

Applying Thermo: an Example of Kinetics - Diffusion



□ Fundamental Physics of Force and Energy/Work:

✓ Energy and Work:

- In general:
- The work is given by:

$$dw = -F \cdot dr \quad (5)$$

(One can argue that Eqns. 4 and 5 are really one in the same.)

- Work or Energy are scalar potentials (e.g., voltage).
- Force is a Vector field.
- If a potential is constant, there is no FIELD!
- Work is done by a Force!
- Combining equations 4 and 5, we have:

$$dw = -F \cdot dr = -\frac{\partial Y}{\partial r} dr \quad (6)$$

- **Key Point:** If the field potential is not changing, then no work would be done.

Enough fundamentals! Let's apply this physics and thermo!

Applying Thermo: an Example of Kinetics - Diffusion



□ Thermo & Physics as applied to Diffusion:

- ✓ Consider a force/forces acting on an atom producing atomic motion.
- ✓ The applied force is given by the previous equation:

$$F = -\nabla Y \quad (7)$$

- ✓ The motion of the atom will be often interrupted by other atoms and collisions occur.
- ✓ Thus: the velocity of the diffusing atom over a time period larger than the time between collisions is an average velocity.
- ✓ The velocity is proportional to the applied force and can be written as:

$$v = \mu_{mob} F \quad (8)$$

- ✓ The constant of proportionality is called the mobility.
- ✓ Consider:
 - Flux of atoms, A, diffusing at an average velocity, v , through a homogeneous distribution of B atoms.
 - The flux of A atoms through B is equal to the product of:
 - Number of A atoms per unit volume (i.e., concentration, C_A)
 - Average velocity of the A atoms, v_A .
 - This is given by:

$$J_A = C_A v_A \quad (9)$$

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□ Thermo & Physics as applied to Diffusion (cont.):

- ✓ By combining the last two equations, we obtain:

$$J_A = C_A \mu_{mob}^A F_A \quad (10)$$

- ✓ Substituting the *Force Field* Eqn. 7 (field gradient):

$$J_A = -C_A \mu_{mob}^A \nabla Y_A \quad (11)$$

- o This last equation is a general form of *Fick's 1st Law of Diffusion*.
- o That is, the flux of A atoms through a homogeneous distribution of B atoms is due to the *gradient* of some *potential field*.
- o **NOTE:** This potential field can be any of the ones shown in the previous table.
- ✓ Because the gradient of a potential field follows the *superposition principle*, the more general form of *Fick's 1st Law* is:

$$J_A = -C_A \mu_{mob}^A \sum_i \nabla Y_{i,A} \quad (12)$$

- o where the sum indicates the superposition of potential field gradients.

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□ Thermo & Physics as applied to Diffusion (cont.) –

Derivation of *Fick's 1st Law*:

- ✓ In the following slides, *Fick's 1st law*, in which the concentration gradient is obtained from the chemical potential, is explicitly derived.
- ✓ **Key point:** Diffusion in solids is based on this delineation.
- ✓ The chemical potential of atoms A is given by the thermodynamic relation:

$$\mu_A = \left(\frac{\partial E_A}{\partial N_A} \right)_{T,P,N_{\neq A}} \quad (13)$$

where E_A is a *free energy* of the A atoms in B.

- ✓ Examples of *Free Energy, E*:
 - o Gibbs, $G = G(T, P, N)$
 - o Helmholtz, $F = F(T, V, N)$
 - o Enthalpy, $H = H(S, P, N)$
 - o Omega potential or Grand Potential, $\Omega = \Omega(T, V, \mu)$

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Thermo & Physics as applied to Diffusion (cont.):

- ✓ Substituting eqn. 13 into eqn. 11, the flux with respect to the *chemical potential gradient* is obtained:

$$J_A = -C_A \mu_{mob}^A \nabla \mu_A \quad (14)$$

- ✓ Assuming one-dimensional diffusion, equation 14 simplifies to:

$$J_A = -C_A \mu_{mob}^A \frac{\partial \mu_A}{\partial x} \quad (15)$$

- ✓ The chemical potential of the A atoms may be written as a function of the *chemical activity* (i.e., a_A) of A in a distribution of B:

$$\mu_A = \mu_A^\phi + kT \ln a_A \quad (16)$$

- o where a_A is the *activity* of A among B, k is Boltzmann's constant and μ_A is the chemical potential of A in the pure state.
- ✓ The a_A may be described as the amount that the chemical potential of A deviates from the ideal or pure state (i.e., ideality).
- ✓ The ideality can be interpreted as the absence of A-A interaction upon adding an extra A atom to the system.
- ✓ Thus, the *enthalpy change*, ΔH , of the system is zero.

