EMA5001 Lecture 4
Self-Diffusion &
Vacancy Diffusion

FLORIDA INTERNATIONAL UNIVERSITY

Self-Diffusion (1)

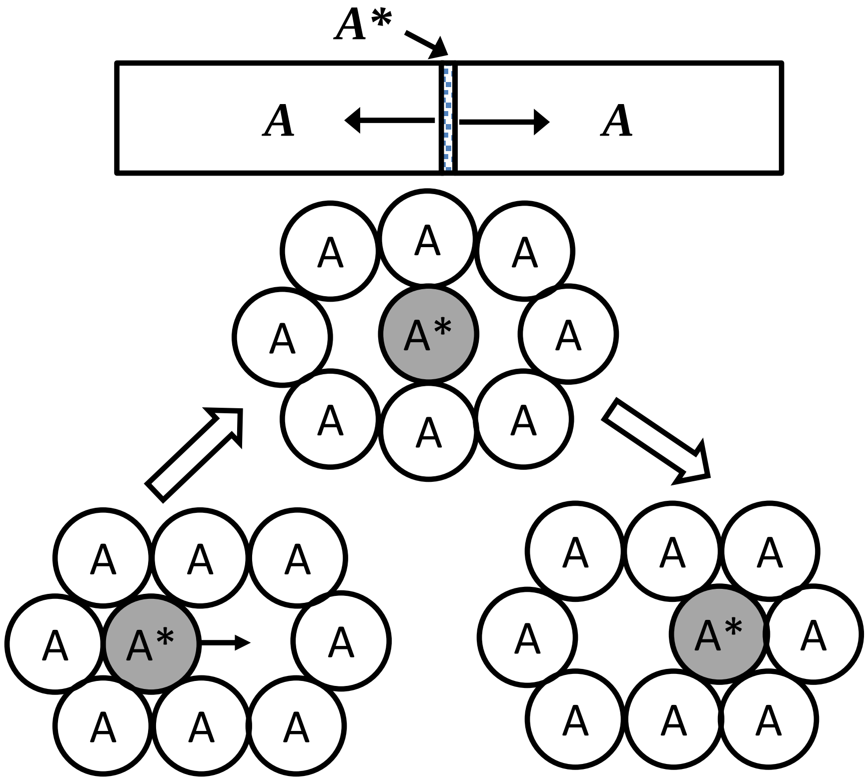
❑Self-Diffusion

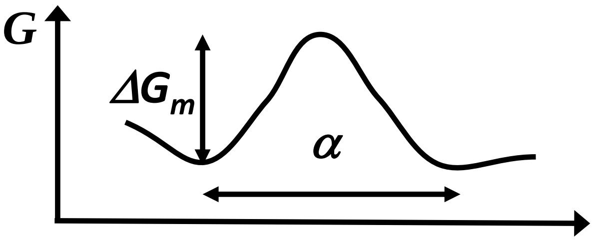
Introducing radioactive atoms A*, then measure penetration at different time

- A* and A chemically identical
- Assuming
  - A* and A have the same jump frequency
  - Each jump is unrelated to the previous jump even for the case of jumping into a vacancy

$$D_A^* = D_A = \frac{1}{6}\Gamma\alpha^2$$

- "Successful" jump frequency depend on
  - Thermal activation:
    Portion of atoms with energy higher than equilibrium by ΔG_m
  - Availability of vacancy
    - X_v Vacancy concentration





Self-Diffusion (2)

❑Continue from p. 2

"Successful" substitutional diffusion jump frequency depend on

- Thermal activation:
  - ν : Thermal vibration frequency
  - $\exp\left(-\frac{\Delta G_m}{RT}\right)$: Portion of atoms with energy higher than equilibrium by G_m
- Availability of vacancy
  - X_v : Probability of one site is vacant (i.e., vacancy molar fraction)

Therefore,

$$\Gamma = \nu \exp\left(-\frac{\Delta G_m}{RT}\right) \cdot X_v = \nu X_v \exp\left(-\frac{\Delta G_m}{RT}\right)$$

If the vacancies are in thermodynamic equilibrium, $X_v = X_v^{eq} = \exp\left(-\frac{\Delta G_v}{RT}\right)$

in which ΔG_v is the free energy change (positive value) needed to create vacancies

Self-Diffusion (3)

