# ChE-402: Diffusion and Mass Transfer

Lecture 5

# Intended Learning Outcome

- To solve transient problems involving both convection and diffusion.
- To further analyze origin of convection.
- To evaluate diffusion coefficients by theory as well as by using empirical models.

# Transient convection and diffusion

**Component 2 does not mix with liquid phase of 1** $\Rightarrow$ **At z = 0, $n_2 = 0$**

- **In the steady case, we could use $v_2 = 0$ (stagnant air);**
- **In this unsteady case, the flux of 1 varies with time and position (for example, 1 displaces 2 immediately after t =0, so $v_2 \neq 0$).**

**Define your system -** Capillary tube

**Define an element to do mass balance**

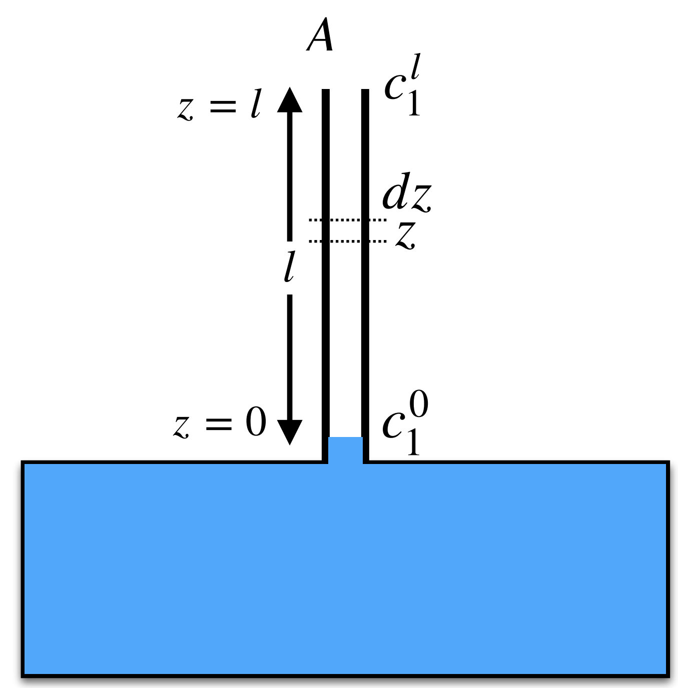
**Apply mass balance**

$$Accumulation * dV = Flux\,|_{in} * A - Flux\,|_{out} * A + Generation * dV - Consumption * dV$$

$$\frac{\partial}{\partial t}(c_1 A \Delta z) = A\ n_1\,|_z - A\ n_1\,|_{z+dz} + 0 - 0$$

$$\frac{\partial c_1}{\partial t} = -\frac{\partial n_1}{\partial z} \qquad n_1 = -D\frac{\partial c_1}{\partial z} + c_1 v^v$$

$$\Rightarrow \frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} - \frac{\partial}{\partial z}(c_1 v^v)$$




**Fast evaporation by diffusion and convection**

# Transient convection and diffusion

$$\frac{\partial c_1}{\partial t} = -\frac{\partial n_1}{\partial z}$$

$$v^v = c_1\bar{V}_1 v_1 + c_2\bar{V}_2 v_2 = \bar{V}_1 n_1 + \bar{V}_2 n_2$$

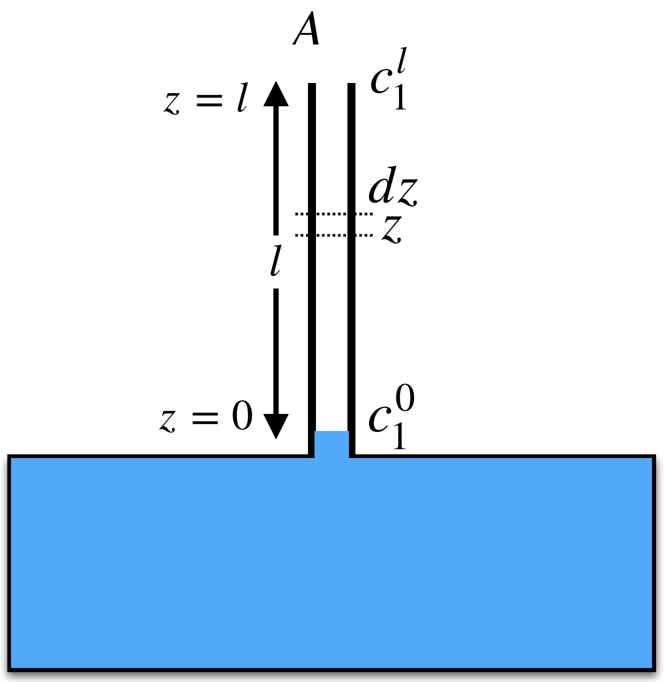
$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} - \frac{\partial}{\partial z}(c_1 v^v)$$

**Apply mass balance for component 2**

$$\overset{o}{Accumulation} * dV = \overset{o}{Flux}\,|_{in} * A - \overset{o}{Flux}\,|_{out} * A + \overset{o}{Generation} * dV - \overset{o}{Consumption} * dV$$

$$\frac{\partial}{\partial t}(c_2 A \Delta z) = A\ n_2\,|_z - A\ n_2\,|_{z+dz} + 0 - 0$$

$$\frac{\partial c_2}{\partial t} = -\frac{\partial n_2}{\partial z}$$



Fast evaporation by diffusion and convection

# Transient convection and diffusion

$$\frac{\partial c_1}{\partial t} = -\frac{\partial n_1}{\partial z}$$

$$\frac{\partial c_2}{\partial t} = -\frac{\partial n_2}{\partial z}$$

$$v^v = c_1\bar{V}_1 v_1 + c_2\bar{V}_2 v_2 = \bar{V}_1 n_1 + \bar{V}_2 n_2$$

**Multiply each term with molar volume and add**

$$\frac{\partial}{\partial t}(\bar{V}_1 c_1 + \bar{V}_2 c_2) = -\frac{\partial}{\partial z}(\bar{V}_1 n_1 + \bar{V}_2 n_2) = -\frac{\partial v^v}{\partial z}$$

