Thermally Activated Processes

- ❑ General Description of Activated Process:

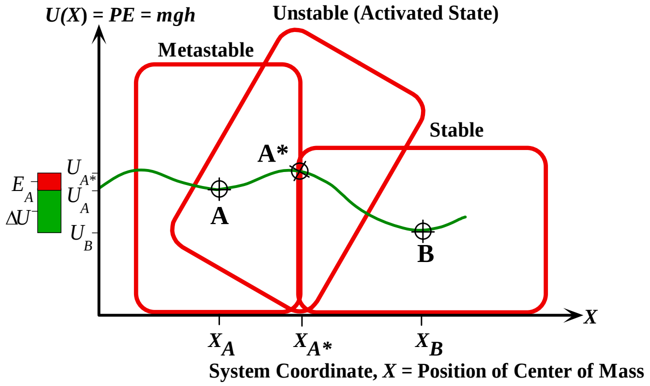

Fig. 1.27: Tilting a filing cabinet from state *A* to its edge in state *A** requires an energy E_A. After reaching *A**, the cabinet spontaneously drops to the stable position *B*. *PE* of state *B* is lower than *A* and therefore state *B* is more stable than *A*.

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Thermally Activated Processes
- Arrhenius Behavior -

- ❑ Diffusion:

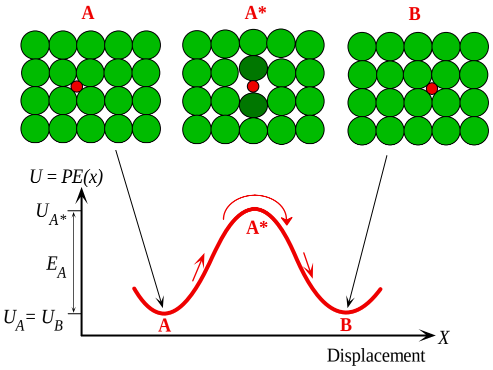

Fig. 1.28: Diffusion of an interstitial impurity atom in a crystal from one void to a neighboring void. The impurity atom at position *A* must posses an energy E_A to push the host atoms away and move into the neighboring void at *B*.

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- ☐ **Diffusion:** Thermally Activated Processes
  - ✓ Temperature Plays a significant role in diffusion
  - ✓ Temperature is not the driving force.
  - ✓ **Remember:**

  DRIVING FORCE = GRADIENT of a FIELD VARIABLE

  - ✓ Remember: Driving force for diffusion is a difference in the chemical potential. $\mu_{phase1} \neq \mu_{phase2}$ i.e. $\Delta\mu \neq 0$ or $\nabla\mu \neq 0$
  - ✓ HOWEVER: Temperature increases the activity of a diffusing species.
  - ✓ **Question:** What is the probability that an atom will diffuse?
    - o Atoms are *Bosons*
    - o Use *Maxwell-Boltzmann Statistics*!

$$\boxed{N(\varepsilon)d\varepsilon = f(\varepsilon)g(\varepsilon)d\varepsilon = \frac{Ne^{-\beta\varepsilon}g(\varepsilon)d\varepsilon}{\int e^{-\beta\varepsilon}g(\varepsilon)d\varepsilon}}$$

→

$$\boxed{\begin{aligned} f(\varepsilon) &= \frac{Ne^{-\beta\varepsilon}}{\int e^{-\beta\varepsilon}g(\varepsilon)d\varepsilon} \\ &= \frac{\text{No. Impurities with } E > E_A}{\text{Total No. of Impurities}} \\ &= Ae^{-E_A/kT} \end{aligned}}$$

Thermally Activated Processes
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- ☐ Diffusion:

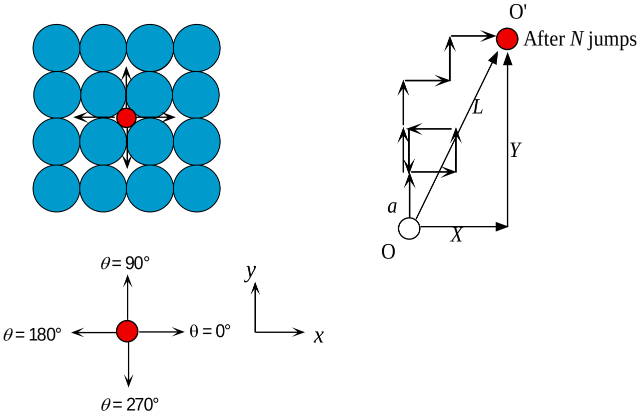

Fig. 1.29: An impurity atom has four site choices for diffusion to a neighboring interstitial vacancy. After *N* jumps, the impurity atom would have been displaced from the original position at O.

