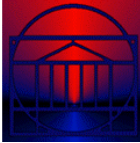
A diagram illustrating diffusion. It shows a collection of blue and red circles representing atoms. The blue circles are concentrated on the left side, and the red circles are concentrated on the right side. A central white box with a black border contains the word "Diffusion". Below it, another white box with a black border contains the text "MSE 201" and "Callister Chapter 5".

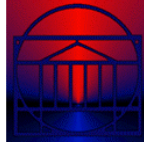
# Diffusion

MSE 201  
Callister Chapter 5



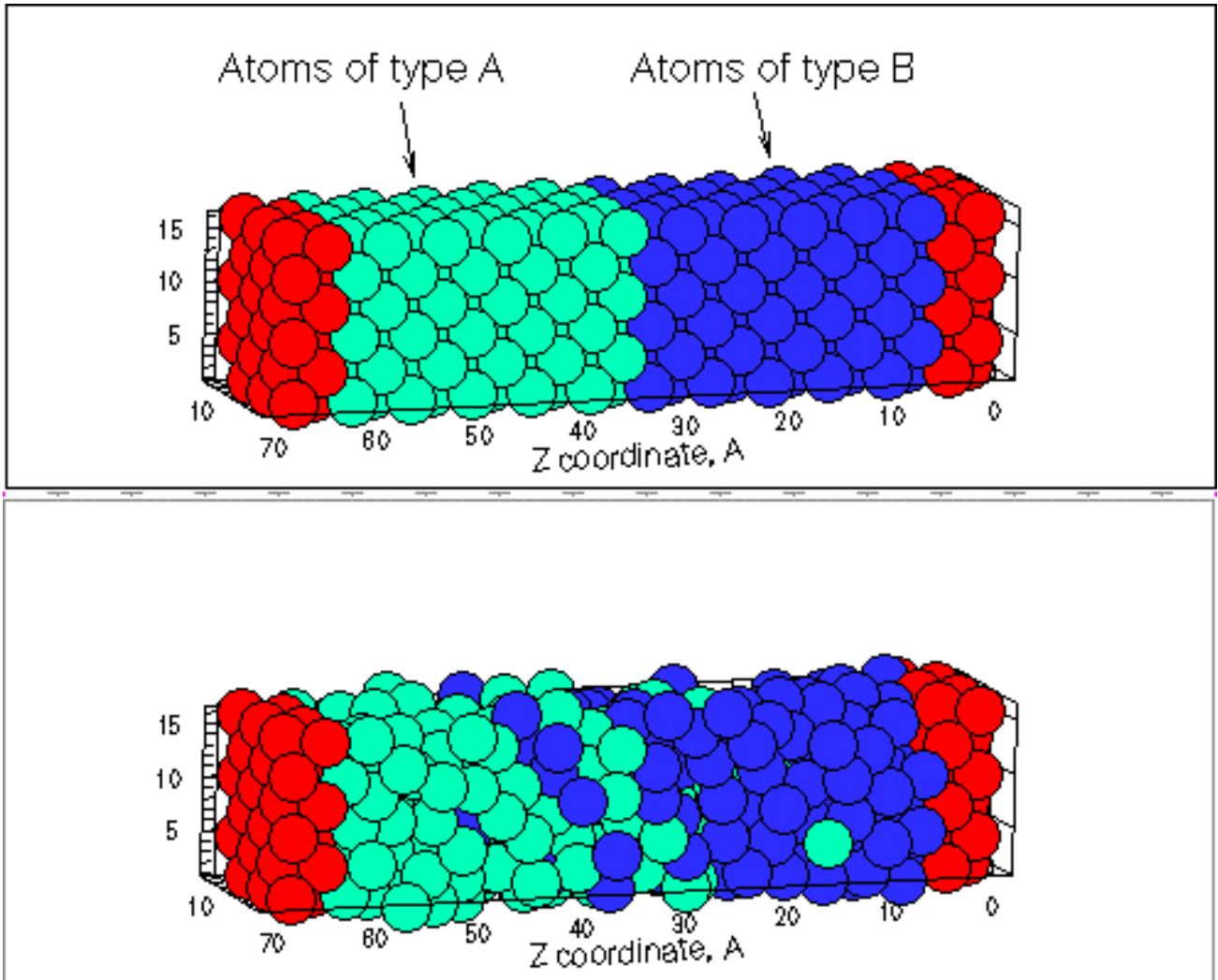
***Goals: Diffusion - how do atoms move through solids?***

- Fundamental concepts and language
- Diffusion mechanisms
  - Vacancy diffusion
  - Interstitial diffusion
  - Impurities
- Diffusion equations
  - Fick's first law
  - Fick's second law
- Factors that influence diffusion
  - Diffusing species
  - Host solid
  - Temperature
  - Microstructure

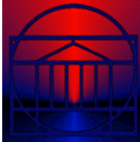


## What is diffusion?

Diffusion is material transport by atomic motion.



Inhomogeneous materials can become homogeneous by diffusion. For an active diffusion to occur, the temperature should be high enough to overcome energy barriers to atomic motion.



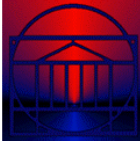
## Atomic Vibrations

- Heat causes atoms to vibrate
- Vibration amplitude increases with temperature
- Melting occurs when vibrations are sufficient to rupture bonds
- Vibrational frequency  $\sim 10^{13}$  Hz
- Average atomic / electronic energy due to thermal excitation is of order  $kT$  [*with a distribution around this average energy,  $P(E) \sim \exp(-E/kT)$* ]

***k* : Boltzmann's constant**

***( $1.38 \times 10^{-23}$  J/K or  $8.62 \times 10^{-5}$  eV/K)***

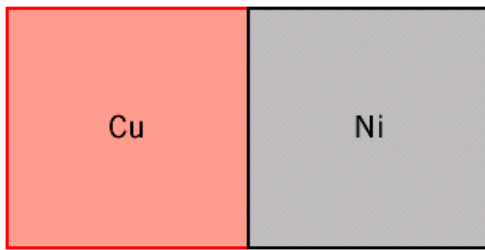
***T* : Absolute temperature (Kelvin)**



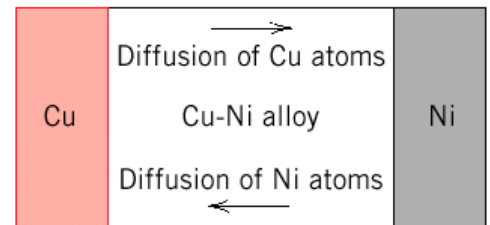
# What is diffusion?

