 174)

For very small particles, the fluid molecules may not be that much smaller than the particles, and the fluid flow around the particles begins to appear as if it had a lot of holes through which the particle may more easily pass. This leads to a reduced drag.

The drag force is then reduced (divided) by a factor, called the **Cunningham slip factor**, and denoted \(C_c\):

\[
F_d = \frac{\text{uncorrected drag force}}{C_c} = \frac{3\pi\mu_f d_p V_p}{C_c}
\]

To get \(C_c\), either use formula or graph:

\[
C_c = 1 + \frac{d_p}{\lambda_g} \left[ 2.51 + 0.80 \exp \left( -\frac{0.55d_p}{\lambda_g} \right) \right]
\]

where \(\lambda_g = 0.066\ \mu m\)

![Graph of drag coefficient as a function of particle Reynolds number](image1)

![Correction for very small particles](image2)
When moving relatively to a fluid, a particle is subject to 3 forces:
- its own weight
- a buoyancy force
- a drag force.

After a brief period of acceleration, a terminal velocity is reached, and a balance is achieved between these 3 forces:

\[ F_g = F_b + F_d \]

weight of particle: \( F_g = m_{\text{particle}} g = \rho_p \frac{\pi d_p^3}{6} g \)

buoyancy force: \( F_b = m_{\text{displaced fluid}} g = \rho_f \frac{\pi d_p^3}{6} g \)

drag force: \( F_d = C_d \frac{\pi d_p^3}{4} \frac{1}{2} \rho_f V^2 \)

Note the difference: \( \rho_p \) = density of material making up the particle, \( \rho_f \) = fluid density.
Two extreme (and most common) situations:
(Nazaroff & Alvarez-Cohen, page 176)

Small particles (Stokes’ regime $Re_p < 0.3$):

$$V_p = \frac{C_v g d_p^2}{18} \left( \frac{\rho_p - \rho_f}{\mu_f} \right)$$

Large particles (Newton’s regime $1000 < Re_p$):

$$V_p = \sqrt{\frac{3.0 g d_p}{\mu_f} \left( \frac{\rho_p - \rho_f}{\rho_f} \right)}$$

Some useful numbers in this context:

Air: $\rho_f = 1.20 \text{ kg/m}^3$ $\mu_f = 1.8 \times 10^{-5} \text{ kg/(m} \cdot \text{s)}$

Water: $\rho_f = 997 \text{ kg/m}^3$ $\mu_f = 1.0 \times 10^{-3} \text{ kg/(m} \cdot \text{s)}$

Sand, grit: $\rho_f = 2650 \text{ kg/m}^3$

Figure 4.8.4 Terminal settling velocity for rigid spherical particles in air ($P = 1 \text{ mm}$, $T = 298 \text{ K}$). For the upper pair of curves, read the particle diameter from the upper scale and the settling velocity from the left-hand scale. For the lower pair of curves, read the particle diameter from the lower scale and the settling velocity from the right-hand scale.
EXAMPLE
(Nazaroff & Alvarez-Cohen, pages 179-180)

Studies have shown that a white surface becomes noticeably soiled when 0.2% of its area is covered by black particles, such as soot.

Estimate the time required for an initially clean, horizontal surface to appear soiled if it is exposed to an atmosphere containing 10 \( \mu \text{g/m}^3 \) of soot particles of diameter 5 \( \mu \text{m} \).

Assume that the particles are spherical and have a density of 2.5 \( \text{g/cm}^3 \).

SOLUTION

Soot particles are small particles. So, assume Stokes drift, but there is no need to apply the Cunningham slip correction factor (particle diameter > 1 \( \mu \text{m} \)). The settling speed is:

\[
V_p = \frac{C_w g d_p^2 \left( \rho_p - \rho_f \right)}{18 \mu_f}
\]

\[
= \frac{(1)(9.81 \text{ m/s}^2)(5\times10^{-6} \text{ m})^2}{18} \left( \frac{2.5 - 1.2 \times 10^{-3} \text{ g/cm}^3}{1.8 \times 10^{-4} \text{ g/cm.s}} \right)
\]

\[
= 0.189 \text{ cm/s}
\]
Determine the mass of each particle

\[ m_p = \rho_p \frac{\pi}{6} d_p^3 = (2.5 \text{ g/cm}^3) \frac{\pi}{6} (5 \times 10^{-4} \text{ cm})^3 = 1.636 \times 10^{-10} \text{ g} \]

Next, determine the number of particles per unit volume of air:

\[ C = \frac{\text{mass concentration in the air}}{\text{mass of each particle}} = \frac{10 \times 10^{-6} \text{ g/m}^3}{1.636 \times 10^{-10} \text{ g/particle}} = \frac{61,116 \text{ particles}}{\text{m}^3} = 0.0611 \text{ particles/cm}^3 \]

The flux of falling particles is

\[ J = C V_p = (0.0611 \text{ particles/cm}^3)(0.189 \text{ cm/s}) = 0.0116 \text{ particles/cm}^3 \cdot \text{s} \]

Each particle has a footprint equal to its cross-sectional area

\[ A_p = \frac{\pi}{4} d_p^2 = \frac{\pi}{4} (5 \times 10^{-4} \text{ cm})^2 = 1.963 \times 10^{-7} \text{ cm}^2 \]

Take 1 cm² of the surface. It has become soiled when 0.2% of its surface is covered by particles, which is 0.002 cm².

This surface coverage necessitates the deposition of a certain number of particles:

\[ N = \frac{\text{surface}}{\text{surface per particle}} = \frac{0.002 \text{ cm}^2}{1.963 \times 10^{-7} \text{ cm}^2 / \text{particle}} = 10,186 \text{ particles} \]

At the rate the particles are falling down, this will take a time equal to

\[ \frac{10,186 \text{ particles per cm}^2 \text{ of surface}}{0.0116 \text{ particles falling per cm}^2 \text{ per second}} = 881,157 \text{ s} = 244.8 \text{ hours} = 10.2 \text{ days} \]