Mechanisms of Diffusion in Materials
A final point on interdiffusion...

- The composition profiles resulting from interdiffusion are generally constrained by phase equilibria. Consider the an Ir–Re diffusion couple annealed at 2400°C:

**Equilibrium diagram**

**Diffusion couple**
Now consider the Os–W system at 2200°C :

In this case, a couple initially between pure Os and pure W can form an *intermediate phase*, $\sigma$, in the interdiffusion zone. If $\sigma$ forms, the resulting composition curve will have *two* discontinuities.
Illustration of interphase layer growth in X–Y alloy interdiffusion…

Atomistic mechanisms for diffusion in crystals

- Given sufficient thermal energy, an atom can move from one site to another in a crystal.
- Most diffusion in crystals occurs by either the vacancy mechanism or the interstitial mechanism.

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Additional mechanisms include the *interstitialcy mechanism* in crystals containing significant numbers of self-interstitials (e.g., produced by irradiation); and the *reptation* mechanism in molten (hence non-crystalline) polymers.

Interstitialcy

Reptation
Atomistic mechanisms, cont’d

- Jumps of vacancies and interstitials are thermally activated, and jumps occur at a jump rate, $\Gamma'$,

\[
\Gamma' = \nu \exp\left[-\frac{G_m}{kT}\right]
\]

$\nu$ is an “attempt frequency” typically $\sim 10^{13} \text{ s}^{-1}$; and $G_m$ is the free energy of migration.

The total jump frequency, $\Gamma$, is $\Gamma = z \Gamma'$, where $z$ is the coordination number ($z = 12$ in f.c.c.).
Diffusion and random walks

During self-diffusion, vacancies and interstitials execute a *random walk* among sites in the crystal structure: the trajectories they follow involve a series of discrete jumps, and each jump is uncorrelated with the previous jump.

Illustrate the effects of a vacancy executing a random walk in a diffusion couple via Java applet...
Diffusion & random walks, cont’d

- Mean-square displacement from a random walk of \( n \) jumps each of length \( r \):

\[
\langle R^2 \rangle = nr^2
\]

and for a random-walking vacancy or interstitial, the self-diffusivity in three-dimensional systems is given by:

\[
D = \frac{\Gamma r^2}{6}
\]
Diffusion & random walks, cont’d

- Diffusion in alloys: intrinsic diffusivity and interdiffusivity

These can involve correlated jumps and the resulting value of the mean square displacement can be either greater than, or less than, that for self-diffusion. The correlation factor, $f$, accounts for the extent of correlation, with $f = 1$ for uncorrelated jumps:

$$\langle R^2 \rangle = nr^2 \cdot f \quad \text{and} \quad D = \frac{G r^2}{6} f$$
Self-diffusion of interstitials

- Involves only random walk of the interstitial species, and thus

\[
D_I = \frac{\Gamma_I r^2}{6} f = \frac{z\Gamma'_I r^2}{6} f = \frac{z\nu r^2}{6} \exp[-G^m_I/(kT)] \cdot 1
\]

\[
= \frac{z\nu r^2}{6} \exp[S^m_I/k] \cdot \exp[-H^m_I/(kT)]
\]

Note that interstitial motion is uncorrelated, so \( f = 1 \).
Self-diffusion of vacancies

- Involves only random walk of vacancies, and thus

\[ D_V = \frac{\Gamma_V r^2}{6} f = \frac{z\Gamma_V' r^2}{6} f = \frac{zvr^2}{6} \exp\left[-\frac{G_V^m}{kT}\right] \cdot 1 \]

\[ = \frac{zvr^2}{6} \exp\left[\frac{S_V^m}{k}\right] \cdot \exp\left[-\frac{H_V^m}{kT}\right] \]

Note that vacancy motion is uncorrelated, so \( f = 1 \).
Self-diffusion of solute atoms via vacancy mechanism

- Involves exchange of randomly walking vacancies with the solute atom, A, and thus the atom jump frequency must relate to both the vacancy jump frequency and the probability that a site adjacent to the solute atom is vacant, $X_V$. $X_V$ is equal to the equilibrium fraction of vacant sites,

$$X_V = \exp\left[-\frac{G^f_V}{kT}\right] = \exp\left[\frac{S^f_V}{k}\right] \exp\left[-\frac{H^f_V}{kT}\right]$$
Self-diffusion of solute atoms via vacancy mechanism, cont’d

Using equations for $D$ and $\Gamma_A = X_V \Gamma_V = X_V z \Gamma'_V$

\[
D_A = \frac{X_v z \Gamma_v r^2}{6} f = \frac{z r^2 \nu}{6} \exp\left[ -\frac{(G_V^f + G_V^m)}{(kT)} \right] f
\]

\[
= \frac{z r^2 \nu}{6} \exp\left[ \frac{(S_V^f + S_V^m)}{k} \right] \exp\left[ -\frac{(H_V^f + H_V^m)}{(kT)} \right] f
\]

The correlation factor, $f$, for vacancy diffusion in metals is about 0.7 and can be calculated more precisely for various specific cases.