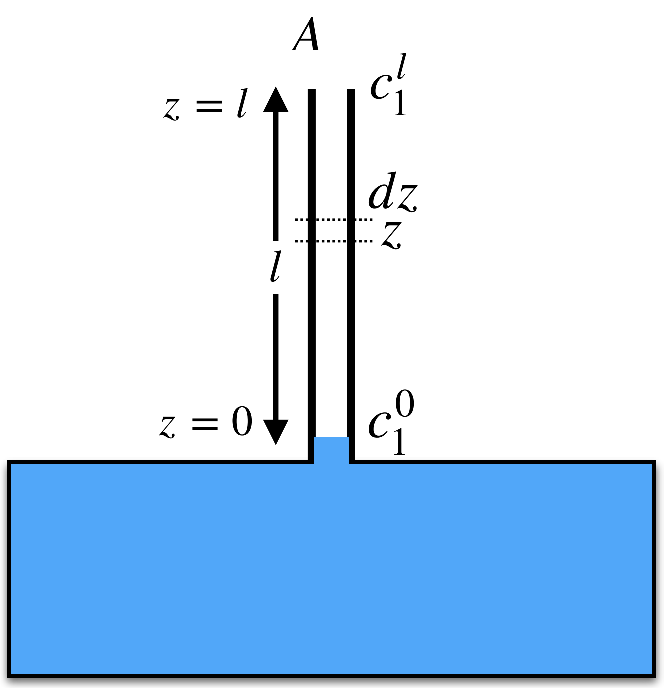
$$\bar{V}_1 c_1 + \bar{V}_2 c_2 \approx y_1 + y_2 = 1$$

**We are dealing with vapor phase**

**Implications**

$$\frac{\partial}{\partial t}(\bar{V}_1 c_1 + \bar{V}_2 c_2) = 0 = -\frac{\partial v^v}{\partial z}$$

- Volume average velocity, $v^v$, is constant, and does not change with z



Fast evaporation by diffusion and convection

$$v^v = \bar{V}_1 n_1 + \bar{V}_2 n_2 = \bar{V}_1 n_1 |_{z=0}$$

- At z = 0, $n_2 = 0$

$$\Rightarrow n_1 |_{z=0} = -D\frac{\partial c_1}{\partial z}|_{z=0} + c_1 v^v |_{z=0} = -D\frac{\partial c_1}{\partial z}|_{z=0} + c_1 \bar{V}_1 n_1 |_{z=0}$$

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# Transient convection and diffusion

$$n_1 \,|_{z=0} = -D\frac{\partial c_1}{\partial z}\,|_{z=0} + c_1 \bar{V}_1 n_1 \,|_{z=0} \qquad \Rightarrow n_1 \,|_{z=0} = \left(\frac{-D\frac{\partial c_1}{\partial z}}{1 - c_1 \bar{V}_1}\right)|_{z=0}$$

**Constant**

$$v^v = \bar{V}_1 n_1 + \bar{V}_2 n_2 = \bar{V}_1 n_1 \,|_{z=0}$$

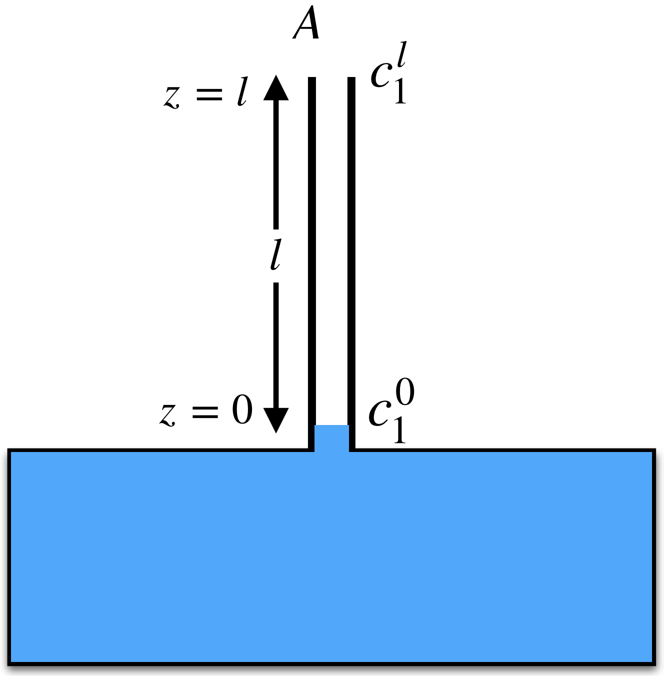
$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} - \frac{\partial}{\partial z}(c_1 v^v)$$

$$\Rightarrow \frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} - v^v \frac{\partial c_1}{\partial z}$$

$$\Rightarrow \frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} - \bar{V}_1 n_1 \,|_{z=0} \frac{\partial c_1}{\partial z}$$

$$\Rightarrow \frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} - \bar{V}_1 \left(\frac{-D\frac{\partial c_1}{\partial z}}{1 - c_1 \bar{V}_1}\right)|_{z=0} \frac{\partial c_1}{\partial z}$$

$$\Rightarrow \frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} + D\left(\frac{\bar{V}_1\frac{\partial c_1}{\partial z}}{1 - c_1 \bar{V}_1}\right)|_{z=0} \frac{\partial c_1}{\partial z}$$