- **Continue from p.3**

We have $D_A^* = D_A = \frac{1}{6}\Gamma\alpha^2$ $\quad \Gamma = \nu X_v \exp\left(-\frac{\Delta G_m}{RT}\right)$ $\quad X_v = X_v^{eq} = \exp\left(-\frac{\Delta G_v}{RT}\right)$

Therefore, diffusion coefficient is

$$D_A = \frac{1}{6}\left\{\nu\left[\exp\left(-\frac{\Delta G_v}{RT}\right)\right]\exp\left(-\frac{\Delta G_m}{RT}\right)\right\}\alpha^2 = \frac{1}{6}\alpha^2\nu\exp\left(-\frac{\Delta G_m + \Delta G_v}{RT}\right)$$

$$D_A = \frac{1}{6}\alpha^2\nu\exp\left(\frac{\Delta S_m + \Delta S_v}{R}\right)\exp\left(-\frac{\Delta H_m + \Delta H_v}{RT}\right)$$

Define

Frequency factor $\quad D_0 = \frac{1}{6}\alpha^2\nu\exp\left(\frac{\Delta S_m + \Delta S_v}{R}\right)$

Substitutional diffusion activation energy $\quad Q_{SD} = \Delta H_m + \Delta H_v$

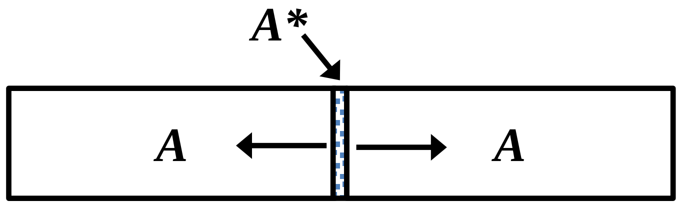
We have

$$D_A = D_0 \exp\left(-\frac{Q_{SD}}{RT}\right)$$

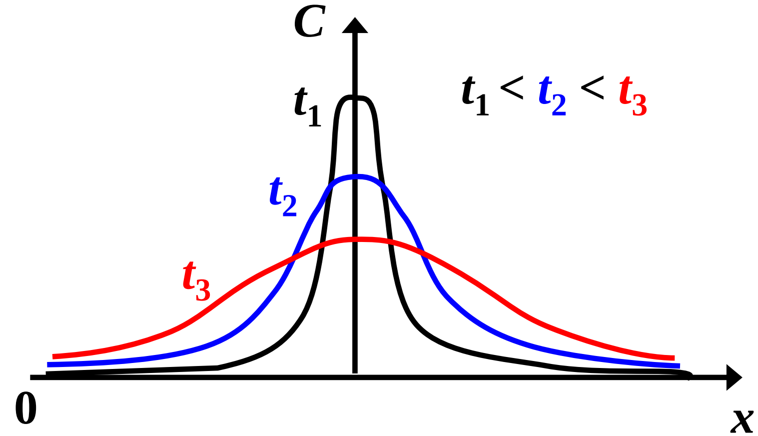
Representation of "self-diffusion" coefficient has similar formality as that for interstitial diffusion coefficient

Measurement of Self-Diffusion using Radioactive Tracer Element

- **Experiment**
  - Radio active atoms sputtered onto surface weld together into a diffusion couple
  - Measure concentration profile with time and temperature



- **Illustrate concentration profile and how it changes with time**



- **What is the analytical concentration profile?**
  - Similar to special case solution to Fick's 2nd Law of "spin on dopant"
  - If M is total amount of radio active atoms