## Interdiffusion and Self-diffusion

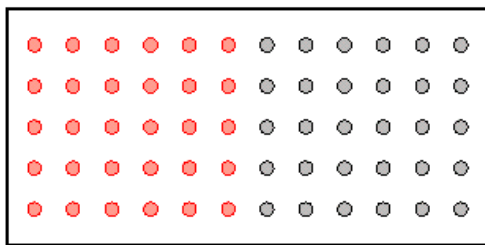
- Diffusion is material transport by atomic motion
- *Interdiffusion* occurs in response to a concentration gradient (more rigorously, to a gradient in chemical potential)



(a)

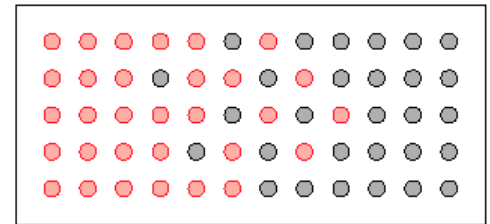


(a)

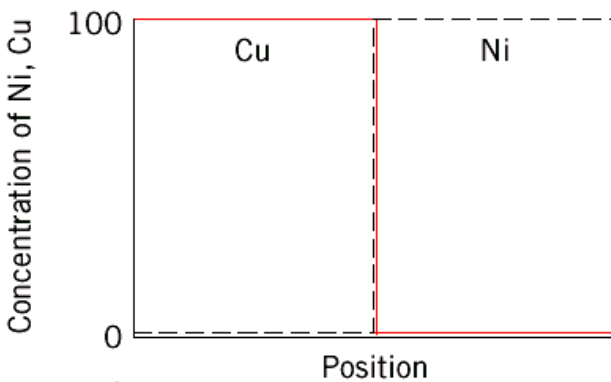


(b)

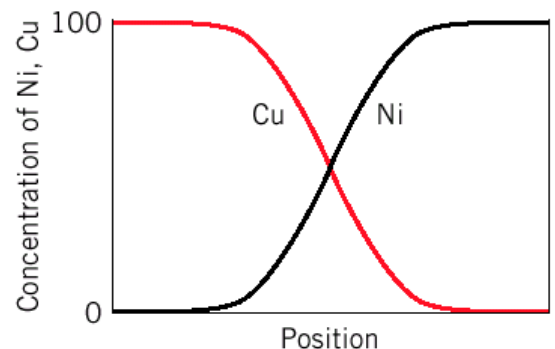
**(Heat)**



(b)



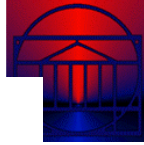
(c)



(c)

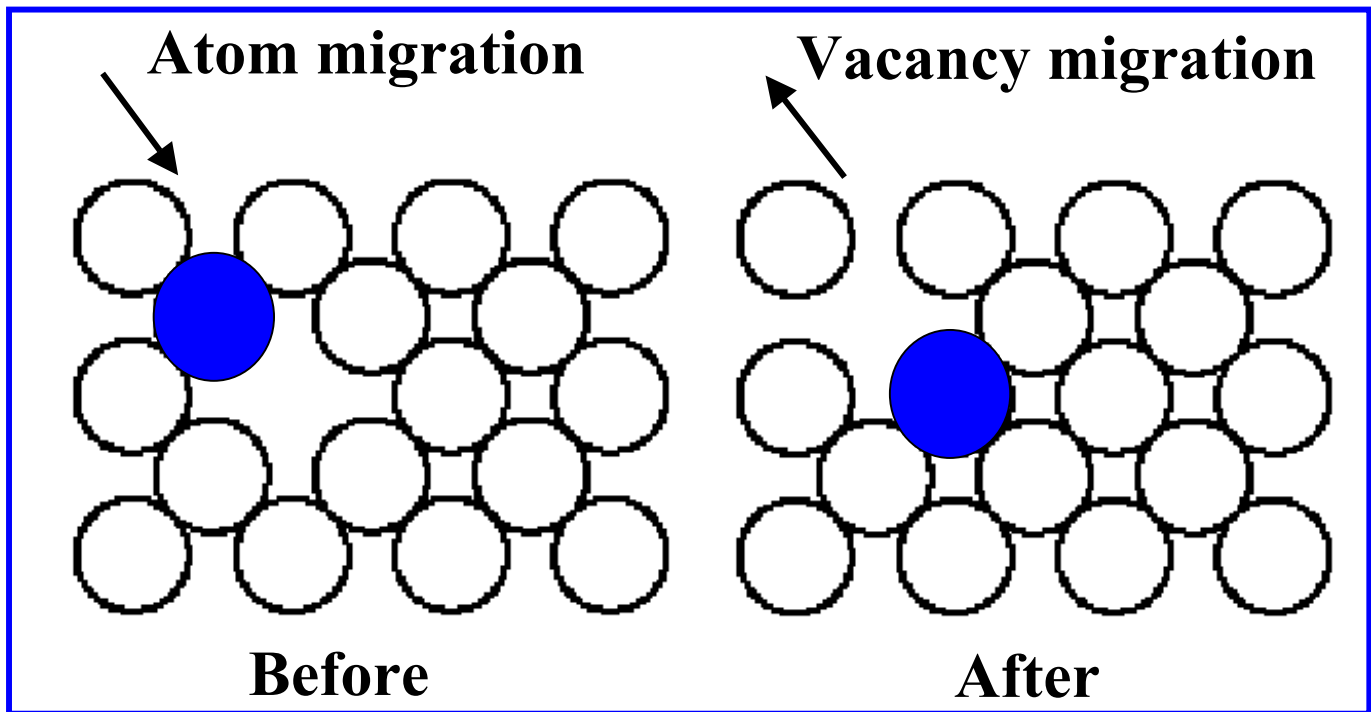
**Before**

**After**

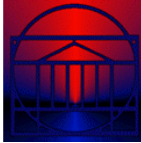


## Diffusion Mechanisms

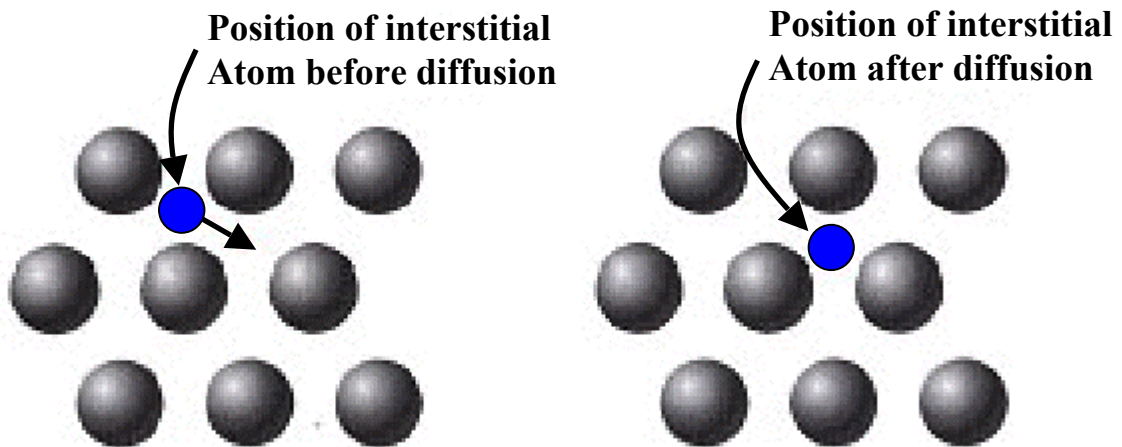
- To move from lattice site to lattice site, atoms need energy to break bonds with neighbors, and to cause the necessary lattice distortions during motion from site to another. This energy comes from atomic vibrations ( $E_{av} \sim kT$ )