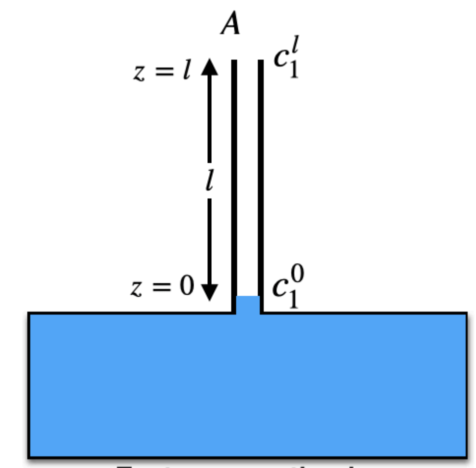


Fast evaporation by diffusion and convection

# Transient convection and diffusion

$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} + D\left(\frac{\bar{V}_1\frac{\partial c_1}{\partial z}}{1 - c_1\bar{V}_1}\right)\Big|_{z=0} \frac{\partial c_1}{\partial z}$$

$$\zeta = \frac{z}{\sqrt{4Dt}}$$




**Initial condition:** $t = 0, \; c_1 = 0$

**Boundary conditions**

$t > 0 \qquad c_1\,|_{z=0} = c_1^{sat}$

**Boundary/Initial conditions:**

$c_1\,|_{\zeta=0} = c_1^{sat}$

$c_1\,|_{\zeta=\infty} = 0$

$$\frac{d^2 c_1}{d\zeta^2} + 2(\zeta - \phi)\frac{dc_1}{d\zeta} = 0$$

$$\frac{c_1}{c_1^{sat}} = \frac{1 - \text{erf}\,(\zeta - \phi)}{1 + \text{erf}\,\phi}$$

$$\bar{V}_1 c_1^{sat} = \left(1 + \frac{1}{\sqrt{\pi}(1 + \text{erf}\,\phi)\phi e^{\phi^2}}\right)^{-1}$$

$$\phi = -\frac{1}{2}\left(\frac{\bar{V}_1\frac{\partial c_1}{\partial \zeta}}{1 - c_1\bar{V}_1}\right)\Big|_{z=0}$$

Dimensionless velocity, which determines extent of diffusion-led convection and the movement of the interface (z= 0).

- Higher diffusive flux leads to convection.
- Higher concentration leads to convection.

**When there is no convection**

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}$$

$$\frac{d^2 c_1}{d\zeta^2} + 2\zeta\frac{dc_1}{d\zeta} = 0$$

$$\frac{c(z,t) - c_S}{c_\infty - c_S} = erf\,\zeta$$

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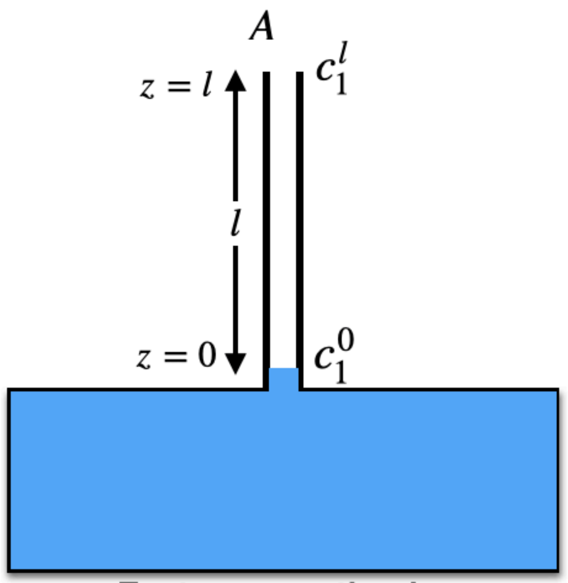
# Summary: transient convection and diffusion

$$\phi = -\frac{1}{2}\left(\frac{\bar{V}_1 \frac{\partial c_1}{\partial \zeta}}{1 - c_1 \bar{V}_1}\right)\Big|_{z=0}$$

$$\bar{V}_1 c_1^{sat} = \left(1 + \frac{1}{\sqrt{\pi}(1 + \text{erf}\,\phi)\phi e^{\phi^2}}\right)^{-1}$$



Fast evaporation by diffusion and convection

$$\zeta = \frac{z}{\sqrt{4Dt}}$$

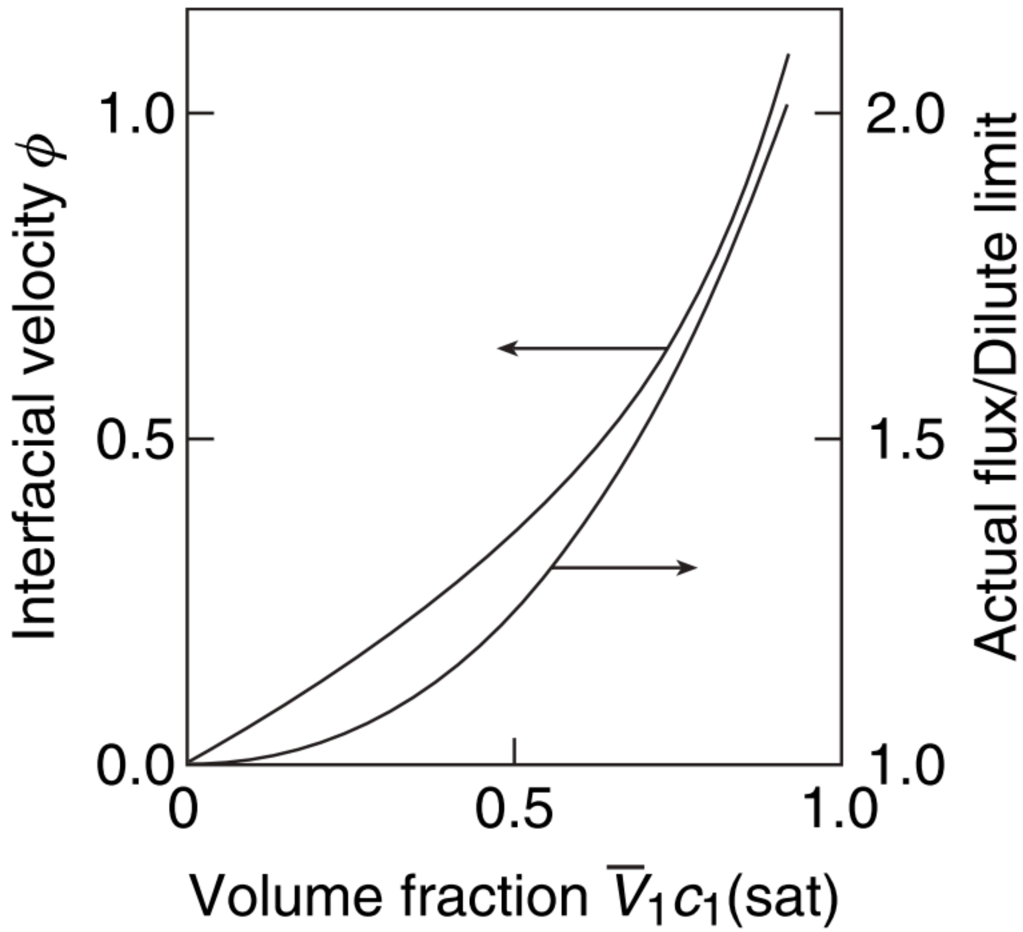
$$\frac{c_1}{c_1^{sat}} = \frac{1 - \text{erf}\,(\zeta - \phi)}{1 + \text{erf}\,\phi}$$

