DIFFUSION IN SOLIDS

WHY STUDY DIFFUSION?

• Materials often heat treated to improve properties

• Atomic diffusion occurs during heat treatment

• Depending on situation higher or lower diffusion rates desired

• Heat treating temperatures and times, and heating or cooling rates can be determined using the mathematics/physics of diffusion

Example: steel gears are “case-hardened” by diffusing C or N to outer surface

Courtesy of P. Alpay
DIFFUSION IN SOLIDS

ISSUES TO ADDRESS...

• Atomic mechanisms of diffusion

• Mathematics of diffusion

• Influence of temperature and diffusing species on Diffusion rate
DIFFUSION

Phenomenon of material transport by atomic or particle transport from region of high to low concentration

• What forces the particles to go from left to right?
• Does each particle “know” its local concentration?
• Every particle is equally likely to go left or right!
• At the interfaces in the above picture, there are more particles going right than left → this causes an average “flux” of particles to the right!
• Largely determined by probability & statistics

Courtesy of P. Alpay
• Glass tube filled with water.
• At time $t = 0$, add some drops of ink to one end of the tube.
• Measure the diffusion distance, $x$, over some time.

**DIFFUSION DEMO**

![Diagram showing time $t_0$, $t_1$, $t_2$, $t_3$ and diffusion distances $x_0$, $x_1$, $x_2$, $x_3$]

Courtesy of P. Alpay
• Case Hardening:
  -- Example of interstitial diffusion is a case hardened gear.
  -- Diffuse carbon atoms into the host iron atoms at the surface.

• Result: The "Case" is
  --hard to deform: C atoms "lock" planes from shearing.
  --hard to crack: C atoms put the surface in compression.

Fig. 5.0, Callister 6e. (Fig. 5.0 is courtesy of Surface Division, Midland-Ross.)
**PROCESSING USING DIFFUSION (2)**

- **Doping** Silicon with P for n-type semiconductors:
- **Process**
  1. Deposit P rich layers on surface.
  2. Heat it.
  3. Result: Doped semiconductor regions.

Fig. 18.0, Callister 6e.

Courtesy of P. Alpay
Driving force of sintering process = reduction of energy associated with particles surfaces

Reducing scattering losses implies control of ceramic microstructure

Porosity = 0
Transparent material
(if no refractive index mismatch between grains)

Porosity ≠ 0
Translucent material

Two processes in competition: densification and coarsening

Reducing scattering losses implies control of ceramic microstructure
Factors affecting solid-state sintering:
- Temperature, pressure
- Green density
- Uniformity of green microstructure
- Atmosphere composition
- Impurities
- Particles size and size distribution
DIFFUSION: THE PHENOMENA (1)

- **Self-diffusion**: In an elemental solid, atoms also migrate.

\[ D^* = B^* \kappa_8 T \]

**B***: self diffusion mobility

**Self – diffusion coefficient in a simple cubic lattice**

\[ D^* = \frac{1}{6} \delta^2 \nu \]

\( \delta \): interatomic distance

\( \nu \): jump frequency

Courtesy of P. Alpay
Tracer atom studies may not give the true self-diffusion coefficient, $D_i^*$

\[ D_i^T = fD_i^* \]  \hspace{1cm} (12.6)

$f$: correlation coefficient

$D_i^*$: true self-diffusion coefficient

<table>
<thead>
<tr>
<th>Structure</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>0.500</td>
</tr>
<tr>
<td>Simple cubic</td>
<td>0.655</td>
</tr>
<tr>
<td>Body-centered cubic</td>
<td>0.721</td>
</tr>
<tr>
<td>Face-centered cubic</td>
<td>0.781</td>
</tr>
</tbody>
</table>

Fig. 12.4 Diffusion coefficients in gold-nickel alloys. \( \bar{D} \) is the interdiffusion coefficient and \( D^* \) the self-diffusion coefficient. (From J. E. Reynolds, B. L. Averbach, and M. Cohen, *Acta Met.* 5, 29 (1957).)
• **Interdiffusion**: In an alloy or “diffusion couple”, atoms tend to migrate from regions of large to lower concentration.

Initially (diffusion couple)

After some time

Adapted from Figs. 5.1 and 5.2, *Callister 6e*.

Courtesy of P. Alpay
FICK’S LAW AND DIFFUSIVITY OF MATERIALS
DEFINITION OF FLUXES – FICK’S FIRST LAW

Fig. 12.1 Establishment of steady-state concentration gradient; Fick’s first law.
If the concentration of component A is given in mass units, the rate equation for diffusion is:

\[ W_{Ax} = -D_A \left[ \frac{\partial \rho_A}{\partial x} \right] \]  \hspace{1cm} (12.1)

\( W_{Ax} \): mass flux of A in the x-direction, kg (of A) m\(^{-2}\)s\(^{-1}\)

\( \rho_A \): mass concentration of A, kg (of A) m\(^{-3}\) (of total material)

\( D_A \): diffusion coefficient, or diffusivity of A, m\(^2\)s\(^{-1}\)

(intrinsic diffusion coefficient)

In the materials field, the rate equation is usually written in terms of molar concentrations:

\[ j_{Ax} = -D_A \left[ \frac{\partial C_A}{\partial x} \right] \]  \hspace{1cm} (12.2)

\( j_{Ax} \): molar flux of A in the x-direction, mol (of A) m\(^{-2}\)s\(^{-1}\)

\( C_A \): molar concentration of A, mol (of A) m\(^{-3}\) (of total material)
Fick’s first law of diffusion states that species A diffuses in the direction of decreasing concentration of A, similarly as heat flows by conduction in the direction of decreasing temperature, and momentum is transferred in viscous flow in the direction of decreasing velocity.

Eq. (12.1) and (12.2) are convenient forms of the rate equation when the density of the total solution is uniform (in solid or liquid solutions, or in dilute gaseous mixture).