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- **Diffusion:**
  - ✓ *Frequency of Jump* is proportional to the probability
  - ✓ *Coefficient of Diffusion* is proportional to *Jump Frequency*

$$\begin{aligned}\nu &= \nu_0 f(\varepsilon) \\ &= A\nu_0 e^{-\frac{E}{kT}}\end{aligned} \quad \Rightarrow \quad \begin{aligned}D &\propto \nu \\ &\propto A\nu_0 e^{-\frac{E}{kT}}\end{aligned}$$

- ✓ ***Diffusivity*** or ***Diffusion Coefficient (Arrhenius Rate Equation)***:

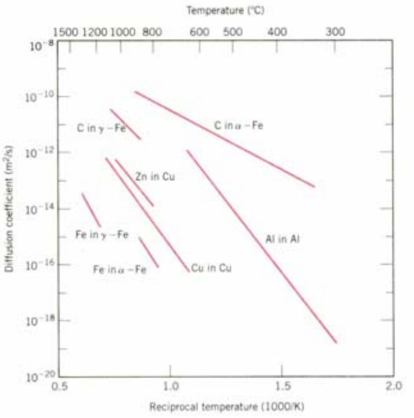
$$D = D_o e^{-E_A/kT}$$

- E_{act} is the *activation energy* for diffusion
- $k_b\,T$ is the *thermal energy*
- D_o, the *pre-exponential factor*, contains a number of physical constants and properties including:
  - » *entropy of formation* of the defect
  - » *attempt frequency* for jumps into available neighboring sites
  - » *lattice constant*
  - » *crystal structure* dependence

Thermally Activated Processes
- Arrhenius Behavior -

- **Diffusion:** Thermally Activated Processes
  - ✓ *Diffusivity* or *Diffusion Coefficient*:

$$D = D_o e^{-E_A/kT}$$



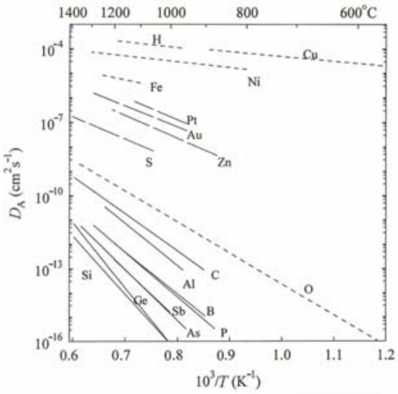


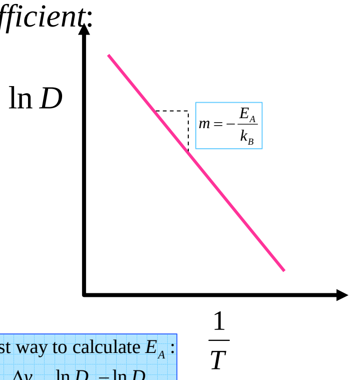
Figure 2. Temperature dependence of the diffusion coefficient of foreign atoms (A) in silicon, compared with self-diffusion. Solid lines represent diffusion data of elements that are mainly dissolved substitutionally and diffuse via the vacancy or interstitialcy mechanism. Long-dashed lines (— —) illustrate diffusion data for hybrid elements, which are mainly dissolved on the substitutional lattice site, but their diffusion proceeds via a minor fraction in an interstitial configuration. The short-dashed lines (- - - -) indicate the elements that diffuse via the direct interstitial mechanism.

Thermally Activated Processes
- Arrhenius Behavior -

❑ **Diffusion:** *Diffusivity* or *Diffusion Coefficient*:

- ✓ **Question:** How does one obtain:
  - o Activation energy
  - o Pre-exponential

$$D = D_o e^{-E_{act}/k_B T}$$



Linearize Diffusivity:

$$\ln D = \ln\left(D_o e^{-E_{act}/k_B T}\right)$$

$$= \boxed{-\frac{E_A}{k_B T} + \ln D_o}$$

Has form of Equation of a Line!