$$n_1\big|_{z=0} = \left(\frac{-D\frac{\partial c_1}{\partial z}}{1 - c_1 \bar{V}_1}\right)\Big|_{z=0} = \sqrt{\frac{D}{\pi t}}\left(\frac{1}{1 - \bar{V}_1 c_1^{sat}}\right)\frac{e^{-\phi^2}}{1 + erf\,\phi} c_1^{sat}$$

# Summary: transient convection and diffusion

$$\phi = -\frac{1}{2}\left(\frac{\bar{V}_1 \frac{\partial c_1}{\partial \zeta}}{1 - c_1 \bar{V}_1}\right)\Big|_{z=0}$$

$$n_1\,|_{z=0} = \sqrt{\frac{D}{\pi t}}\left(\frac{1}{1 - \bar{V}_1 c_1^{sat}}\right)\frac{e^{-\phi^2}}{1 + erf\,\phi}c_1^{sat}$$



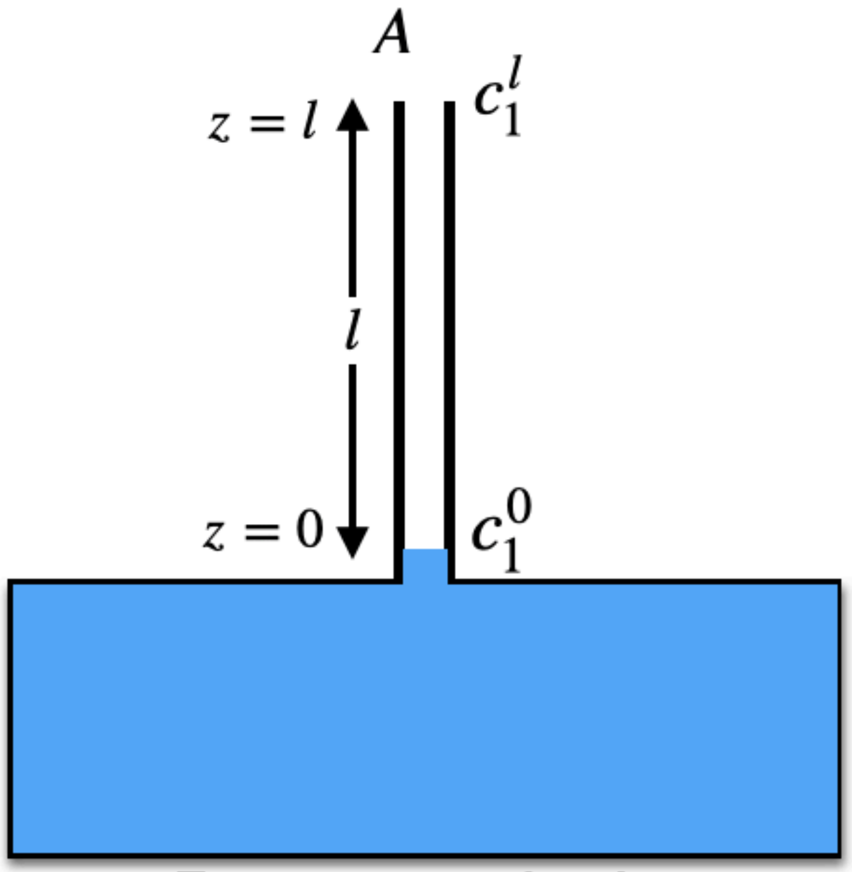
# In which of the following cases, convection can not be neglected

a) Diffusive flux at z = 0 is high

b) $y_1$ at z =0 is 0.05

c) $y_1$ at z = L is 0.5

$$\phi = -\frac{1}{2}\left(\frac{\bar{V}_1 \frac{\partial c_1}{\partial \zeta}}{1 - c_1 \bar{V}_1}\right)\Big|_{z=0}$$

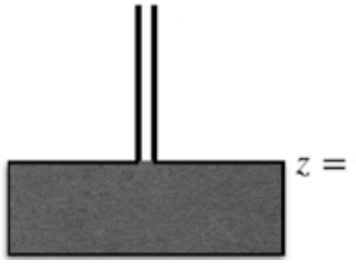



Fast evaporation by diffusion and convection

# In-class exercise problem

A container filled with liquid aniline (molar mass: 93.13 g/mol) is stored in a large room. The container has a cylindrical tube with length of 10 cm and a diameter of 1 cm. Initially, the cylindrical tube is filled with air (pressure of 1 atm), and aniline is prevented from evaporation. At time t = 0, the evaporation of aniline is allowed.

- Saturation vapor pressure of aniline: 10 kPa
- The diffusion coefficient of the aniline vapor in air: $9 \times 10^{-2}$ cm²/s.
- Aniline vapor can be treated as ideal gas.
- Assume a concentration of 0 at z = 10 cm, and saturation conditions at z =0.