When the density is not uniform:

\[ W_A = -\rho D_A \left( \frac{\partial \rho_A^*}{\partial x} \right) \]

\[ j_A = -CD_A \left[ \frac{\partial X_A}{\partial x} \right] \]

\( \rho \): density of the entire solution, kg/m\(^3\)

\( \rho_A^* \): mass fraction of A

C: local molar concentration in the solution at the point where the gradient is measured
DIFFUSION IN SOLIDS

1. Self-diffusion

Self-diffusion data apply to homogenous alloys in which there is no gradient in chemical composition.

Fig. 12.2 Self-diffusion in materials. (a) Condition before diffusion. (b) Condition after some diffusion. (c) Uniform condition after prolonged diffusion.
\[ D^* = B^* \kappa_B T \]

Fig. 12.3 Self-diffusion in an alloy.
Fig. 12.5—Self-diffusion coefficients for pure metals, plotted as log $D$ versus $T_n/T$, where $T_n$ is the melting temperature. (From O. D. Sherby and M. T. Simnad, Trans. ASM 54, 227 (1961).)
Fig. 12.6 Effect of dilute alloying on self-diffusion and rate of solute substitutional diffusion for a number of metallic systems. $T_M$ is the temperature halfway between the liquidus and solidus of the alloy. (From O. D. Sherby and M. T. Simnad, *ibid.*)
DIFFUSION IN SOLIDS

2. Diffusion under the influence of a composition gradient

- Vacancy mechanism
- Ring mechanism
- Interstitialcy mechanism
Fig. 12.7 The interdiffusion of gold and nickel, and the resulting bulk flow and composition profiles.
Flux of gold atoms (according to an observer sitting on a plane moving with the solid’s velocity):

\[ j_{Au} = -D_{Au} \frac{\partial C_{Au}}{\partial x} \]

Total flux of gold atoms (according to an observer sitting on an unattached plane in space):

\[ N_{Au} = -D_{Au} \frac{\partial C_{Au}}{\partial x} + v_x C_{Au} \]  \hspace{1cm} (12.7)

The accumulation of gold as a function of time within a unit volume:

\[ \Delta x \left( \frac{\partial C_{Au}}{\partial t} \right) = N_{Au|t_0} - N_{Au|t_0} \ast \Delta x \]  \hspace{1cm} (12.8)
Accumulation of nickel in the same unit volume:

\[
\frac{\partial C_{\text{Ni}}}{\partial t} = -\frac{\partial}{\partial x} \left[ D_{\text{Ni}} \frac{\partial C_{\text{Ni}}}{\partial x} - v_x C_{\text{Ni}} \right] \quad (12.11)
\]
If the vacancy concentration within the unit volume is constant, then the volume is approximately constant and:

\[
\frac{\partial C}{\partial t} = \frac{\partial C_{Ni}}{\partial t} + \frac{\partial C_{Au}}{\partial t} = 0
\]  \hspace{1cm} (12.12)

\[
\nu_x = \frac{1}{(C_{Au} + C_{Ni})} \left[ D_{Au} \left( \frac{\partial C_{Au}}{\partial x} \right) + D_{Ni} \left( \frac{\partial C_{Ni}}{\partial x} \right) \right] \hspace{1cm} (12.13)
\]

Only in terms of the gold concentration gradient:

\[
\nu_x = \frac{1}{C} \left[ D_{Au} - D_{Ni} \right] \left( \frac{\partial C_{Au}}{\partial x} \right) \hspace{1cm} (12.14)
\]
Accumulation of gold solely in terms of diffusion coefficients and concentration gradients:

\[
\frac{\partial C_{Au}}{\partial t} = \frac{\partial}{\partial x} \left[ \left( X_{Ni} D_{Au} + X_{Au} D_{Ni} \right) \frac{\partial C_{Au}}{\partial x} \right] \tag{12.15}
\]

Fick’s first law in its simplest form, for gold:

\[
j_{Au} = -D \left( \frac{\partial C_{Au}}{\partial x} \right) \tag{12.16}
\]

\( \bar{D} \) indicates that the flux is proportional to the concentration gradient but side-steps the issue of bulk flow.

The accumulation of gold within the unit volume:

\[
\Delta x \left( \frac{\partial C_{Au}}{\partial t} \right) = [j_{Au}|_{x} - j_{Au}|_{x - \Delta x}] \tag{12.17}
\]
The unsteady-state equation for unidirectional diffusion in solids (*Fick’s second law*):

\[
\frac{\partial C_{Au}}{\partial t} = \frac{\partial}{\partial x} \left( \tilde{D} \frac{\partial C_{Au}}{\partial x} \right) \tag{12.18}
\]

Equation (12.18) is used to obtain analytical solutions for diffusion problems

\[
\tilde{D} = X_{Ni} D_{Au} + X_{Au} D_{Ni} \tag{12.19}
\]

\(D_{Au}\) and \(D_{Ni}\): Intrinsic diffusion coefficients

\(\tilde{D}\): Interdiffusion, mutual diffusion, or chemical diffusion
3. Darken’s equation

\[
\dot{n}_{Ax} = -\frac{n_A B_A}{N_0} \left( \frac{\partial \overline{G}_A}{\partial x} \right)
\]

$n_{Ax}$: flux of A atoms passing through an unit area in the x-direction

$n_A$: the number of A atoms per unit volume

$B_A$: mobility of A atoms in the presence of the energy gradient

$N_0$: Avogadro’s number

$\overline{G}_A$: partial molar free energy of A (chemical potential of A)

\[
\overline{G}_A = G_A^0 + RT \ln a_A
\]
(12.21)

\[ n_{Ax} = \frac{-n_A B_A RT}{N_0} \left( \frac{\partial \ln a_A}{\partial x} \right) \]

\( a_x \): activity of A

(12.22)

\[ D_A = B_A \kappa_B T \left( \frac{\partial \ln a_A}{\partial \ln X_A} \right) \]