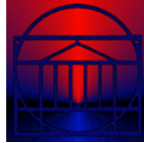
**Atomic migration by a mechanism of vacancy migration. Materials flow (the atom) is opposite the vacancy flow direction.**



- **Interstitial diffusion (depends on temperature). This is generally faster than vacancy diffusion because there are many more interstitial sites than vacancy sites to jump to. Requires small impurity atoms (e.g. C, H, O) to fit into interstices in host.**



**Self diffusion (motion of atoms within a pure host) also occurs. Predominantly vacancy in nature (difficult for atoms to “fit” into interstitial sites because of size.**

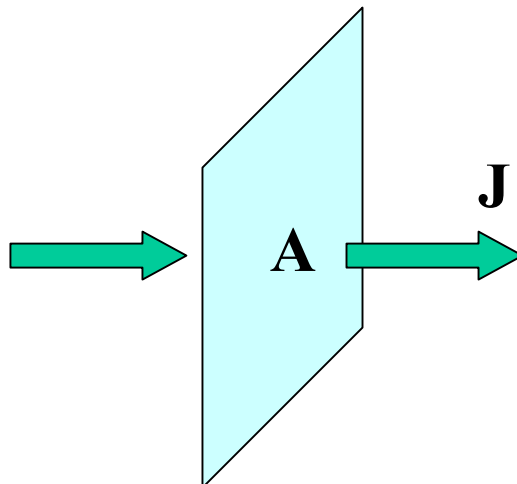


## Diffusion Flux

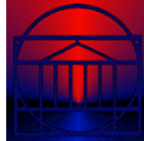
**The flux of diffusing atoms,  $J$** , is used to quantify how fast diffusion occurs. The flux is defined as either in number of atoms diffusing through unit area and per unit time (e.g., atoms/m<sup>2</sup>-second) or in terms of the mass flux - mass of atoms diffusing through unit area per unit time, (e.g., kg/m<sup>2</sup>-second).

$$\mathbf{J} = \mathbf{M} / \mathbf{A}t \cong (1/\mathbf{A}) (\mathbf{dM}/\mathbf{dt}) (\text{Kg m}^{-2} \text{s}^{-1})$$

where  $M$  is the mass of atoms diffusing through the area  $A$  during time  $t$ .







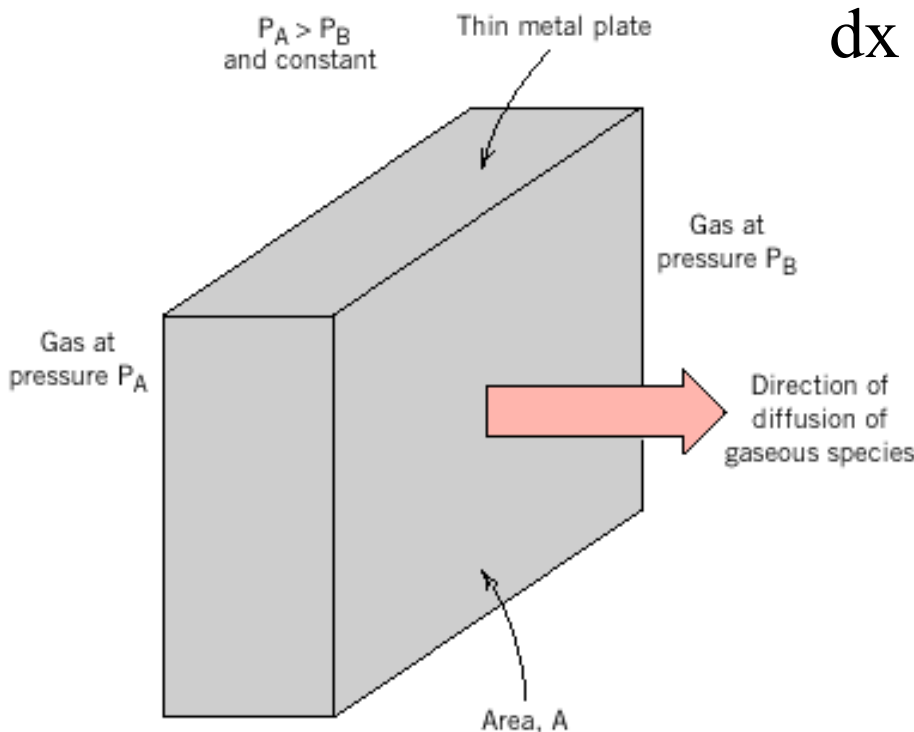
## Steady-State Diffusion

**Steady state diffusion:** the diffusion flux does not change with time.

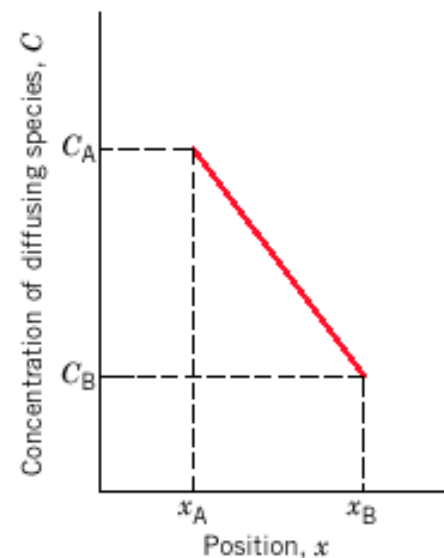
**Concentration profile:** concentration of atoms/molecules of interest as function of position in the sample.

**Concentration gradient:  $dC/dx$  ( $\text{Kg.m}^{-4}$ ):** the slope at a particular point on concentration profile.

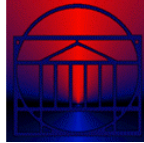
$$\frac{dC}{dx} \approx \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$



(a)