1. Neglecting convection, calculate the partial pressure of aniline vapor at z =1.5 cm after 25 seconds.

2. Estimate the error in neglecting convection.

**When convection is neglected;** $\frac{c(z,t) - c_S}{c_\infty - c_S} = erf\ \zeta$

$c_\infty = 0$

t = 25 s, z = 0.015 m

D = $9 \times 10^{-2}$ cm²/s

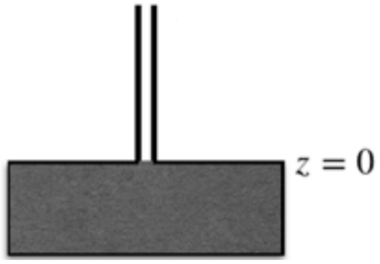
$\Rightarrow \zeta = 0.5$

$$\Rightarrow \frac{c(z,t) - c_S}{0 - c_S} = erf\ \zeta \qquad \Rightarrow \frac{c(z,t)}{c_S} = (1 - erf\ \zeta) = 0.48$$

**Partial pressure = 4.8 kPa**

# In-class exercise problem

**When convection is considered** $\bar{V}_1 c_1^{sat} = \left(1 + \frac{1}{\sqrt{\pi}(1+\text{erf}\ \phi)\phi e^{\phi^2}}\right)^{-1}$




**In vapor phase,** $\bar{V}_1 c_1^{sat} = y_1^{sat} = 10/100 = 0.1$

$$\Rightarrow \left(1 + \frac{1}{\sqrt{\pi}(1+\text{erf}\ \phi)\phi e^{\phi^2}}\right) = 10$$

$$\Rightarrow \frac{1}{\sqrt{\pi}(1+\text{erf}\ \phi)\phi e^{\phi^2}} = 9$$

$$\Rightarrow \sqrt{\pi}(1+\text{erf}\ \phi)\phi e^{\phi^2} = \frac{1}{9} = 0.11$$

$$\Rightarrow (1+\text{erf}\ \phi)\phi e^{\phi^2} = 0.06$$

$\phi$ is positive (dimensionless velocity), $\Rightarrow 1 + \text{erf}\ \phi > 1$, also $\exp(\phi^2) > 1$

$\Rightarrow \phi$ is small $\approx 0.06$

**Check LHS;** $(1 + erf 0.06) 0.06 e^{0.06*0.06} = 0.064$

$LHS \approx RHS$

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# In-class exercise problem

$$\frac{c_1}{c_1^{sat}} = \frac{1 - \text{erf}\,(\zeta - \phi)}{1 + \text{erf}\,\phi}$$

$\zeta = 0.5$ $\phi = 0.06$

$$\frac{c_1}{c_1^{sat}} = \frac{1 - \text{erf}\,0.44}{1 + \text{erf}\,0.06} = 0.5$$

**Partial pressure comes out to be 5.0 kPa**

**Neglecting convection, we got partial pressure of 4.8 kPa**

**Very small error because $y_1^{sat}$ is only 0.1**

# Diffusion coefficients in gases, liquids and solids

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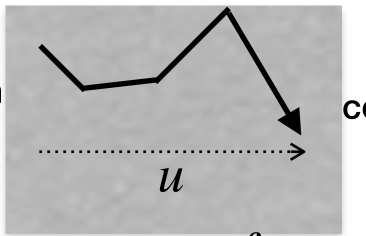
# Understanding the driving force for diffusion

- Diffusion flux is essentially a flow driven by force (the gradient of chemical potential).
- If there is a flow, there should be frictional force opposing the flow.

Frictional drag = chemical potential force




$$fu = -\frac{d\mu}{dz} \quad \Rightarrow \quad u = -\frac{1}{f}\frac{d\mu}{dz}$$

$$\text{flux} = uc = -\frac{c}{f}\frac{d\mu}{dz} = -\left[\frac{k_BT}{f}\frac{d\ln(\hat{f}/P)}{d\ln c}\right]\frac{dc}{dz} = -D\frac{dc}{dz}$$

$$D = \frac{k_BT}{f}\frac{d\ln(\hat{f}/P)}{d\ln c} = D_o\frac{d\ln(\hat{f}/P)}{d\ln c}$$

$$D_o = \frac{k_BT}{f}$$

Diffusivity is inversely proportional to frictional force

<u>Stoke's Einstein Equation</u>

# Comparison of diffusion coefficients

$$D_o = \frac{RT}{f}$$

$$f_{gas} \qquad f_{liquid} \qquad f_{solid}$$

$$D_{gas} \qquad D_{liquid} \qquad D_{solid}$$

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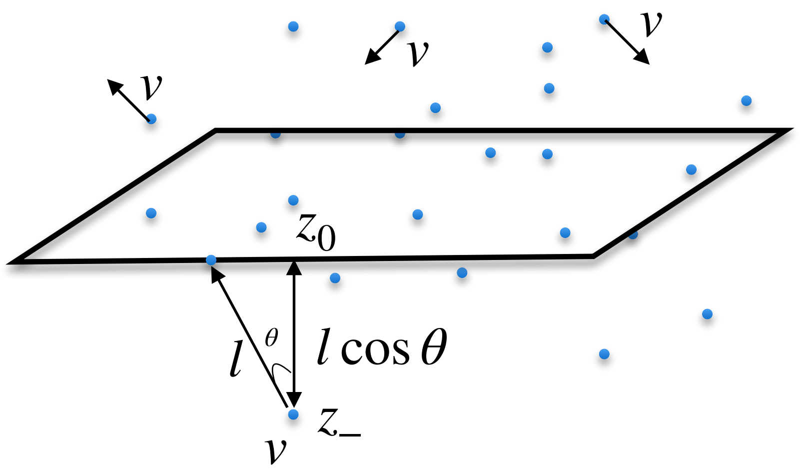
# Diffusion coefficient of gas

$l \; = \;$ mean free path




$$z_0 \; = \; z_- \; + \; l\cos\theta$$

$$\frac{dn}{dt}\uparrow \; = \; c|_{z_-}\, v_z \qquad v_z = v\cos\theta$$

**Velocity of particles are thermally distributed**

$$g(v) \;\; = \;\; \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}}$$

$$\left\langle \frac{dn}{dt}\uparrow \right\rangle \; = \; \int c|_{z_-}\, v_z \;\; g(v)\; d^3v \;\; = \;\; \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{0}^{\infty} c|_{z_-}\, v_z \;\; g(v)\; dv_z$$

$$J\,|_{z=z_0} = \left\langle \frac{dn}{dt}\uparrow \right\rangle - \left\langle \frac{dn}{dt}\downarrow \right\rangle \; = -\,D\frac{dc}{dz}\,|_{z=z_0}$$