\( K_B \): Boltzmann’s constant = \( R/N_0 \)

\( X_A \): Mole fraction of A

\( a_A = X_A \) (for a thermodynamically ideal solution)

(12.23)

\[ D_A = B_A \kappa_B T \]

NERNST-EINSTEIN EQUATION
Gibbs – Duhem equation:

\[ \begin{pmatrix} \frac{\partial \ln a_B}{\partial \ln X_B} \\ \frac{\partial \ln a_A}{\partial \ln X_A} \end{pmatrix} = \begin{pmatrix} \frac{\partial \ln a_A}{\partial \ln X_A} \end{pmatrix} \]  

(12.24)

And only if \( B_A = B_A^* \) and \( B_B = B_B^* \), then Eq. (12.19) can be written as:

\[ \tilde{D} = (X_A D_A^* + X_B D_B^*) \begin{pmatrix} \frac{\partial \ln a_A}{\partial \ln X_A} \end{pmatrix} \]  

(12.25)

If the system is ideal:

\[ \tilde{D} = X_A D_A^* + X_B D_B^*. \]  

(12.26)
Fig. 12.8 Concentration and partial molar free-energy curves at various times for Fe-C and Fe-C-Si alloys welded together and annealed.
DIFFUSION IN SOLIDS

4. Temperature dependence of diffusion in solids

\[ D = D_0 e^{-Q/RT} \]  \hspace{1cm} (12.27)

\[ \text{(Arrhenius equation)} \]

According to Zener, if the jump process is an activated one, jump frequency \( \nu \) can be described by:

\[ \nu = \nu_0 Z e^{-\Delta G^*/RT} \]  \hspace{1cm} (12.28)

\( \nu_0 \) = vibrational frequency of the atom in the lattice
\( Z \) = coordination number
\( \Delta G^* \) = free energy of activation required for the atom to jump from one site into the next
\[ \Delta G^* = \Delta H^* - T \Delta S^*, \]

\[ D^* = D_0 e^{(\Delta H^*/RT)}, \quad (12.29) \]

\[ D_0 = \frac{\delta^2 \nu_0 Z}{6} e^{(\Delta S^*/R)}. \]
Fig. 12.9 Interdiffusion coefficients in nonferrous metals.
Fig. 12.10 Interdiffusion coefficients of interstitial elements through ferrous materials.
Fig. 12.11 Interdiffusion coefficients in ferrous materials.
Sherby and Simnad developed a correlation equation for predicting self-diffusion data in pure metals:

\[ D^* = D_0 e^{-(K_0 + V/T_M)} \]  

12.30

- \( K_0 \) depends only on the crystal structure
- \( V \) = normal valence of the metal
- \( T_M \) = absolute melting point
- \( D_0 \) is approximated as \( 1 \times 10^{-4} \) m2 s\(^{-1}\) for estimation purposes

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>( K_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc</td>
<td>14</td>
</tr>
<tr>
<td>fcc</td>
<td>17</td>
</tr>
<tr>
<td>hcp</td>
<td>17</td>
</tr>
<tr>
<td>Diamond</td>
<td>21</td>
</tr>
</tbody>
</table>

\[ Q = RT_M(K_0 + V) \]  

12.31
<table>
<thead>
<tr>
<th>Diffusing ion</th>
<th>Crystal in which diffusion takes place</th>
<th>$D_0$, m$^2$/s$^{-1}$</th>
<th>$Q$, J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^+$</td>
<td>$\alpha$-Cu$_2$S</td>
<td>$38 \times 10^{-9}$</td>
<td>19 100</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>$\alpha$-Ag$_2$S</td>
<td>$12 \times 10^{-9}$</td>
<td>13 300</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>$\alpha$-Cu$_2$Te</td>
<td>$2.4 \times 10^{-5}$</td>
<td>87 300</td>
</tr>
<tr>
<td>Cu$^+$</td>
<td>$\alpha$-AgI</td>
<td>$16 \times 10^{-9}$</td>
<td>9420</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>$\alpha$-AgI</td>
<td>$50 \times 10^{-9}$</td>
<td>19 100</td>
</tr>
<tr>
<td>Se$^{-}$</td>
<td>$\alpha$-Ag$_2$S</td>
<td>$17 \times 10^{-9}$</td>
<td>83 850</td>
</tr>
<tr>
<td>Pb$^{++}$</td>
<td>PbCl$_2$</td>
<td>$7.8 \times 10^{-4}$</td>
<td>150 000</td>
</tr>
<tr>
<td>Pb$^{++}$</td>
<td>PbI$_2$</td>
<td>$10.6 \times 10^{-4}$</td>
<td>126 000</td>
</tr>
<tr>
<td>O$^-$</td>
<td>Fe$_2$O$_3$</td>
<td>$1 \times 10^{-7}$</td>
<td>611 000</td>
</tr>
<tr>
<td>Fe$^{+++}$</td>
<td>Fe$_3$O$_4$</td>
<td>$4 \times 10^{+1}$</td>
<td>469 000</td>
</tr>
<tr>
<td>Co$^{++}$</td>
<td>CoO</td>
<td>$2.15 \times 10^{-1}$</td>
<td>144 000</td>
</tr>
<tr>
<td>Ni$^{++}$</td>
<td>NiO</td>
<td>$1.83 \times 10^{-7}$</td>
<td>192 000</td>
</tr>
<tr>
<td>O$^-$</td>
<td>NiO</td>
<td>$1.0 \times 10^{-9}$</td>
<td>226 000</td>
</tr>
<tr>
<td>Cr$^{+++}$</td>
<td>Cr$_2$O$_3$</td>
<td>$1.37 \times 10^{-5}$</td>
<td>256 000</td>
</tr>
</tbody>
</table>
The general equation for the transport of the species in the $x$-direction under the influence of an electric field and a concentration gradient in the $x$-direction:

$$
\dot{n}_x = -D_i \left[ \frac{\partial n_i}{\partial x} \right] - B_i n_i z_i e \left[ \frac{\partial \phi}{\partial x} \right], \quad \text{i ions m}^{-2} \text{s}^{-1} \tag{12.32}
$$

- $z_i$ = number of charges on the diffusing species,
- $n_i$ = concentration of diffusing species, ions m$^{-3}$,
- $B_i$ = mobility of species $i$ (steady-state velocity of the particle under the influence of a unit force), m$^2$ s$^{-1}$ V$^{-1}$ C$^{-1}$,
- $D_i$ = the diffusion coefficient of species $i$, m$^2$ s$^{-1}$
- $e = 1.6 \times 10^{-19}$ C charge$^{-1}$,
- $\phi$ = electrical potential, V.

