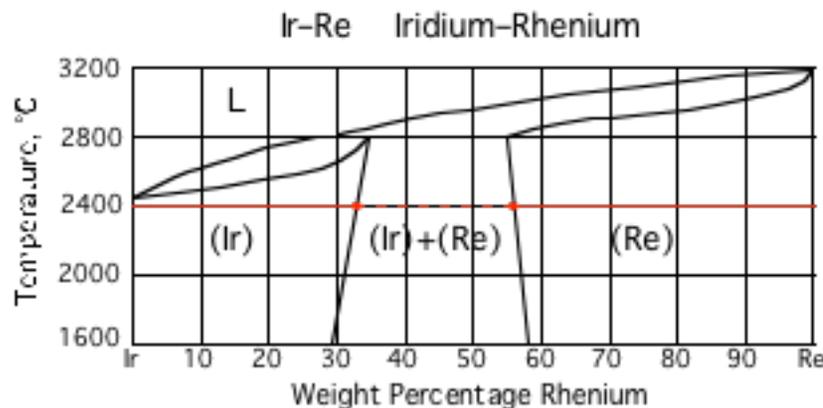


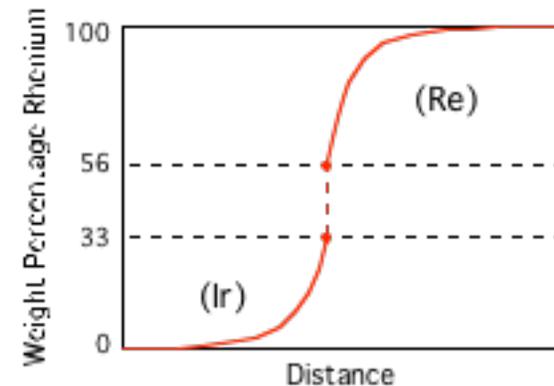
# Mechanisms of Diffusion in Materials

# 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:

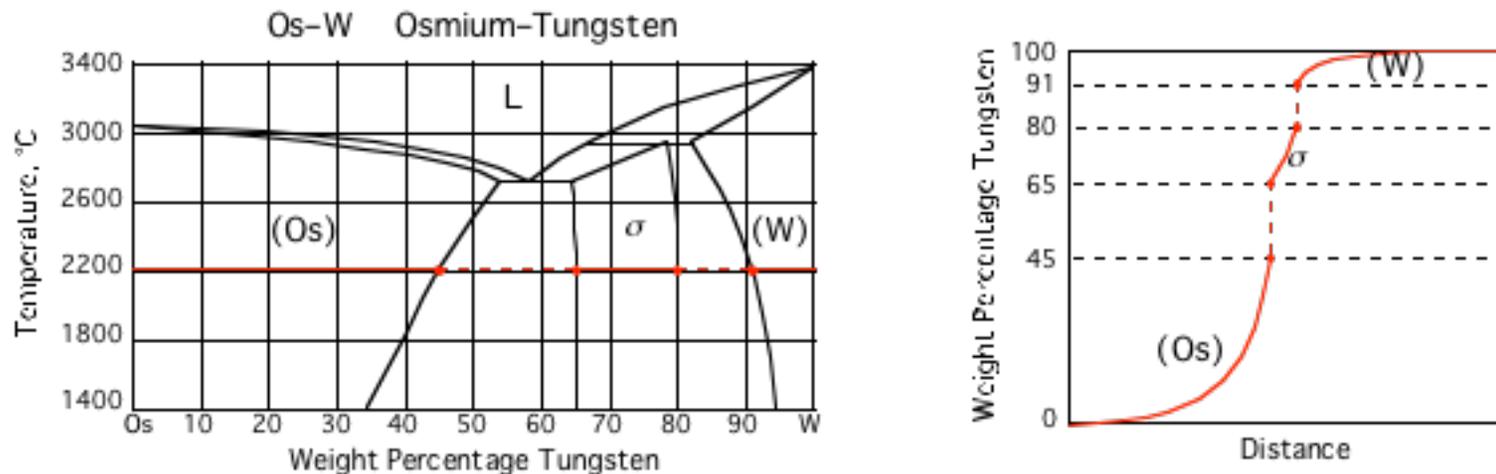


Equilibrium diagram



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...