**Employ Taylor series for** $c\,|_{z_-}$ $\qquad f(x) = f(x_0) + (x - x_0)\dfrac{df}{dx}\,|_{x=x_0}$

$$c|_{z_-} = c\;|_{z_0} + \; (z_- - z_0)\frac{dc}{dz}|_{z=z_0}$$

$$c\,|_{z_-} \; = c\;|_{z_0} - \; l\cos\theta\frac{dc}{dz}|_{z=z_0}$$

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# Diffusion coefficient of gas

$$J\,|_{z=z_0} = \left\langle \frac{dn}{dt}\uparrow \right\rangle - \left\langle \frac{dn}{dt}\downarrow \right\rangle$$

$$J\,|_{z=z_0} = \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} \left( c\,|_{z_-}\, v_z \;-\; c\,|_{z_+}\, v_z \right) g(v)\, dv_z$$

$$c\,|_{z_-}\, v_z \;=\; c\,|_{z_0}\, v_z \;-\; l\cos\theta \frac{dc}{dz}|_{z=z_0}\, v_z$$

$$c\,|_{z_+}\, v_z \;=\; c\,|_{z_0}\, v_z \;+\; l\cos\theta \frac{dc}{dz}|_{z=z_0}\, v_z$$

$$\Rightarrow\; J\,|_{z=z_0} = -\int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} \left( 2l\cos\theta \frac{dc}{dz}|_{z=z_0}\, v_z \right) g(v)\, dv_z$$

$$\Rightarrow\; J\,|_{z=z_0} = -\,2l\frac{dc}{dz}|_{z=z_0} \left( \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} \cos\theta\; v_z\; g(v)\, dv_z \right) = -\,D\frac{dc}{dz}\,|_{z=z_0}$$

$$\to\; \frac{\bar{v}}{6}$$

$$\bar{v} = \sqrt{\frac{8k_BT}{\pi m}}$$

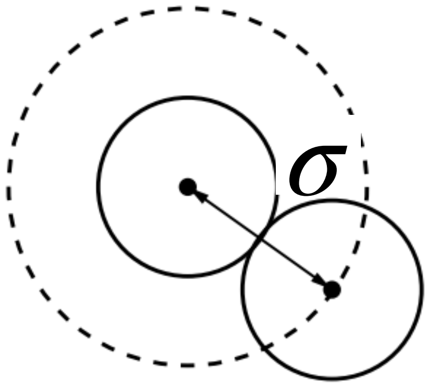
$$\Rightarrow\; J\,|_{z=z_0} = -\,2l\frac{dc}{dz}|_{z=z_0} \left( \frac{\bar{v}}{6} \right) = -\,D\frac{dc}{dz}\,|_{z=z_0}$$

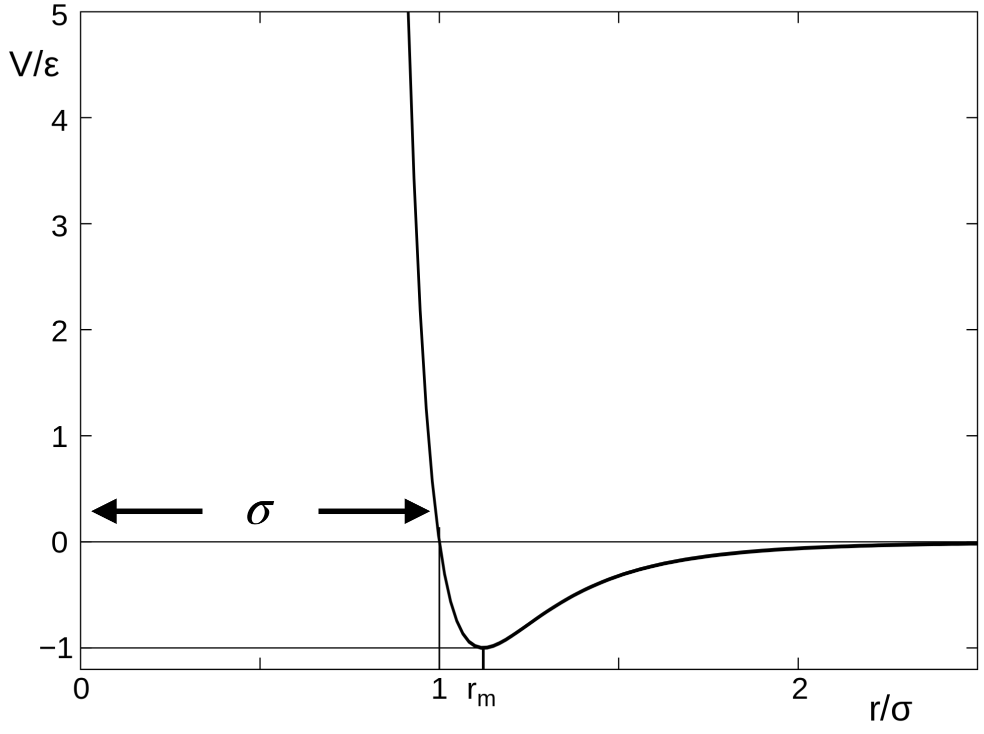
$$D = \frac{1}{3}\,\bar{v}\,l$$

# Diffusion coefficient of gas

$$D = \frac{1}{3}\bar{v}\,l$$

$$\bar{v} = \sqrt{\frac{8k_BT}{\pi m}}$$




$$V_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$l = \frac{k_BT/P}{\left(\frac{\pi}{4}\sigma^2\right)} = \frac{\text{volume of space per molecule}}{\text{cross-sectional area}}$$

**Mean free path is much bigger than average distance between gas molecules**

$$D = \frac{1}{3}\bar{v}\,l = \frac{8}{3}\sqrt{\frac{2}{m}}\left(\frac{k_BT}{\pi}\right)^{3/2}\frac{1}{P\sigma^2}$$