In the absence of a concentration gradient, the flux is:

$$
\dot{n}_x = -B_i n_i z_i e \left[ \frac{\partial \phi}{\partial x} \right], \quad \text{i ions m}^{-2} \text{s}^{-1} \tag{12.33}
$$
The current density:

\[ I = \dot{n}_i z_i e, \quad \text{A m}^{-2} \quad (12.34) \]

\[ I = -B_i n_i (z_i e)^2 \left[ \frac{\partial \phi}{\partial x} \right] \quad (12.35) \]

The electrical conductivity \( \sigma \):

\[ \sigma_i = \frac{1}{- \left( \frac{\partial \phi}{\partial x} \right)} = -B_i n_i (z_i e)^2, \quad \text{ohm}^{-1} \text{ m}^{-1} \quad (12.36) \]

\[ \frac{\sigma_i}{D_i} = \frac{n_i (z_i e)^2}{\kappa_B T} \quad (12.37) \]

This equation is known as the “extended” Nernst-Einstein equation.
\[
\sum_{\text{cation species}} t_{\text{cation } i} + \sum_{\text{anion species}} t_{\text{anion } i} + t_{\text{electron}} = 1
\]  \hspace{1cm} (12.38)

\( t_i \): transference number of species \( i \)

\[
\sigma_i = t_i \sigma_{\text{total}}, \quad \text{ohm}^{-1} \text{ m}^{-1}
\]  \hspace{1cm} (12.39)

For NaCl:

\[
D_{\text{Na}} = \frac{\sigma_{\text{total}} k_B T}{n_{\text{Na}^+} e^2}
\]  \hspace{1cm} (12.40)
Fig. 12.12 Log $D$ versus $1/T$ for sodium in NaCl as determined with radioactive sodium (o), and as calculated from the conductivity (*). (From D. Mapother, H. N. Crooks, and R. Mauer, J. Chem. Phys. 18, 1231 (1950).)

$$\frac{1}{2}O_2(g) = O_\delta + V_{co} + h^*$$
For CoO:

![Graph showing phase stability of CoO with respect to oxygen pressure and temperature.](image)

Fig. 12.13 The stable phase field of cobaltous oxide with respect to oxygen pressure and temperature.

\[ K = \frac{[h^*][V_{Co}']}{P_{O_2}^{1/2}} \]
\[ \bar{D} = 4.33 \times 10^{-7} \exp (-24000/RT), \text{ m}^2 \text{ s}^{-1} \]

\[ \bar{D} \approx D^*_C X_0 \left\{ \frac{\partial \ln a_C}{\partial \ln X_{C_0}} \right\} \]

Thermodynamic factor can be calculated by:

\[ \left\{ \frac{\partial \ln a_C}{\partial \ln X_{C_0}} \right\} = - \left\{ \frac{\partial \ln a_o}{\partial \ln X_{C_0}} \right\} \]

\[ a_o = \left( \frac{P_{O_2}}{P^0_{O_2}} \right)^{1/2} \cdot \]

\[ P^0_{O_2}: \text{ standard oxygen pressure, 1 atm} \]
\[- \left( \frac{\partial \ln a_o}{\partial \ln X_{Co}} \right) \equiv - \left( \frac{\Delta \log a_o}{\Delta \log X_{Co}} \right) = - \left[ \frac{1}{2} \left( \log P_{O_2,\text{initial}} - \log P_{O_2,\text{final}} \right) \right] \]

\[- \left[ \frac{1}{2} \left( \log 4.7 \times 10^{-2} - \log 5.1 \times 10^{-1} \right) \right] = \log \left( \frac{0.4963}{0.4936} \right) = +1.45 \times 10^2 \]

At 1000°C, \( \tilde{D} = 2.16 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \), and \( X_o \equiv 0.50 \). Substituting into Eq. (12.25) as simplified above, we find \( D^*_c \) to be \( 2.98 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \). Applying the correlation coefficient, \( f = 0.78 \) for the fcc cation sublattice, then

\[ D^{T}_{Co} = 0.78 D^*_c = 2.33 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \quad \text{(calculated)} \]

\[ D^{T}_{Co} = 2.60 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \quad \text{(measured)} \]
Fig. 12.14 Diffusion of Na⁺ in a sodium silicate glass. (From W. D. Kingery, *Introduction to Ceramics*, John Wiley, New York, 1960, page 239.)
## Table 12.3 Diffusion constants in Ge