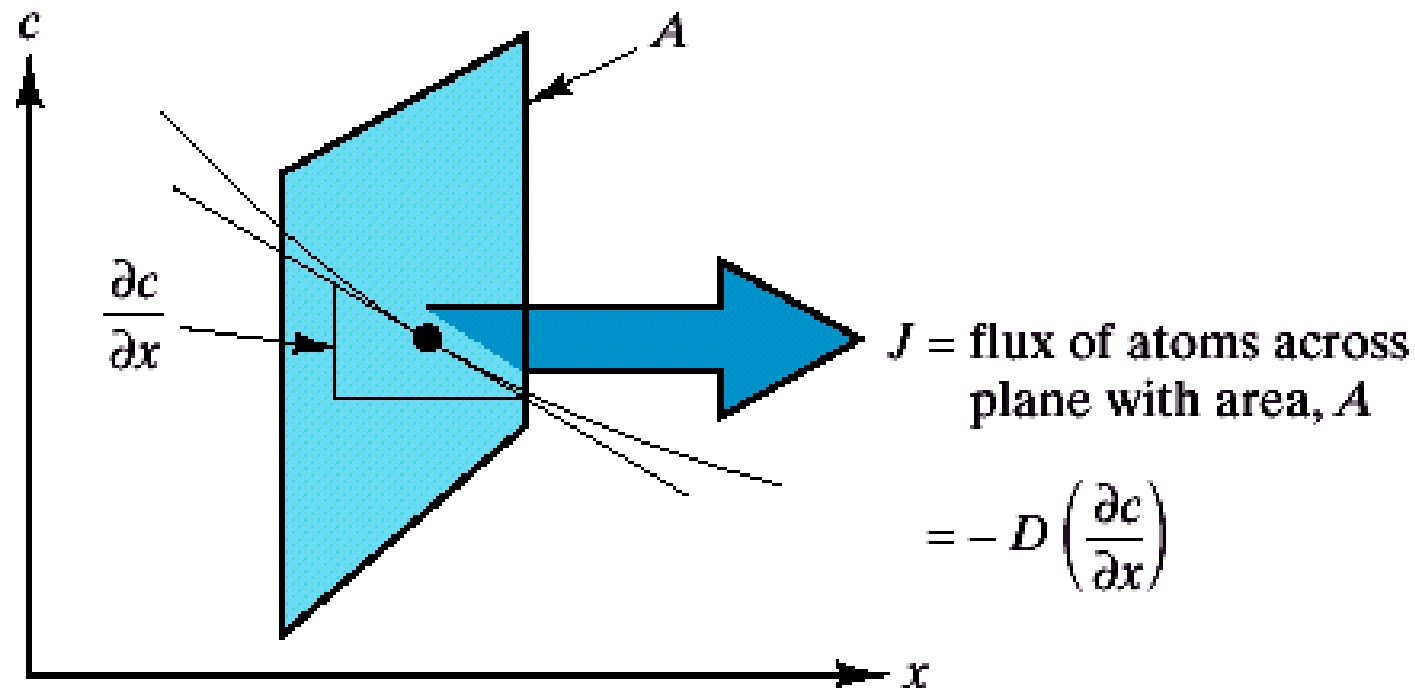
(b)



## Steady-State Diffusion: Fick's first law

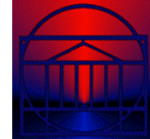
**Fick's first law:** the diffusion flux along direction  $x$  is proportional to the concentration gradient

$$J = -D \frac{dC}{dx} \quad \text{where } \mathbf{D} \text{ is the diffusion coefficient}$$



The concentration gradient is often called the *driving force* in diffusion (but it is not a force in the mechanistic sense).

The minus sign in the equation means that diffusion is down the concentration gradient.



## Diffusion – Temperature Dependence (I)

$$J = -D \frac{dC}{dx}$$

Diffusion coefficient is the measure of mobility of diffusing species.

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$D_0$  – temperature-independent preexponential ( $\text{m}^2/\text{s}$ )

$Q_d$  – the activation energy for diffusion ( $\text{J/mol}$  or  $\text{eV/atom}$ )

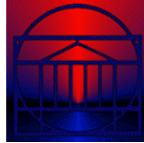
$R$  – the gas constant ( $8.31 \text{ J/mol-K}$  or  $8.62 \times 10^{-5} \text{ eV/atom-K}$ )

$T$  – absolute temperature (K)

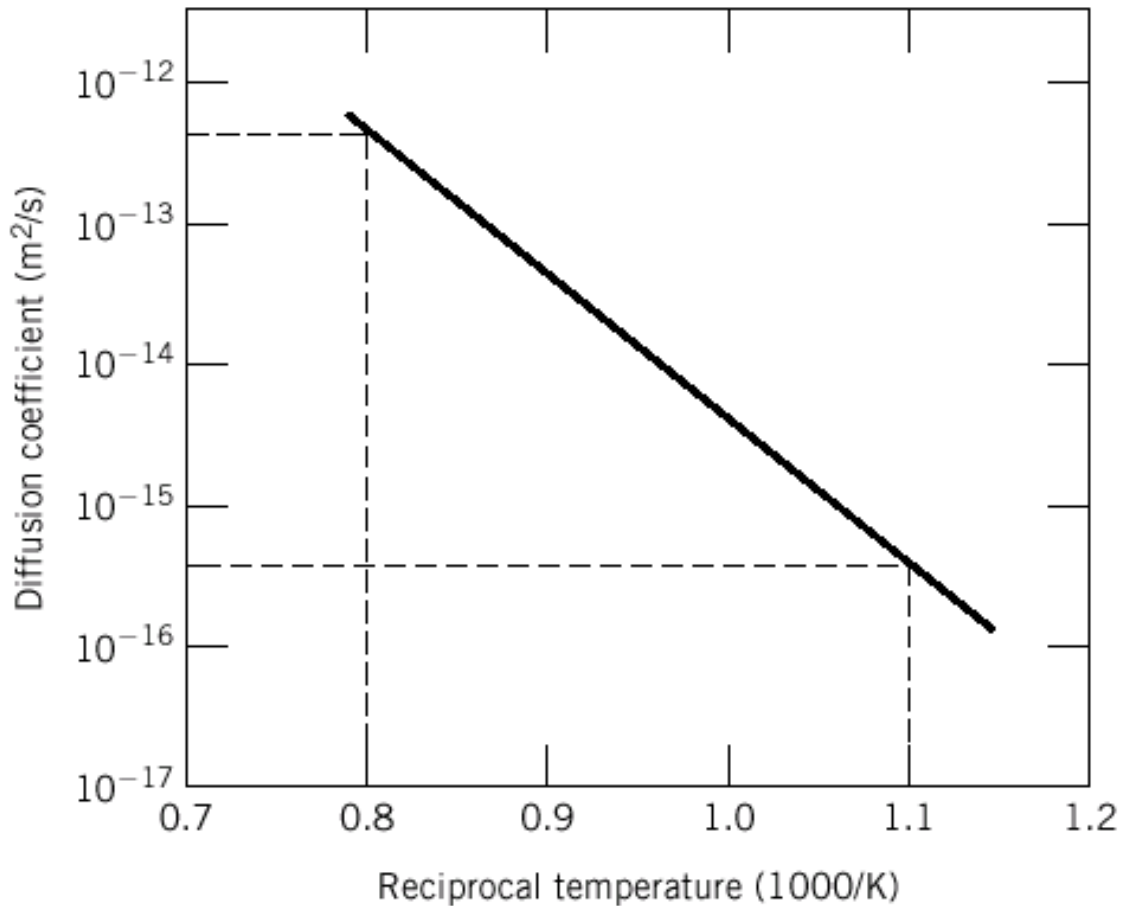
The above equation can be rewritten as

$$\ln D = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T}\right) \quad \text{or} \quad \log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T}\right)$$

The activation energy  $Q_d$  and preexponential  $D_0$ , therefore, can be estimated by plotting  $\ln D$  versus  $1/T$  or  $\log D$  versus  $1/T$ . Such plots are Arrhenius plots.