$y = mx + b$

Thus:

$$y = \ln D;\ x = \frac{1}{T};\ m = -\frac{E_A}{k_B};\ b = \ln D_o$$

Best way to calculate E_A:

$$m = \frac{\Delta y}{\Delta x} = \frac{\ln D_2 - \ln D_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$So:$

$$E_A = -k_B \cdot slope$$

$$= -k_B \cdot \frac{\ln D_2 - \ln D_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

Thermally Activated Processes
- Arrhenius Behavior -

❑ **KINETICS: Diffusion and "Chemical Reactions:** Thermally Activated Processes

- ✓ We will use Si as an example of a system with various ***diffusion mechanisms.***
- ✓ Two types of diffusion mechanisms:
  - o Direct diffusion mechanisms: diffusion without the aid of point defects.
    - Interstitial diffusion
  - o Indirect diffusion mechanisms: diffusion with the aid of point defects

$A_s + V \Leftrightarrow AV$ Vacancy mechanism
$A_s + I \Leftrightarrow AI$ Interstitialcy mechanism
$A_s + I \Leftrightarrow A_i$ Kick-out mechanism
$A_s \Leftrightarrow A_i + V$ Dissociative (Frank-Turnbull) mechanism

Thermally Activated Processes
- Arrhenius Behavior -

- ❑ **KINETICS: Diffusion and "Chemical Reactions:** Thermally Activated Processes
  - ✓ Chemical reaction causes a change in concentration, C_I, of interstitials

$$A_s + I \overset{k_f}{\underset{k_r}{\leftrightarrow}} AI$$

$$\frac{\partial C_I^{reac}}{\partial t} = k_r C_{AI} - k_f C_I C_{A_s}$$

k_r & k_f:
forward & reverse
Coefficients
of reaction

$$k = k_o e^{E_A/kT}$$

  - ✓ For the equation that describes the total kinetics, that is, the total change in the concentration of C, or C_{total}:

$$\frac{\partial C_{total}}{\partial t} = \frac{\partial C_{diff}}{\partial t} + \frac{\partial C_{rctn}}{\partial t}$$

Thermally Activated Processes
- Arrhenius Behavior -

Extra notes for those that are interested

- ❑ Arrhenius behavior is observed in many areas of science
  - ✓ Conduction in solids

Thermally Activated Processes
- Arrhenius Behavior -

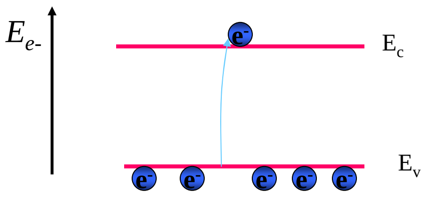
Extra notes for those that are interested

- ☐ Other Examples of Arrhenius Rate Behavior:
  - ✓ Much of Kinetics shows this behavior
    - o Carrier concentration and conduction in semiconductors and insulators
    - o Mass Transport
    - o Defect Formation
    - o Rates of Chemical Reactions (Coefficient of Reaction Rate)
    - o Creep Rate
    - o Dislocation motion

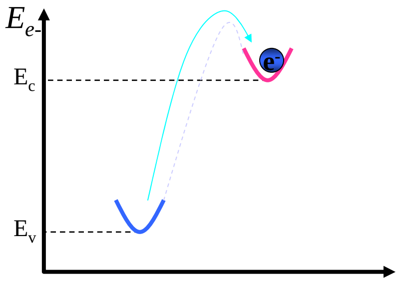
Thermally Activated Processes
- Arrhenius Behavior -

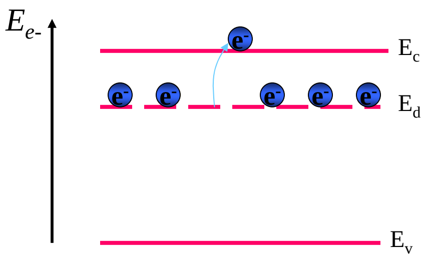
- ☐ Carrier Concentration in Semiconductors:

Intrinsic



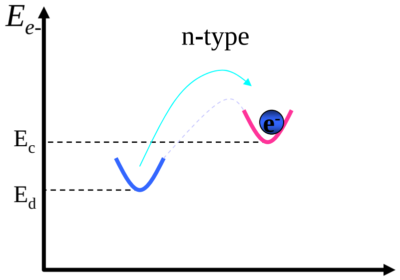
Intrinsic





n-type

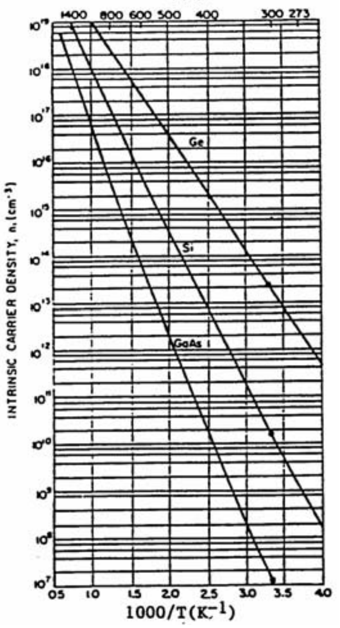
n-type



Thermally Activated Processes
- Arrhenius Behavior -

❑ Carrier Concentration:

$$n = n_o e^{-E_G/2k_BT}$$



Intrinsic carrier concentration as a function of 1/T (Arrhenius plot).