<table>
<thead>
<tr>
<th>Element</th>
<th>$D_0$, m$^2$ s$^{-1}$</th>
<th>$Q$, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>$1.85 \times 10^{-3}$</td>
<td>296</td>
</tr>
<tr>
<td>B</td>
<td>$1.1 \times 10^{-3}$</td>
<td>438</td>
</tr>
<tr>
<td>Al</td>
<td>$1.6 \times 10^{-2}$</td>
<td>313</td>
</tr>
<tr>
<td>Ga</td>
<td>$4.0 \times 10^{-3}$</td>
<td>304</td>
</tr>
<tr>
<td>In</td>
<td>$3.3 \times 10^{-3}$</td>
<td>292</td>
</tr>
<tr>
<td>P</td>
<td>$2.5 \times 10^{-4}$</td>
<td>240</td>
</tr>
<tr>
<td>As</td>
<td>$1.03 \times 10^{-1}$</td>
<td>242</td>
</tr>
<tr>
<td>Sb</td>
<td>$3.2 \times 10^{-4}$</td>
<td>234</td>
</tr>
<tr>
<td>Li</td>
<td>$3.1 \times 10^{-7}$</td>
<td>49</td>
</tr>
<tr>
<td>Cu</td>
<td>$4.0 \times 10^{-7}$</td>
<td>32</td>
</tr>
</tbody>
</table>

(From R. J. Borg and G. J. Dienes, ibid., page 197.)
Fig. 12.15 Diffusion coefficients for Group III and Group V elements in Ge. (From R. J. Borg and G. J. Dienes, *ibid.*, page 196.)
<table>
<thead>
<tr>
<th>Element</th>
<th>$D_0$, m$^2$ s$^{-1}$</th>
<th>$Q$, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>$5.1 \times 10^{-4}$</td>
<td>357</td>
</tr>
<tr>
<td>Al</td>
<td>$8.0 \times 10^{-4}$</td>
<td>335</td>
</tr>
<tr>
<td>Ga</td>
<td>$3.6 \times 10^{-4}$</td>
<td>339</td>
</tr>
<tr>
<td>In</td>
<td>$16.5 \times 10^{-4}$</td>
<td>377</td>
</tr>
<tr>
<td>P</td>
<td>$10.5 \times 10^{-4}$</td>
<td>356</td>
</tr>
<tr>
<td>As</td>
<td>$60.0 \times 10^{-4}$</td>
<td>405</td>
</tr>
<tr>
<td>Sb</td>
<td>$12.9 \times 10^{-4}$</td>
<td>384</td>
</tr>
<tr>
<td>Bi</td>
<td>$1.03 \times 10^{-1}$</td>
<td>447</td>
</tr>
</tbody>
</table>

(From R. J. Borg and G. J. Dienes, *ibid.*, page 201.)
Fig. 12.16 Diffusion coefficients for Group III and Group V elements in Si. (From R. J. Rys and G. J. Dieke, *ibid.* page 201.)
DIFFUSION IN LIQUIDS

1. Liquid state diffusion theories

Hydrodynamical theory:

The force on a sphere moving at steady-state in laminar flow:

\[ F = 6\pi R \eta V_\infty \]

and since \( B = V_\infty / F \),

\[ B = \frac{1}{6\pi R \eta} \]

\[ D = \frac{\kappa_n T}{6\pi R \eta} \quad (12.41) \]

Stokes – Einstein equation
\[ D = \frac{\kappa_n T}{4\pi R \eta} \] (12.42)

Sutherland – Einstein equation

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature range, °C</th>
<th>Sutherland model, nm</th>
<th>Pauling radii, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>110-630</td>
<td>0.151-0.453</td>
<td>0.157</td>
</tr>
<tr>
<td>Hg</td>
<td>274-364</td>
<td>0.120-0.124</td>
<td>0.139</td>
</tr>
<tr>
<td>In</td>
<td>448-1013</td>
<td>0.136-0.306</td>
<td>0.142</td>
</tr>
<tr>
<td>Ag</td>
<td>977-1397</td>
<td>0.137-0.137</td>
<td>0.134</td>
</tr>
<tr>
<td>Zn</td>
<td>394-837</td>
<td>0.129-0.075</td>
<td>0.121</td>
</tr>
<tr>
<td>Sn</td>
<td>575-956</td>
<td>0.130-0.222</td>
<td>0.142</td>
</tr>
</tbody>
</table>

\[ D^* = A \left( \frac{T_M}{M} \right)^{1/2} V_M^{1/3} \]  \hspace{1cm} (12.43)

A is a constant

\( M \) = atomic weight or molecular weight

\( T_M \) = melting point

\( D^* \) = self-diffusion coefficient

\( V_M \) = molar (or atomic) volume

If it is assumed that the atoms in the liquid are in a cubic array, then for materials generally the simple theory predicts that:

\[ 2R = \left( \frac{\bar{V}}{N_0} \right)^{1/3} \]

\[ D^* = \frac{\kappa n T}{2\pi} \left( \frac{N_0}{\bar{V}} \right)^{1/3} \]  \hspace{1cm} (12.44)
**Hole theory:** This theory presumes the existence of holes or vacancies randomly distributed throughout the liquid and providing ready diffusion paths for atoms and ions. The concentration of these holes would have to be very great in order to account for the volume increase upon melting, thus resulting in much higher diffusion rates in liquids than in solids just below the melting point.

**Eyring theory:**

If the liquid is considered quasi-crystalline, and the atoms are in a cubic configuration, then an expression relating $D^*$ and $\eta$ results:

$$D^* = \frac{\kappa_\eta T}{2R\eta}$$  \hspace{1cm} (12.45)
**Fluctuation theory:**

In this theory, the ‘extra’ volume (over that of the solid) in the liquid is distributed evenly throughout the liquid, making the average nearest neighbour distance increase.