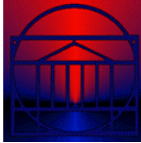
## Diffusion – Temperature Dependence (II)



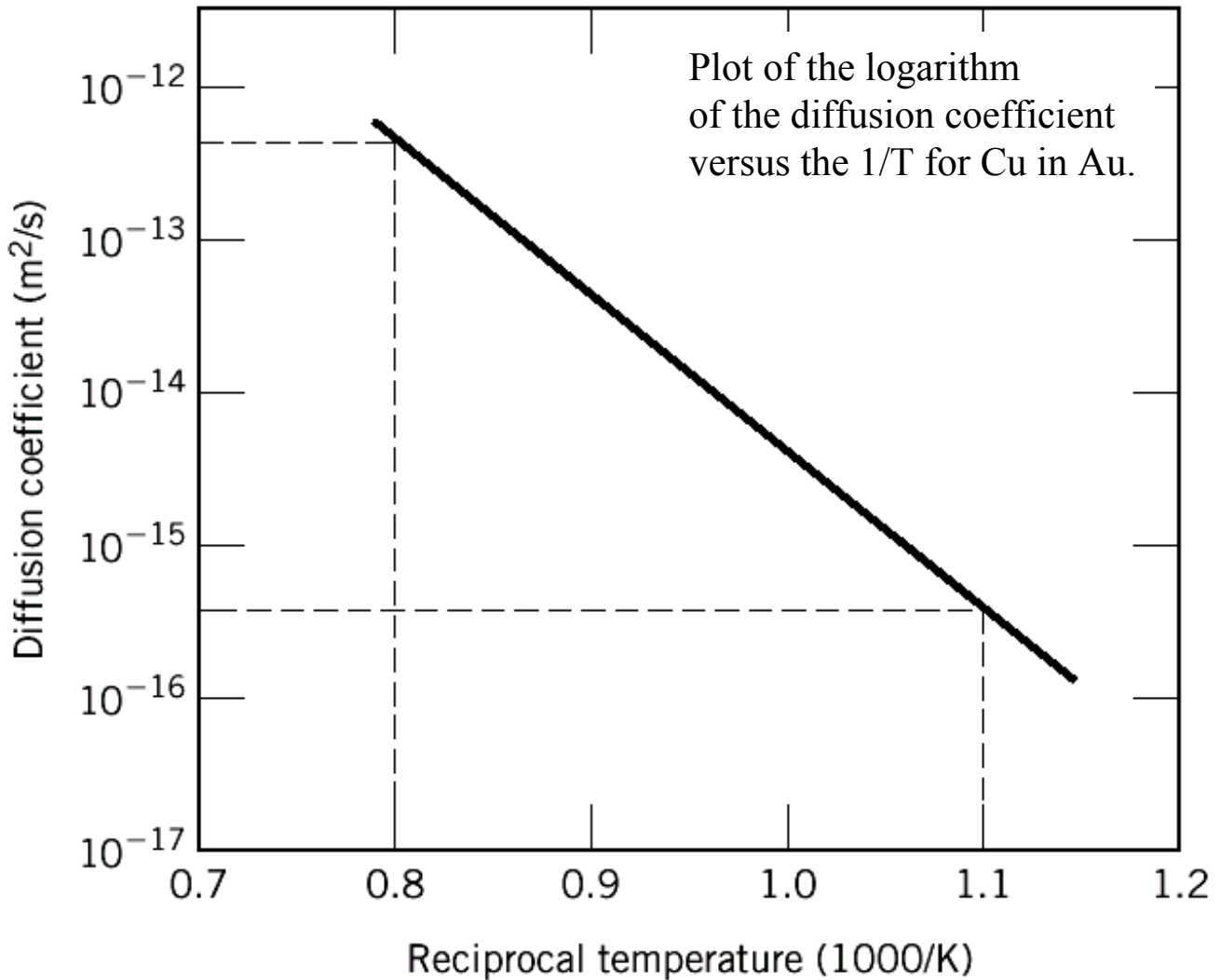
Graph of  $\log D$  vs.  $1/T$  has slope of  $-Q_d/2.3R$ ,  
intercept of  $\ln D_0$

$$\log D = \log D_0 - \frac{Q_d}{2.3R} \left( \frac{1}{T} \right)$$

$$Q_d = -2.3R \left[ \frac{\log D_1 - \log D_2}{1/T_1 - 1/T_2} \right]$$



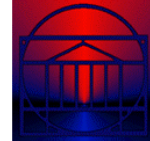
# Diffusion Coefficient



**Determine activation energy,  $Q_d$ :**

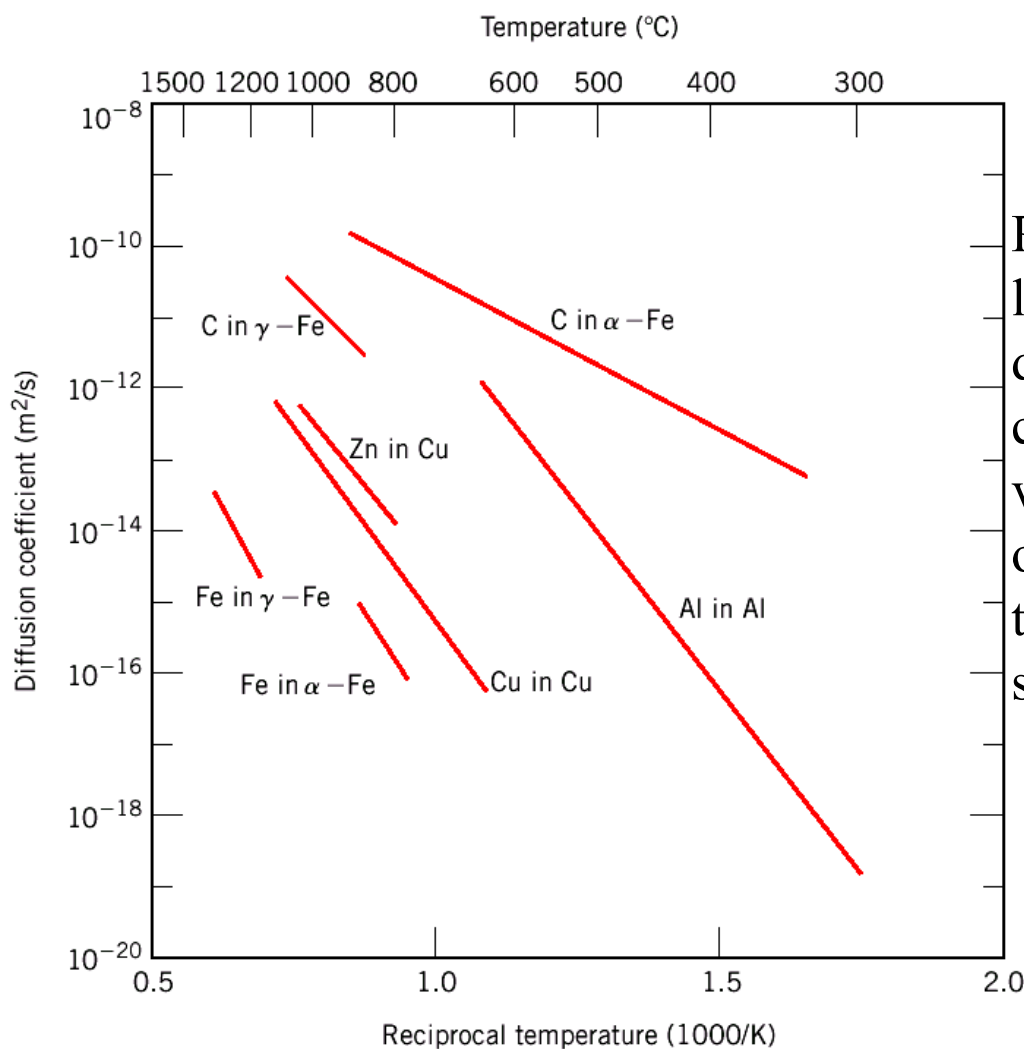
$$D = D_0 \exp(-Q_d/kT), \ln D = [\ln D_0] - Q_d/kT,$$