Video clip from “Diffusion in solid metal—multiphase system,” V. Ruth (Universität Oldenburg), K. Schaar, J. Thienel, and H.G. Graske (Institut für de Wissenschaftlichen, Göttingen) ©IWF, Göttingen 1986



# 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*.

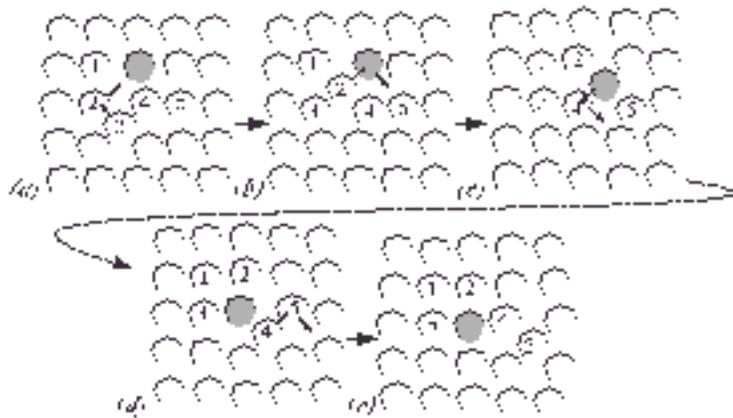
Figures removed due to copyright restrictions.

See Figures 8.2 and 8.7 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.

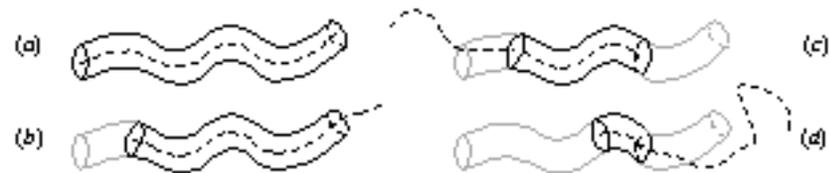
*Kinetics of Materials*. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

# Atomistic mechanisms, cont'd

- 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

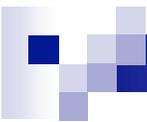
- Jumps of vacancies and interstitials are *thermally activated*, and jumps occur at a jump rate,  $\Gamma'$ ,

$$\Gamma' = \nu \exp\left[-G^m / (kT)\right]$$

Figure removed due to copyright restrictions.  
See Figure 7.2 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.  
*Kinetics of Materials*. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

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

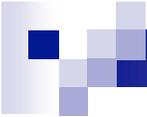
The total jump frequency,  $\Gamma$ , is  $\Gamma = z \Gamma'$ , where  $z$  is the coordination number ( $z = 12$  in f.c.c.).



# 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...



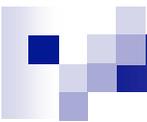
## Diffusion & random walks, cont'd

- 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:

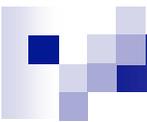
$$\langle R^2 \rangle = nr^2 \cdot f \quad \text{and} \quad D = \frac{\Gamma r^2}{6} f$$

# Self-diffusion of interstitials

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

$$\begin{aligned} D_I &= \frac{\Gamma_I r^2}{6} f = \frac{z \Gamma'_I r^2}{6} f = \frac{z \nu r^2}{6} \exp\left[-G_I^m / (kT)\right] \cdot 1 \\ &= \frac{z \nu r^2}{6} \exp\left[S_I^m / k\right] \cdot \exp\left[-H_I^m / (kT)\right] \end{aligned}$$

Note that interstitial motion is uncorrelated, so  $f = 1$ .

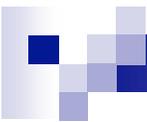


# Self-diffusion of vacancies

- Involves only random walk of vacancies, and thus

$$\begin{aligned} D_V &= \frac{\Gamma_V r^2}{6} f = \frac{z\Gamma'_V r^2}{6} f = \frac{z\nu r^2}{6} \exp\left[-G_V^m / (kT)\right] \cdot 1 \\ &= \frac{z\nu r^2}{6} \exp\left[S_V^m / k\right] \cdot \exp\left[-H_V^m / (kT)\right] \end{aligned}$$

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,

$$X_V = \exp\left[-G_V^f / (kT)\right] = \exp\left[S_V^f / k\right] \exp\left[-H_V^f / (kT)\right]$$

# Self-diffusion of solute atoms via vacancy mechanism, cont'd

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

$$D_A = \frac{X_v z \Gamma_v r^2}{6} f = \frac{z r^2 v}{6} \exp\left[-\left(G_V^f + G_V^m\right)/(kT)\right] f$$
$$= \frac{z r^2 v}{6} \exp\left[\left(S_V^f + S_V^m\right)/k\right] \exp\left[-\left(H_V^f + H_V^m\right)/(kT)\right] f$$

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