Reynik’s fluctuation model:

\[ D^* = a + bT, \quad \text{cm}^2 \text{s}^{-1} \quad (12.46) \]

where \( a = 1.72 \times 10^{24} ZX_0 K \), \( b = 2.08 \times 10^9 ZX_0 \), \( Z \) = number of nearest neighbors, \( X_0 \) = maximum diffusive displacement due to normal vibrations, Å, and \( K \) = a force constant.

\[ X_0 = \bar{d} - 2R, \quad (12.47) \]
Fig. 12.17 Simulations of trajectories of molecules in solid, liquid, and gas. (Reproduced from T. Iida and R. I. L. Guthrie, *ibid.*, page 5.)
DIFFUSION IN LIQUIDS

2. Liquid diffusion data

Diffusion in liquid metals:

Fig. 12.18. Self-diffusion data in liquid metals.
Fig. 12.19 Interdiffusion coefficients in liquid nonferrous alloys.
Fig. 12.20 Interdiffusion coefficients in ferrous liquid alloys
(--- carbon-saturated; --- pure Fe).
**Diffusion in molten salts and silicates:**

<table>
<thead>
<tr>
<th>Diffusate</th>
<th>Melt</th>
<th>Temp. range, °C</th>
<th>$D_0 \times 10^8$, m² s⁻¹</th>
<th>$Q$, kJ mol⁻¹</th>
<th>Typical $D^*$ value, m² s⁻¹</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>NaCl</td>
<td>845-916</td>
<td>8</td>
<td>16.7</td>
<td>$14.2 \times 10^{-9}$</td>
<td>906</td>
</tr>
<tr>
<td>Cl</td>
<td>NaCl</td>
<td>825-942</td>
<td>23</td>
<td>29.7</td>
<td>$8.8 \times 10^{-9}$</td>
<td>933</td>
</tr>
<tr>
<td>Na</td>
<td>NaNO₃</td>
<td>315-375</td>
<td>12.88</td>
<td>20.8</td>
<td>$2.00 \times 10^{-9}$</td>
<td>328</td>
</tr>
<tr>
<td>NO₃</td>
<td>NaNO₃</td>
<td>315-375</td>
<td>8.97</td>
<td>21.2</td>
<td>$1.26 \times 10^{-9}$</td>
<td>328</td>
</tr>
<tr>
<td>Tl</td>
<td>TiCl</td>
<td>487-577</td>
<td>7.4</td>
<td>19.2</td>
<td>$3.89 \times 10^{-9}$</td>
<td>502</td>
</tr>
<tr>
<td>Zn</td>
<td>ZnBr₂</td>
<td>394-650</td>
<td>790</td>
<td>67.2</td>
<td>$0.22 \times 10^{-9}$</td>
<td>500</td>
</tr>
</tbody>
</table>

¹Data from L. Yang and G. Derge, *ibid.*
<table>
<thead>
<tr>
<th>System</th>
<th>Temp. range, °C</th>
<th>$D_0 \times 10^4$, m$^2$ s$^{-1}$</th>
<th>$Q$, kJ mol$^{-1}$</th>
<th>$D^*$, m$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca in CaO-Al$_2$O$_3$-SiO$_2$ (39/21/40)</td>
<td>1350-1540</td>
<td>—</td>
<td>290</td>
<td>$6.7 \times 10^{-11}$ (1673 K)</td>
</tr>
<tr>
<td>Ca in CaO-Al$_2$O$_3$-SiO$_2$ (40/20/40)</td>
<td>1350-1450</td>
<td>—</td>
<td>290</td>
<td>$6.2-6.7 \times 10^{-11}$ (1673 K)</td>
</tr>
<tr>
<td>Si in CaO-Al$_2$O$_3$-SiO$_2$ (40/20/40)</td>
<td>1350-1460</td>
<td>—</td>
<td>290</td>
<td>$1 \times 10^{-11}$ (1703 K)</td>
</tr>
<tr>
<td>O in CaO-Al$_2$O$_3$-SiO$_2$ (40/20/40)</td>
<td>1370-1520</td>
<td>—</td>
<td>40</td>
<td>$4 \times 10^{-10}$ (1703 K)</td>
</tr>
<tr>
<td>Fe in CaO-Al$_2$O$_3$-SiO$_2$ (30/15/55)</td>
<td>1500</td>
<td>—</td>
<td>—</td>
<td>$2.4-3.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>Fe in CaO-Al$_2$O$_3$-SiO$_2$ (43/22/35)</td>
<td>1500</td>
<td>—</td>
<td>—</td>
<td>$2.1-5.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>Fe in FeO-SiO$_2$ (61/39)</td>
<td>1250-1305</td>
<td>—</td>
<td>170</td>
<td>$9.6 \times 10^{-9}$ (1548 K)</td>
</tr>
<tr>
<td>P in CaO-Al$_2$O$_3$-SiO$_2$ (40/21/39)</td>
<td>1300-1500</td>
<td>—</td>
<td>195</td>
<td>$2 \times 10^{-10}$ (1673 K)</td>
</tr>
<tr>
<td>Fe in Fe-S (33.5%)</td>
<td>1150-1238</td>
<td>65.7</td>
<td>56.9</td>
<td></td>
</tr>
<tr>
<td>Fe in Fe-S (31.0%)</td>
<td>1164-1234</td>
<td>298</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>Fe in Fe-S (29.0%)</td>
<td>1158-1254</td>
<td>20200</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>Fe in Fe (48.1%)-Cu (20.5%)-S (31.9%)</td>
<td>1160-1250</td>
<td>1440</td>
<td>90.0</td>
<td></td>
</tr>
<tr>
<td>Fe in Fe (32.0%)-Cu (40.0%)-S (28.0%)</td>
<td>1168-1244</td>
<td>35.7</td>
<td>57.3</td>
<td></td>
</tr>
<tr>
<td>Cu in Cu-S (19.8%)</td>
<td>1160-1256</td>
<td>69.3</td>
<td>53.6</td>
<td></td>
</tr>
<tr>
<td>Cu in Fe (32.0%)-Cu (40.0%)-S (28.0%)</td>
<td>1160-1245</td>
<td>564</td>
<td>82.4</td>
<td></td>
</tr>
</tbody>
</table>