**Graph of  $\ln D$  vs.  $1/kT$  has gradient of  $-Q_d$ , intercept  $\ln D_0$**

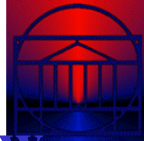


# Diffusion Properties for Several Materials

Diffusing Species	Host Metal	$D_0(m^2/s)$	Activation Energy $Q_d$		Calculated Values	
			$kJ/mol$	$eV/atom$	$T(^{\circ}C)$	$D(m^2/s)$
Fe	$\alpha$ -Fe (BCC)	$2.8 \times 10^{-4}$	251	2.60	500	$3.0 \times 10^{-21}$
					900	$1.8 \times 10^{-15}$
Fe	$\gamma$ -Fe (FCC)	$5.0 \times 10^{-5}$	284	2.94	900	$1.1 \times 10^{-17}$
					1100	$7.8 \times 10^{-16}$
C	$\alpha$ -Fe	$6.2 \times 10^{-7}$	80	0.83	500	$2.4 \times 10^{-12}$
					900	$1.7 \times 10^{-10}$
C	$\gamma$ -Fe	$2.3 \times 10^{-5}$	148	1.53	900	$5.9 \times 10^{-12}$
					1100	$5.3 \times 10^{-11}$
Cu	Cu	$7.8 \times 10^{-5}$	211	2.19	500	$4.2 \times 10^{-19}$
Zn	Cu	$2.4 \times 10^{-5}$	189	1.96	500	$4.0 \times 10^{-18}$
Al	Al	$2.3 \times 10^{-4}$	144	1.49	500	$4.2 \times 10^{-14}$
Cu	Al	$6.5 \times 10^{-5}$	136	1.41	500	$4.1 \times 10^{-14}$
Mg	Al	$1.2 \times 10^{-4}$	131	1.35	500	$1.9 \times 10^{-13}$
Cu	Ni	$2.7 \times 10^{-5}$	256	2.65	500	$1.3 \times 10^{-22}$



Plot of the logarithm of the diffusion coefficient vs. the reciprocal of the absolute temperature for several metals.

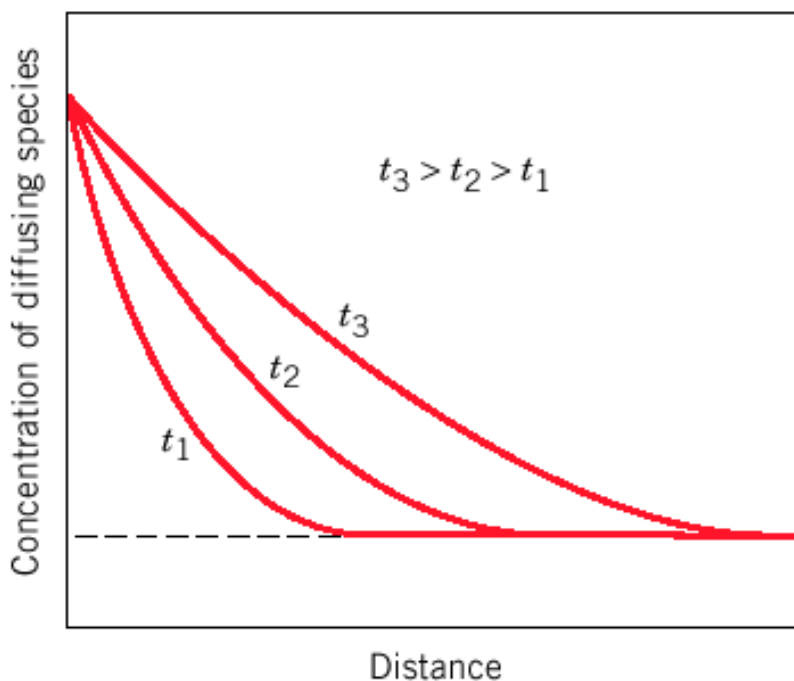


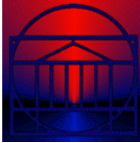
## Nonsteady-State Diffusion: Fick's second law (*not tested*)

In most real situations the concentration profile and the concentration gradient are changing with time. The changes of the concentration profile is given in this case by a differential equation, *Fick's second law*.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2}$$

Solution of this equation is concentration profile as function of time,  $C(x,t)$ :



*(not tested)*

## Equations Governing Diffusion

### 2. Time Varying - Fick's 2nd Law

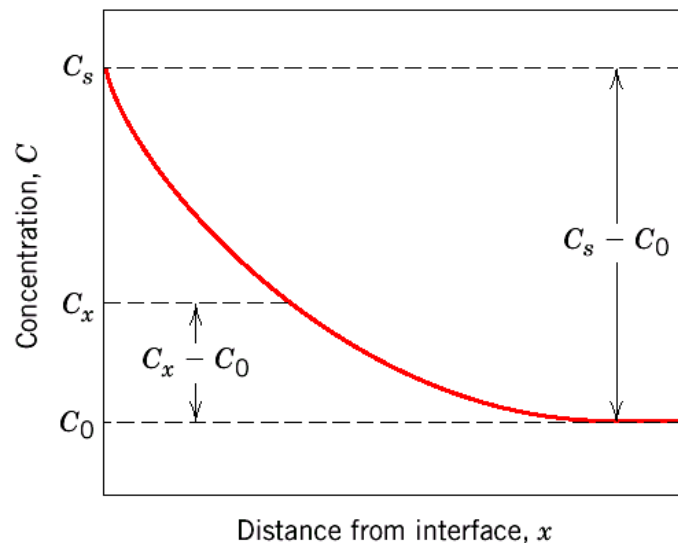
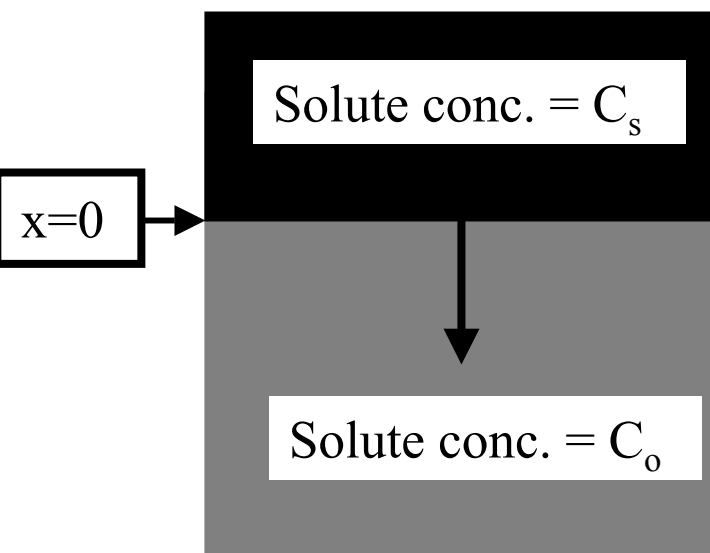
- Time varying diffusion equation (i.e. non steady state):

$$\partial C / \partial t = \partial / \partial x (D \partial C / \partial x) = \partial^2 C / \partial x^2 *$$