# Binary diffusion coefficient for gas

**Chapman-Enskog theory: Empirically derived (accurate to 8%)**

$$D_{12} = \frac{1.86 * 10^{-3} * T^{1.5} * (1/M_1 + 1/M_2)^{0.5}}{P\sigma_{12}^2\Omega}$$

$\Omega =$ Collision Integral
*D* in cm²/s
*T* in Kelvin
*P* in atm
*M* in g/mole
$\sigma_{12}$ in Angstrom

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$$

$$\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}$$

$$V_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Table 5.1-2 *Lennard–Jones potential parameters found from viscosities*

| Substance | | $\sigma$(Å) | $\varepsilon_{12}/k_B$(K) |
|---|---|---|---|
| Ar | Argon | 3.542 | 93.3 |
| He | Helium | 2.551 | 10.2 |
| Kr | Krypton | 3.655 | 178.9 |
| Ne | Neon | 2.820 | 32.8 |
| Xe | Xenon | 4.047 | 231.0 |
| Air | Air | 3.711 | 78.6 |
| $Br_2$ | Bromine | 4.296 | 507.9 |
| $CCl_4$ | Carbon tetrachloride | 5.947 | 322.7 |
| $CHCl_3$ | Chloroform | 5.389 | 340.2 |
| $CH_2Cl_2$ | Methylene chloride | 4.898 | 356.3 |
| $CH_3Cl$ | Methyl chloride | 4.182 | 350.0 |
| $CH_3OH$ | Methanol | 3.626 | 481.8 |
| $CH_4$ | Methane | 3.758 | 148.6 |
| CO | Carbon monoxide | 3.690 | 91.7 |
| $CO_2$ | Carbon dioxide | 3.941 | 195.2 |

Table 5.1-3 *The collision integral* $\Omega$

| $k_BT/\varepsilon_{12}$ | $\Omega$ | $k_BT/\varepsilon_{12}$ | $\Omega$ | $k_BT/\varepsilon_{12}$ | $\Omega$ |
|---|---|---|---|---|---|
| 0.30 | 2.662 | 1.65 | 1.153 | 4.0 | 0.8836 |
| 0.40 | 2.318 | 1.75 | 1.128 | 4.2 | 0.8740 |
| 0.50 | 2.066 | 1.85 | 1.105 | 4.4 | 0.8652 |
| 0.60 | 1.877 | 1.95 | 1.084 | 4.6 | 0.8568 |
| 0.70 | 1.729 | 2.1 | 1.057 | 4.8 | 0.8492 |
| 0.80 | 1.612 | 2.3 | 1.026 | 5.0 | 0.8422 |
| 0.90 | 1.517 | 2.5 | 0.9996 | 7 | 0.7896 |
| 1.00 | 1.439 | 2.7 | 0.9770 | 9 | 0.7556 |
| 1.10 | 1.375 | 2.9 | 0.9576 | 20 | 0.6640 |
| 1.30 | 1.273 | 3.3 | 0.9256 | 60 | 0.5596 |
| 1.50 | 1.198 | 3.7 | 0.8998 | 100 | 0.5130 |
| 1.60 | 1.167 | 3.9 | 0.8888 | 300 | 0.4360 |

*Source:* Data from Hirschfelder *et al.* (1954).

# Diffusion at high pressure

$$D = \frac{8}{3}\sqrt{\frac{2}{m}}\left(\frac{k_B T}{\pi}\right)^{3/2}\frac{1}{P\sigma^2}$$

$$DP = \text{constant}$$

$$D_1 P_1 = D_2 P_2$$

$$D_2 = D_1 \frac{P_1}{P_2}$$

# Diffusion coefficient in liquid

**One can primarily use the Stoke's-Einstein equation**

$$D_o = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta R}$$

**Stoke's law** $f = 6\pi\eta R$

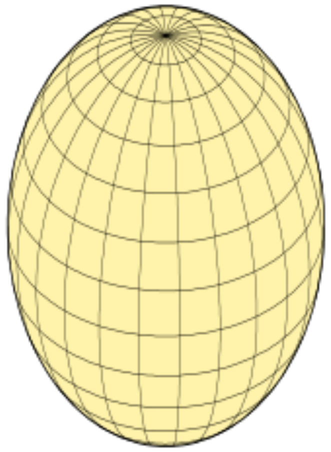
**Valid when** $\frac{R_{solute}}{R_{solvent}} \geq 5$

# Shape effect

**Spherical**

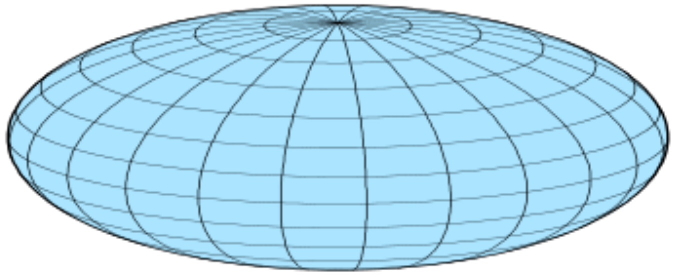
$$D_o = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta R}$$

**Prolate ellipsoid**



$$D_o = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta\left[\dfrac{(a^2-b^2)^{1/2}}{\ln\left(\dfrac{a+(a^2-b^2)^{1/2}}{b}\right)}\right]}$$

**Oblate ellipsoid**



$$D_o = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta\left[\dfrac{(a^2-b^2)^{1/2}}{\tan^{-1}\left(\dfrac{(a^2-b^2)^{1/2}}{b}\right)}\right]}$$

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# Diffusion coefficient in liquid

**When** $R_{solute} \approx R_{solvent}$

$$D = \frac{7.8\ \ 10^{-8}\ T\sqrt{\phi M_2}}{\eta \bar{V}_1^{-0.6}}$$

**Wilke-Chang correlation**

$D$ is diffusion coefficient of solute in cm²/s

$\phi$ is empirical (1 for most organic solvents, 1.5 for alcohols, 2.6 for water)