*Data from L. Yang and G. Derge, *ibid.*
**Diffusion in common liquids:**

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>Concentration</th>
<th>$D$, m$^2$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Water</td>
<td>0.1 M</td>
<td>$3.05 \times 10^{-9}$</td>
</tr>
<tr>
<td>NaCl</td>
<td>Water</td>
<td>0.1 M</td>
<td>$1.48 \times 10^{-9}$</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>Water</td>
<td>0.1 M</td>
<td>$1.10 \times 10^{-9}$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>Water</td>
<td>Dilute</td>
<td>$5.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>Water</td>
<td>Dilute</td>
<td>$2.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>Water</td>
<td>Dilute</td>
<td>$1.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>Water</td>
<td>Dilute</td>
<td>$2.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>Water</td>
<td>Dilute</td>
<td>$1.44 \times 10^{-9}$</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>Water</td>
<td>Dilute</td>
<td>$1.97 \times 10^{-9}$</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>Water</td>
<td>0.01 M</td>
<td>$1.12 \times 10^{-9}$</td>
</tr>
<tr>
<td>K$_4$Fe(CN)$_6$</td>
<td>Water</td>
<td>0.01 M</td>
<td>$1.18 \times 10^{-9}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Water</td>
<td>$X = 0.05$</td>
<td>$1.13 \times 10^{-9}$</td>
</tr>
<tr>
<td>Glucose</td>
<td>Water</td>
<td>0.39%</td>
<td>$0.67 \times 10^{-9}$</td>
</tr>
<tr>
<td>Benzene</td>
<td>CCl$_4$</td>
<td>Dilute</td>
<td>$1.53 \times 10^{-9}$</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>Benzene</td>
<td>Dilute</td>
<td>$2.04 \times 10^{-9}$</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>Benzene</td>
<td>Dilute</td>
<td>$2.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>Kerosene</td>
<td>Dilute</td>
<td>$0.96 \times 10^{-9}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Ethanol</td>
<td>Dilute</td>
<td>$4.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>Ethanol</td>
<td>Dilute</td>
<td>$1.50 \times 10^{-9}$</td>
</tr>
<tr>
<td>Phenol</td>
<td>Ethanol</td>
<td>Dilute</td>
<td>$0.89 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
Based on the kinetic theory of gases, self-diffusivity of spherical A atoms diffusing in pure A can be predicted by:

\[
D_{AA}^* = \frac{2}{3} \left( \frac{\kappa_B^3}{\pi^3 m_A} \right)^{1/2} \frac{T^{3/2}}{P d^2}.
\]  
(12.48)

For the diffusivity of two unequal size spherical atoms A and B, kinetic theory predicts:

\[
D_{AB} = \frac{2}{3} \left( \frac{\kappa_B^3}{\pi^3} \right)^{1/2} \left( \frac{1}{2m_A} + \frac{1}{2m_B} \right)^{1/2} \left( \frac{T^{3/2}}{P \left( \frac{d_A + d_B}{2} \right)^2} \right).
\]  
(12.49)

\(K_B\): Boltzmann’s constant, \(1.38 \times 10^{-16}\) ergs molecule\(^{-1}\) K\(^{-1}\)
Chapman – Enskog theory:

For monoatomic gases

\[
D_{AB} = \frac{0.0018583 T^{3/2}}{P(\sigma_{AB})^2 \Omega_{D,AB}} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}
\]

(12.50)

\[\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) = \text{collision diameter, Å,}\]

\[\Omega_{D,AB} = \text{collision integral for A-B mixture at dimensionless temperature } T^*_A, \text{ for the Lennard-Jones potential},\]

\[
T^*_A = \left( \frac{\kappa_B}{\varepsilon} \right)_{AB} T
\]

\[
\left[ \frac{\varepsilon}{\kappa_B} \right]_{AB} = \left[ \left( \frac{\varepsilon}{\kappa_B} \right)_A \left( \frac{\varepsilon}{\kappa_B} \right)_B \right]^{1/2} = \text{average intermolecular force parameter, } K,
\]

\[M_A, M_B = \text{molecular weights of species A and B},\]

\[T = \text{temperature, K},\]

\[P = \text{pressure, atm.}\]
The collision integral can be calculated by:

\[
\Omega_{D,AB} = \frac{A}{T_{AB}^*} + \frac{C}{\exp DT_{AB}^*} + \frac{E}{\exp FT_{AB}^*} + \frac{G}{\exp HT_{AB}^*}
\]  

(12.51)

where \( A = 1.06036, B = 0.15610, C = 0.19300, D = 0.47635, E = 1.03587, F = 1.52996, G = 1.76474, \) and \( H = 3.89411. \)

\[
\varepsilon / \kappa_B = 1.15 \ T_b, \ K,
\]  

(12.52)

\[
\varepsilon / \kappa_B = 1.92 \ T_M, \ K,
\]  