(\* Assumes  $D$  independent of  $x$  which it isn't really!)

$$t = 0$$

$$t > 0$$

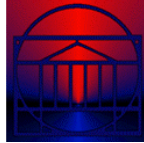


$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dz$$

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \text{erf}(x / 2\sqrt{Dt})$$

Characteristic  
"Diffusion Length"



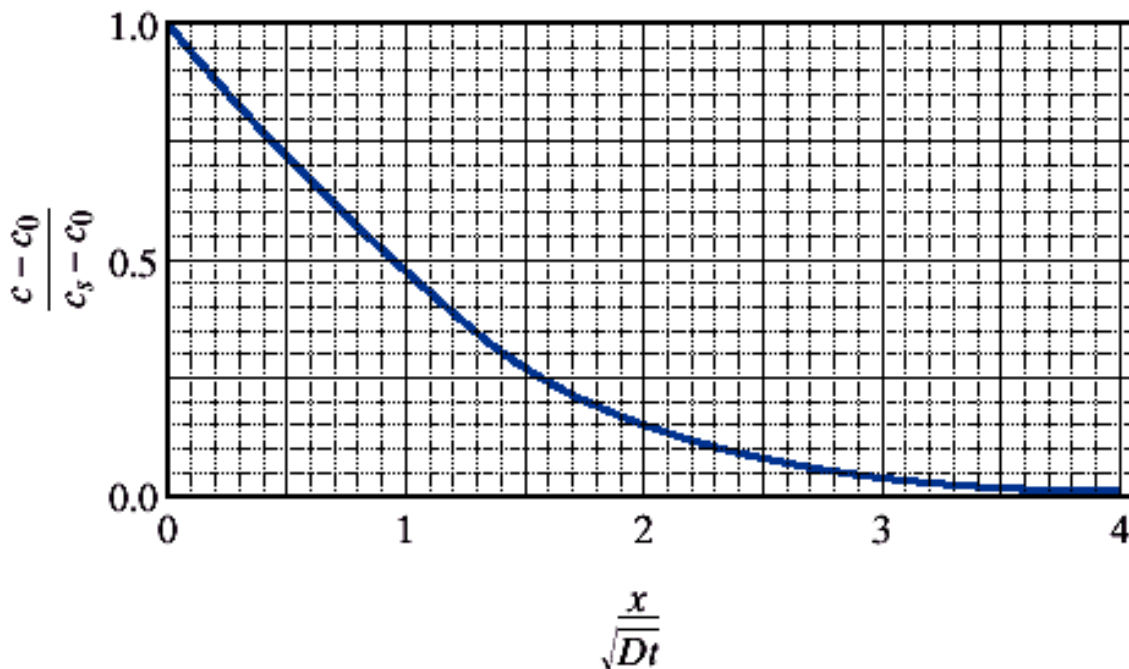


*(not tested)*

The solution to this differential equation with the given boundary condition is:

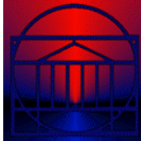
$$\frac{C_x - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

where  $C_s$  is the surface concentration, which remains constant,  $C_o$  is the initial bulk concentration of the diffusing species and erf refers to the Gaussian error function.



$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dz$$

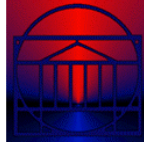
“erf” function – Gaussian error function, based on integration of the “bell shaped” curve



*(not tested)*

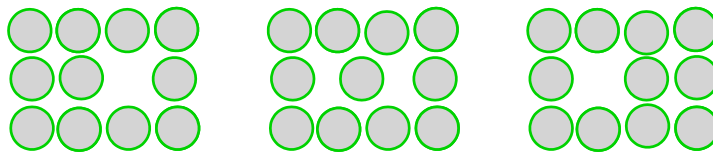
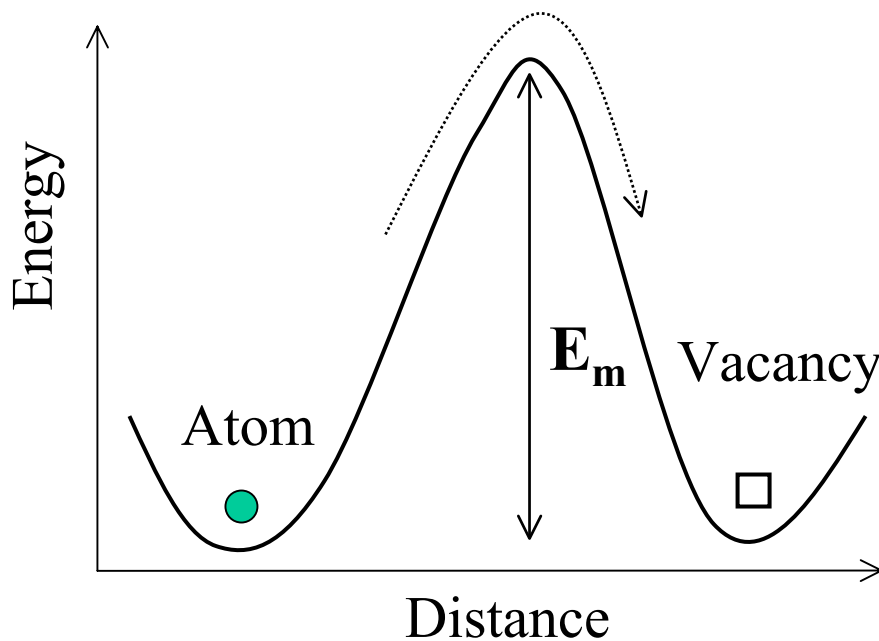
## Tabulation of Error Function Values

$z$	$erf(z)$	$z$	$erf(z)$	$z$	$erf(z)$
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

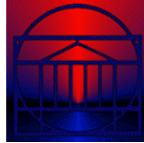


## Diffusion – Thermally Activated Process (I)

In order for atom to jump into a vacancy site, it needs to possess enough energy (thermal energy) to break the bonds and squeeze through its neighbors. The energy necessary for motion,  $E_m$ , is called **the activation energy** for vacancy motion.



Schematic representation of the diffusion of an atom from its original position into a vacant lattice site. At activation energy  $E_m$  has to be supplied to the atom so that it could break inter-atomic bonds and to move into the new position.