$\bar{V}_1$ is molar volume of solute in cm³/mol

$M_2$ is molecular weight of solvent in daltons

$\eta$ is viscosity in centipoise

# Diffusion coefficients in solids

Table 5.3-1 *Diffusion coefficients at 25 °C in some characteristic solids*

| Solid | Solute | $D$ (cm$^2$/sec) |
|---|---|---|
| Iron (α Fe; BCC) | Fe | $3 \cdot 10^{-48}$ |
| | C | $6 \cdot 10^{-21}$ |
| | $H_2$ | $2 \cdot 10^{-9}$ |
| Iron (α Fe; FCC) | Fe | $8 \cdot 10^{-55}$ |
| | C | $3 \cdot 10^{-31}$ |
| Copper | Cu | $8 \cdot 10^{-42}$ |
| | Zn | $2 \cdot 10^{-38}$ |

**Diffusion is activated**

$$D = D_o\, e^{-\frac{\Delta E}{RT}}$$

**Extremely small diffusion coefficient**

1) Almost all transport takes place through defects in the solid, especially along grain-boundaries.
2) Transport approaches the limit of semi-infinite media rather than the thin film.
3) Diffusion of hydrogen in solids is an exception because hydrogen dissociates in atomic hydrogen. The electrons of hydrogen disperse into the metallic electron cloud. The proton being much smaller than inter-atomic distances can reside at the inter-metallic interstitial positions and diffuse relatively fast through the lattice.

# Exercise problem: calculate mean-free path, mean velocity and D of helium at 1 atm and 25 °C.

$$l = \frac{k_B T/P}{\left(\frac{\pi}{4}\sigma^2\right)} = \frac{\text{volume occupied by single molecule}}{\text{cross}-\text{sectional area}}$$

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$$

$$D = \frac{1}{3}\bar{v}\,l = \frac{8}{3}\sqrt{\frac{2}{m}}\left(\frac{k_B T}{\pi}\right)^{3/2}\frac{1}{P\sigma^2}$$

Table 5.1-2 *Lennard–Jones potential parameters found from viscosities*

| Substance | | $\sigma$(Å) | $\varepsilon_{12}/k_B$(K) |
|---|---|---|---|
| He | Helium | 2.551 | 10.2 |

$$l = \frac{1.38 * 10^{-23} * 298/101325}{\left(\frac{3.14}{4}(2.55 * 10^{-10})^2\right)} = 7.95 * 10^{-7}\ m = 795\ nm$$

$$\bar{v} = \sqrt{\frac{8 * 1.38 * 10^{-23} * 298}{3.14 * (0.004/(6.023 * 10^{23}))}} = 1256.05\ \ m/s$$

$$D = \frac{1}{3}\bar{v}\,l = \frac{1}{3}1256.05 * 7.95 * 10^{-7} = 3.33 * 10^{-4}\ m^2\ s^{-1} = 3.33\ cm^2\ s^{-1}$$

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# Exercise problem: calculate the kinetic energy of He using data from the previous problem

# Exercise problem: In previous problem, calculate how fast a gas molecule is colliding. Also, calculate average distance between molecules and compare to mean free path.

Time scale for collision is $\approx \frac{l}{\bar{v}} = 0.63 \text{ ns}$

Volume occupied by 1 mole = 22.4 liter

Volume occupied by 1 molecule = 37.2 nm$^3$

Average distance between molecules = 3.3 nm

Mean free path was calculated as 795 nm

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# Calculate D for helium in argon at 1 atm and 25 °C with the Chapman-Enskog theory

$$D_{12} = \frac{1.86 * 10^{-3} * T^{1.5} * (1/M_1 + 1/M_2)^{0.5}}{P\sigma_{12}^2\Omega}$$

*D* in cm²/s
*T* in Kelvin
*P* in atm
*M* in g/mole
$\sigma_{12}$ in Angstrom

$$\epsilon_{12}/k_B = \sqrt{\epsilon_1/k_B * \epsilon_2/k_B} = \sqrt{93.3 * 10.2} = 30.8$$

Table 5.1-2 *Lennard–Jones potential parameters found from viscosities*

| Substance | | $\sigma$(Å) | $\varepsilon_{12}/k_B$(K) |
|---|---|---|---|
| Ar | Argon | 3.542 | 93.3 |
| He | Helium | 2.551 | 10.2 |

Table 5.1-3 *The collision integral* $\Omega$

| $k_BT/\varepsilon_{12}$ | $\Omega$ | $k_BT/\varepsilon_{12}$ | $\Omega$ | $k_BT/\varepsilon_{12}$ | $\Omega$ |
|---|---|---|---|---|---|
| 0.30 | 2.662 | 1.65 | 1.153 | 4.0 | 0.8836 |
| 0.40 | 2.318 | 1.75 | 1.128 | 4.2 | 0.8740 |
| 0.50 | 2.066 | 1.85 | 1.105 | 4.4 | 0.8652 |
| 0.60 | 1.877 | 1.95 | 1.084 | 4.6 | 0.8568 |
| 0.70 | 1.729 | 2.1 | 1.057 | 4.8 | 0.8492 |
| 0.80 | 1.612 | 2.3 | 1.026 | 5.0 | 0.8422 |
| 0.90 | 1.517 | 2.5 | 0.9996 | 7 | 0.7896 |
| 1.00 | 1.439 | 2.7 | 0.9770 | 9 | 0.7556 |
| 1.10 | 1.375 | 2.9 | 0.9576 | 20 | 0.6640 |
| 1.30 | 1.273 | 3.3 | 0.9256 | 60 | 0.5596 |
| 1.50 | 1.198 | 3.7 | 0.8998 | 100 | 0.5130 |
| 1.60 | 1.167 | 3.9 | 0.8888 | 300 | 0.4360 |

*Source:* Data from Hirschfelder *et al.* (1954).

$$\frac{K_BT}{\epsilon_{12}} = 298/30.8 = 9.67$$

$$\Omega \approx 0.75$$

$$\sigma_{12} = \frac{3.542 + 2.551}{2} = 3.047 \overset{o}{A}$$

$$D_{12} = \frac{1.86 * 10^{-3} * 298^{1.5} * (1/4 + 1/40)^{0.5}}{1 * 3.047^2 * 0.75}$$

$$= 0.72\ cm^2 s^{-1}$$

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