(12.53)
<table>
<thead>
<tr>
<th>Metal</th>
<th>Melting point, °C</th>
<th>Boiling point, °C</th>
<th>( \tilde{V} ) (sol.)</th>
<th>( \tilde{V} ) (liq.)</th>
<th>( \tilde{V}_b ) (liq.)</th>
<th>From ( \tilde{V} ) (sol.)</th>
<th>From ( \tilde{V}_b ) (liq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>960.8</td>
<td>2163</td>
<td>11.02</td>
<td>11.60</td>
<td>13.06</td>
<td>2.72</td>
<td>2.74</td>
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<tr>
<td>Al</td>
<td>660</td>
<td>2057</td>
<td>10.49</td>
<td>11.36</td>
<td>13.26</td>
<td>2.67</td>
<td>2.76</td>
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<tr>
<td>Bi</td>
<td>271</td>
<td>1477</td>
<td>13.34</td>
<td>15.01</td>
<td>14.89</td>
<td>2.90</td>
<td>2.97</td>
</tr>
<tr>
<td>Cd</td>
<td>321</td>
<td>765</td>
<td>7.14</td>
<td>7.68</td>
<td>8.98</td>
<td>2.36</td>
<td>2.43</td>
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<tr>
<td>Co</td>
<td>1493</td>
<td>2877</td>
<td>7.58</td>
<td>8.01</td>
<td>9.15</td>
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<td>2.44</td>
</tr>
<tr>
<td>Cu</td>
<td>1083</td>
<td>2570</td>
<td>7.60</td>
<td>7.94</td>
<td>9.55</td>
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<td>2.47</td>
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<tr>
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<td>2833</td>
<td>23.83</td>
<td>24.54</td>
<td>23.80</td>
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<td>2.80</td>
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<td>13.87</td>
<td>11.43</td>
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<td>Hg</td>
<td>-38.9</td>
<td>357</td>
<td>14.09</td>
<td>15.65</td>
<td>15.71</td>
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<td>3.16</td>
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<td>In</td>
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<td>2087</td>
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<td>16.33</td>
<td>19.98</td>
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<tr>
<td>K</td>
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<td>760</td>
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<td>47.10</td>
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<td>4.54</td>
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<td>186</td>
<td>1317</td>
<td>13.27</td>
<td>13.40</td>
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<td>2.89</td>
<td>2.98</td>
</tr>
<tr>
<td>Mg</td>
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<td>1103</td>
<td>14.66</td>
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<td>Na</td>
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<td>883</td>
<td>24.04</td>
<td>24.79</td>
<td>31.07</td>
<td>3.52</td>
<td>3.66</td>
</tr>
<tr>
<td>Ni</td>
<td>1453</td>
<td>2816</td>
<td>7.11</td>
<td>7.57</td>
<td>9.02</td>
<td>2.34</td>
<td>2.43</td>
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<tr>
<td>Pb</td>
<td>327.4</td>
<td>1717</td>
<td>18.35</td>
<td>19.39</td>
<td>22.47</td>
<td>3.22</td>
<td>3.29</td>
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<td>Pu</td>
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<td>3300</td>
<td>14.20</td>
<td>14.49</td>
<td>18.78</td>
<td>2.95</td>
<td>3.11</td>
</tr>
<tr>
<td>Sb</td>
<td>630.5</td>
<td>1440</td>
<td>18.59</td>
<td>18.74</td>
<td>20.29</td>
<td>3.23</td>
<td>3.18</td>
</tr>
<tr>
<td>Sn</td>
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<td>2770</td>
<td>16.41</td>
<td>17.04</td>
<td>21.63</td>
<td>3.11</td>
<td>3.25</td>
</tr>
<tr>
<td>Tl</td>
<td>303</td>
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<td>18.10</td>
<td>20.64</td>
<td>3.19</td>
<td>2.59</td>
<td>2.51</td>
</tr>
<tr>
<td>Zn</td>
<td>419.5</td>
<td>906</td>
<td>9.56</td>
<td>9.45</td>
<td>10.19</td>
<td>2.59</td>
<td>2.51</td>
</tr>
</tbody>
</table>

*From E. T. Turkdogan, *ibid.*
\[ D_{AB} = \frac{1 \times 10^{-3}T^{1.75}}{P(v_B^{1/3} + v_A^{1/3})^2} \left[ \frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}, \quad \text{cm}^2 \text{ s}^{-1} \] (12.54)

**Table 12.10 Diffusion volumes for simple molecules**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( v )</th>
<th>Molecule</th>
<th>( v )</th>
<th>Molecule</th>
<th>( v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>7.07</td>
<td>Ne</td>
<td>5.59</td>
<td>NH(_3)</td>
<td>14.9</td>
</tr>
<tr>
<td>D(_2)</td>
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<td>Ar</td>
<td>16.1</td>
<td>H(_2)O</td>
<td>12.7</td>
</tr>
<tr>
<td>He</td>
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<td>Kr</td>
<td>22.8</td>
<td>Cl(_2)</td>
<td>37.7</td>
</tr>
<tr>
<td>N(_2)</td>
<td>17.9</td>
<td>CO</td>
<td>18.9</td>
<td>Br(_2)</td>
<td>67.2</td>
</tr>
<tr>
<td>O(_2)</td>
<td>16.6</td>
<td>CO(_2)</td>
<td>26.9</td>
<td>SO(_2)</td>
<td>41.1</td>
</tr>
<tr>
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<td>20.1</td>
<td>N(_2)O</td>
<td>35.9</td>
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<td></td>
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</tbody>
</table>

*From E. N. Fuller, P. D. Schettler, and J. C. Giddings, *ibid.*
Fig. 12.21 Diffusion coefficients in gas mixtures.
Tortuosity is a number greater than one and it ranges from values of 1.5 -2.0 for unconsolidated particles, to as high as 7 or 8 for compacted particles.

An analysis of the flow of molecules through a cylindrical pore radius $r$ under a concentration gradient yields

$$j_A = \frac{2}{3} r \bar{V} \left( \frac{dC_A}{dx} \right)$$
Fig. 12.22 Hydrogen-air diffusion in various unconsolidated porous media. (Adapted from L. N. Satterfield and T. K. Sherwood, *The Role of Diffusion in Catalysts*, Addison-Wesley, Reading, MA, 1963.)
If $r$ and $\lambda$ are of the same order of magnitude, or if the pore diameter is only one order larger, then Knudsen diffusion is presumably important.
If the ratio $D_{AB}/D_K$ is small, then the ordinary diffusion is the rate determining step. Conversely, if $D_{AB}/D_K$ is large, it is presumed that Knudsen diffusion controls.

$$D_{K,eff} = \frac{D_K \omega}{T}$$  \hspace{1cm} (12.57)

<table>
<thead>
<tr>
<th>Material</th>
<th>Gases</th>
<th>$T$, K</th>
<th>$r$, Å</th>
<th>$r$</th>
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<td>Vycor glass</td>
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<td>Cumene</td>
<td>420</td>
<td>(24)</td>
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*From L. N. Satterfield and T. K. Sherwood, *ibid.*