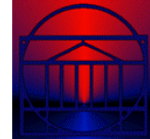
## Diffusion – Thermally Activated Process (II)

The average thermal energy of an atom ( $k_B T = 0.026$  eV for room temperature) is usually much smaller than the activation energy  $E_m$  ( $\sim 1$  eV/atom) and a large fluctuation in energy (when the energy is “pooled together” in a small volume) is needed for a jump.

The probability of such fluctuation or frequency of jumps,  $R_j$ , depends exponentially from temperature and can be described by equation that is attributed to Swedish chemist **Arrhenius** :

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

where  $R_0$  is an attempt frequency proportional to the frequency of atomic vibrations.



## Diffusion – Thermally Activated Process (III)

For the vacancy diffusion mechanism the probability for any atom in a solid to move is the product of

the probability of finding a vacancy in an adjacent lattice site (see Chapter 4):

$$P = C.N. \exp\left(-\frac{Q_v}{k_B T}\right)$$

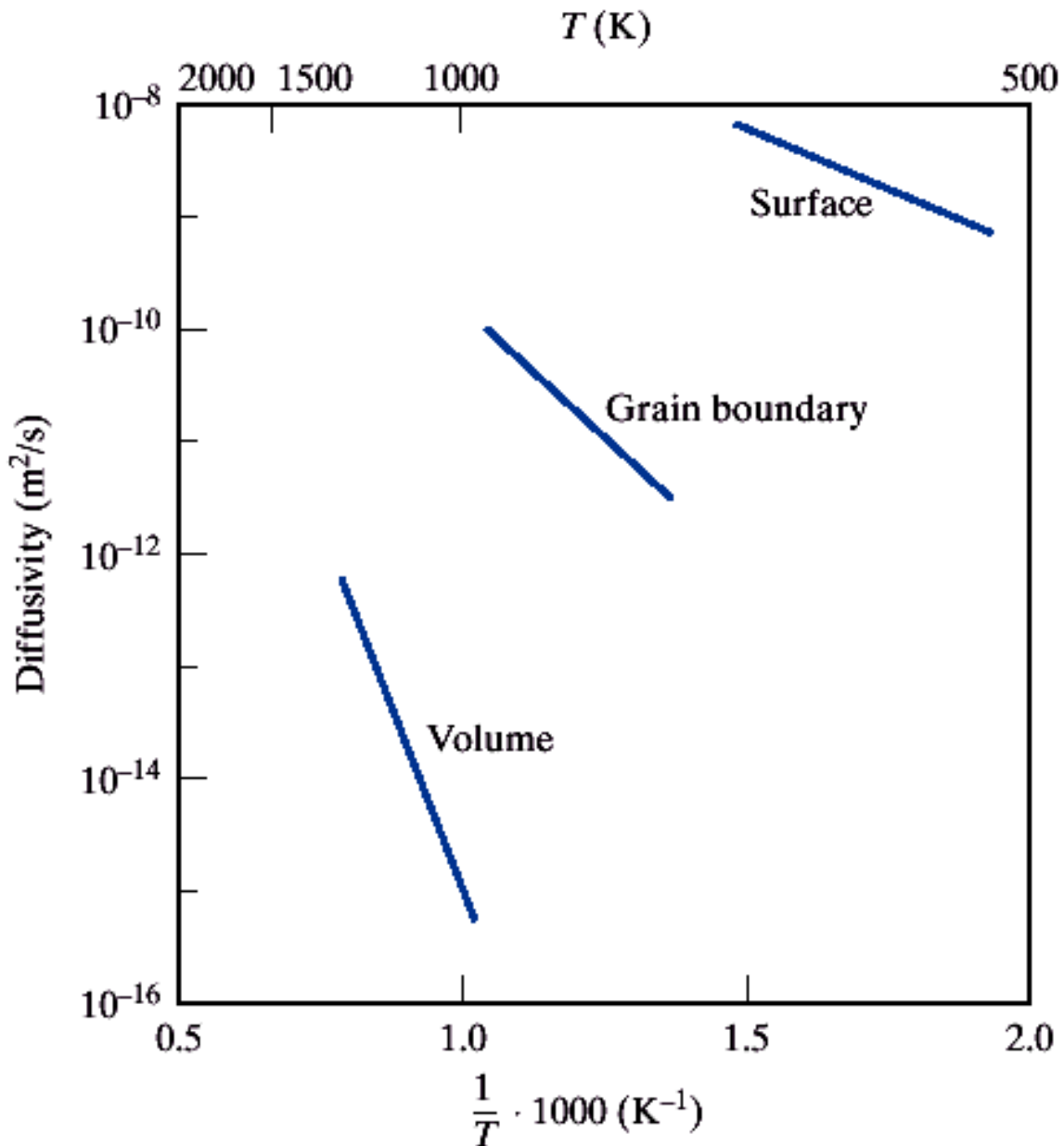
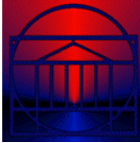
and the probability of thermal fluctuation needed to overcome the energy barrier for vacancy motion

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

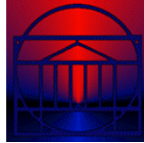
The diffusion coefficient, therefore, can be estimated as

$$\begin{aligned} D &\approx C.N.R_0 a^2 \exp\left(-\frac{E_m}{k_B T}\right) \exp\left(-\frac{Q_v}{k_B T}\right) = \\ &= D_0 \exp\left(-\frac{(E_m + Q_v)}{k_B T}\right) = \underline{D_0 \exp\left(-\frac{Q_d}{k_B T}\right)} \end{aligned}$$

Temperature dependence of the diffusion coefficient, follows the Arrhenius dependence.

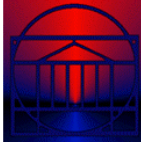


**Self-diffusion coefficients for Ag depend on the diffusion path. In general the diffusivity is greater through less restrictive structural regions.**



## **Factors that Influence Diffusion**

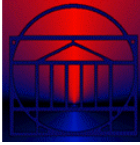
- **Diffusion mechanism - interstitial faster than vacancy**
- **Diffusing and host species:  $D_o$ ,  $Q_d$  is different for every solute, solvent pair**
- **Temperature - diffusion rate increases very rapidly with increasing temperature ( $Q_d \sim 1 - 5 \text{ eV}$ )**
- **Microstructure - diffusion faster in polycrystalline vs. single crystal materials because grain boundary diffusion is faster than bulk diffusion (larger spaces between atoms). Accelerated diffusion can also occur along dislocation cores.**



# Take Home Messages

- Make sure you understand
  - Language: (vacancy diffusion, interstitial diffusion, concentration gradient, interdiffusion, self diffusion, diffusion flux, diffusion length, steady state, non steady state, activation energy)
  - Diffusion mechanisms: vacancy, interstitial
  - Steady state diffusion
  - Non-steady state diffusion
  - Diffusion equations (Fick's 1st law, Fick's 2nd law, Arrhenius eqn.)





# Reading for next class:

- Callister Chapter 6 (Mechanical Properties of Materials)
  - Primary 6.1 - 6.12 (*i.e. whole chapter!*)