$$C_B(x,t) = \frac{M}{2\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

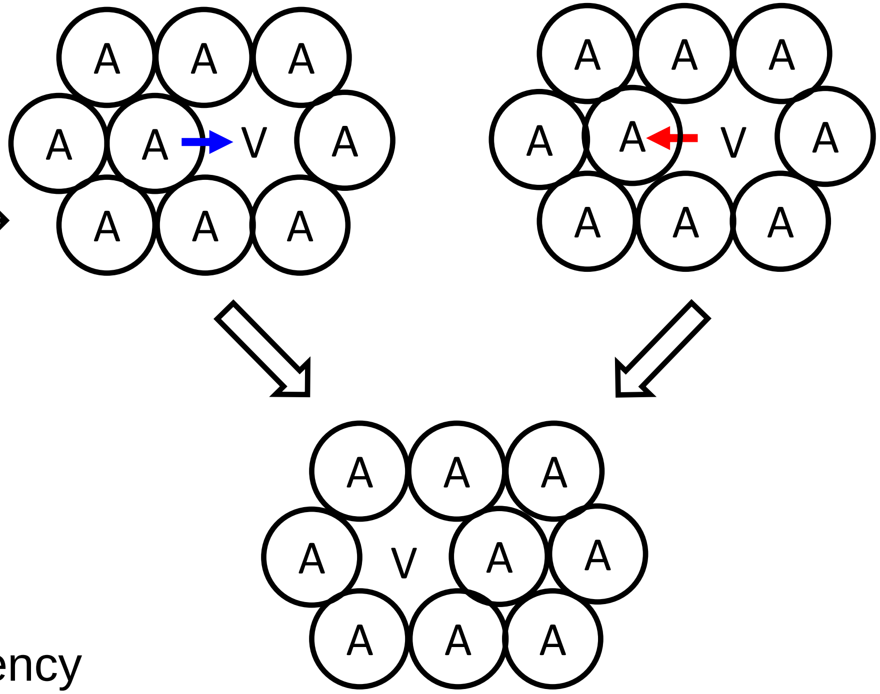
Considerations on Self-Diffusion Coefficients

	Metal	T_m (K)	D_0 (mm^2/s)	Q (kJ/mol)	$\frac{Q}{RT_m}$	$D(T_m)$ ($\mu m^2/s$)
BCC	β-Ce	1071	1.2	90.0	10.1	49
(Rare earth)	γ-La	1193	1.3	102.6	10.4	42
BCC	Rb	312	23	39.4	15.2	5.8
(Alkali metal)	Li	454	23	55.3	14.7	9.9
BCC	α-Fe	1811	200	239.7	15.9	26
(Transition metal)	Zr	2125	134	273.5	15.5	25
FCC	Al	933	170	142.0	18.3	1.9
	γ-Fe	1805	49	284.1	18.9	0.29
	Cu	1356	31	200.3	17.8	0.59
	Ni	1726	190	279.7	19.5	0.65
Diamond	Ge	1211	440	324.5	32.3	4.4×10^{-5}
	Si	1683	9×10^5	496.0	35.5	3.6×10^{-4}

Diffusion of Vacancy

❑Considerations

- An atom jumps into a vacancy can be viewed as a vacancy jumps to a neighboring atom
- Vacancy always surrounded by atoms→ Vacancy diffusion similar to interstitial diffusion



Similar to derivation of interstitial diffusion

We have

$$D_v = \frac{1}{6}\Gamma_v \alpha^2$$

Assuming vacancy thermal vibration frequency the same as atoms, then

$$\Gamma_v = \nu \exp\left(-\frac{\Delta G_m}{RT}\right)$$

Diffusion of Vacancy vs. Substitutional Atoms

- **Continue from p. 7**

$$D_v = \frac{1}{6}\Gamma_v \alpha^2 \qquad \Gamma_v = \nu \exp\left(-\frac{\Delta G_m}{RT}\right)$$

Therefore, $D_v = \frac{1}{6}\left[\nu \exp\left(-\frac{\Delta G_m}{RT}\right)\right]\alpha^2 = \frac{1}{6}\alpha^2 \nu \exp\left(\frac{\Delta S_m}{R}\right)\exp\left(-\frac{\Delta H_m}{RT}\right)$

- **Diffusion coefficient of vacancy vs. substitutional atom**

For self-diffusion $D_A^* = D_A = \frac{1}{6}\Gamma \alpha^2 \qquad \Gamma = \nu X_v \exp\left(-\frac{\Delta G_m}{RT}\right)$

The relationship between jump frequency is $\Gamma = \nu X_v \exp\left(-\frac{\Delta G_m}{RT}\right) = \Gamma_v \cdot X_v$

Since the jump distance is the same

Therefore, $D_A^* = D_A = \frac{1}{6}\Gamma \alpha^2 = \frac{1}{6}(\Gamma_v \cdot X_v)\alpha^2 = \left(\frac{1}{6}\Gamma_v \cdot \alpha^2\right) \cdot X_v = D_v \cdot X_v$

We have $D_v = \frac{D_A}{X_v}$

As X_v << 1, D_v >> D_A