Thermally Activated Processes
- Arrhenius Behavior -

❑ Carrier Conductivity in insulators:

$$\sigma \propto n$$

$$\sigma = \sigma e^{-E_A/k_BT}$$

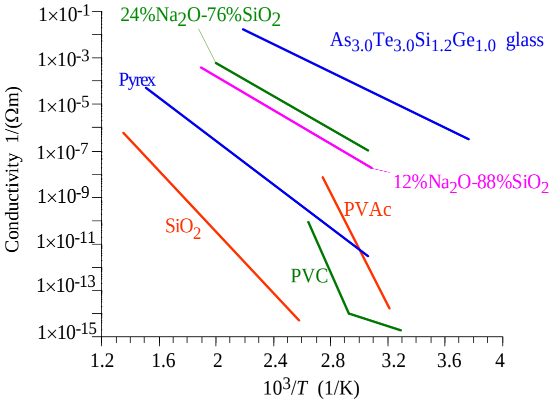


Fig. 2.28: Conductivity vs reciprocal temperature for various low conductivity solids. (PVC = Polyvinyl chloride; PVAc = Polyvinyl acetate.) Data selectively combined from numerous sources.

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Thermally Activated Processes
- Arrhenius Behavior -

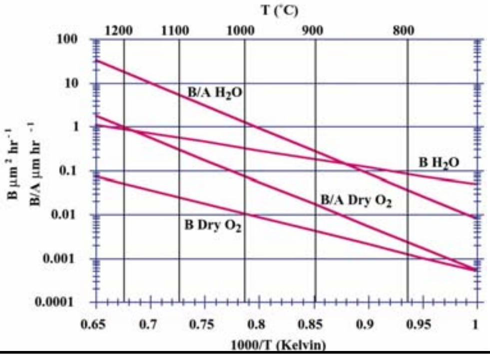
- SiO$_2$ Growth Kinetics Models: *Deal-Grove Model*

A & B/A

$$B = C_1 e^{-E_1/k_b T} \quad \text{(oxidant diffusion)}$$

$$\frac{B}{A} = C_2 e^{-E_2/k_b T} \quad \text{(interface reaction rate)}$$

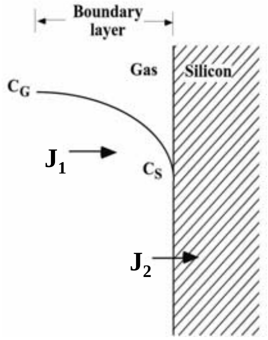
Ambient	B	B/A
Dry O_2	$C_1 = 7.72 \times 10^2\ \mu^2\ hr^{-1}$ $E_1 = 1.23$ eV	$C_2 = 6.23 \times 10^6\ \mu\ hr^{-1}$ $E_1 = 2.0$ eV
Wet O_2	$C_1 = 2.14 \times 10^2\ \mu^2\ hr^{-1}$ $E_1 = 0.71$ eV	$C_2 = 8.95 \times 10^7\ \mu\ hr^{-1}$ $E_1 = 2.05$ eV
H_2O	$C_1 = 3.86 \times 10^2\ \mu^2\ hr^{-1}$ $E_1 = 0.78$ eV	$C_2 = 1.63 \times 10^8\ \mu\ hr^{-1}$ $E_1 = 2.05$ eV

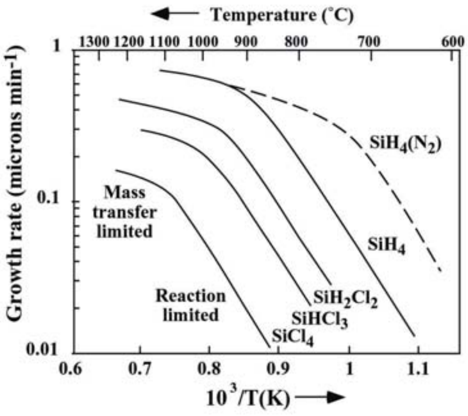


Plots of B & B/A using values in table.

Thermally Activated Processes
- Arrhenius Behavior -

- Chemical Vapor Deposition (CVD)





$$\begin{aligned} J_{rxn} &= J_2 \\ &= k_s C_s \end{aligned}$$

$$\begin{aligned} J_{SBL} &= J_1 \\ &= -D_{gas}\frac{\partial C}{\partial x} \\ &= \frac{D_{gas}}{\delta_S}\left(C_{gas} - C_{\text{waf. surf.}}\right) \\ &= h_g\left(C_{gas} - C_{\text{waf. surf.}}\right) \end{aligned}$$