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Thermo & Physics as applied to Diffusion (cont.):

- ✓ The mathematical description of the activity is given by:

$$a_A = \gamma_A C_A \quad (17)$$

- o where γ_A is the *activity coefficient* and C_A is the *concentration* of the A atoms.
- ✓ **Case I: (Henry's Law)** a range of C_A much smaller than the concentration of B atoms (C_B), γ_A becomes constant.
 - o The chance of interaction between A and B atoms is small since A is so dilute in B.
 - o The primary interaction of A is with B.
 - o This phenomenon is known as *Henry's law*.
 - o Mathematically, as C_A approaches zero, the activity coefficient of A, γ_A , is given by:

$$\gamma_A = \frac{a_A}{C_A} \cong \text{constant} \quad (18)$$

- ✓ **Case II: (Raoult's law)** $C_A \gg C_B$ (i.e., B *rather* than A atoms follow *Henry's law*), *activity coefficient* of A is 1.
 - o The A atoms have a small probability of interacting with B atoms.
 - o The primary interaction of A atoms is with other A atoms.
 - o Hence, the solution of A is effectively *pure*.

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Thermo & Physics as applied to Diffusion (cont.):

- ✓ In this case, and the activity coefficient is given by:

$$\gamma_A = \frac{a_A}{C_A} \cong 1 \quad (19)$$

- o This condition is known as *Raoult's law*.
- o Raoult's law is predominant for most diffusion processes in Si since $C_{Si} \gg C_{dopant}$
- ✓ For either *Henry's* or *Raoult's* law, *Fick's* 1st and 2nd law may still be derived from the *chemical potential*.
- ✓ This eventually can be seen by combining equations 15, 16, and 17 into the following form:

$$J_A = -C_A \mu_{mob}^A \frac{\partial (\mu_A^{\phi} + kT \ln \gamma_A C_A)}{\partial x} \quad (20)$$

- o Since the *chemical potential* of a *pure substance* is constant, its derivative is zero.
- o Furthermore, k and T are constant.
- o Under these circumstances and taking the derivative of the natural logarithm, equation 20 becomes:

$$J_A = -C_A \mu_{mob}^A \frac{kT}{\gamma_A C_A} \frac{\partial (\gamma_A C_A)}{\partial x} \quad (21)$$

- o For *Henry's* and *Raoult's* law, γ_A is a constant or one, respectively.
- o In either case, γ_A may be taken out of the differential.

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Thermo & Physics as applied to Diffusion (cont.):

- ✓ Since the ratios of both γ_A and C_A factor to 1, then:

$$J_A = -\mu_{mob}^A kT \frac{\partial C_A}{\partial x} \quad (22)$$

- ✓ *Einstein's relation* states that the *diffusivity*, D , of an atom is proportional to its *mobility* where the constant of proportionality is kT .
- ✓ Mathematically & in terms of A atoms, this is written as:

$$D_A = kT \mu_{mob}^A \quad (23)$$

- o μ_{mob} units = square of the distance per unit time per unit energy.
- o kT units = energy.
- o Thus, D_A units = square of the distance per unit time.
- ✓ Invoking *Einstein's relation* with respect to equation 23, *Fick's 1st law* is obtained:

$$J_A = -D_A \frac{\partial C_A}{\partial x} \quad (24) \quad \text{Fick's 1st law}$$

Note: It is the concentration gradient that drives the flux of atoms from one area to another.

Fick's 1st law = Steady State Diffusion [$C \neq f(t)$]

- C, at every point, does not change wrt time.

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Thermo & Physics as applied to Diffusion (cont.):

NON-STEADY STATE DIFFUSION

- ✓ It has been found that as the concentration of A atoms in B changes with time, the concentration changes with position.
- ✓ Known as *Fick's 2nd law*, it has the following form:

$$\frac{\partial C_A}{\partial t} = - \frac{\partial J_A}{\partial x} \quad (25)$$

- ✓ Assume that D_A is concentration independent.
- ✓ For diffusion in S/Cs, the concentration of dopant atoms is very small, thus assumption may be comfortably made.
- ✓ Substituting equation 24 into equation 25, *Fick's 2nd law*, is given by:

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \quad (26) \quad \text{Fick's 2nd law}$$

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Diffusion: Solving Fick's 2nd Law

- ✓ Solve for $C(x,t)$
- ✓ Infinite Solutions
- ✓ Need Boundary Conditions

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2}$$

- ✓ Two Primary Boundary Conditions:
 - o Fixed Surface Concentration (*Infinite Source*)
 - Solution: Complimentary Error Function
 - o Redistribution of a constant total number of diffusing atoms (*Finite Source*)
 - Solution: Gaussian Function

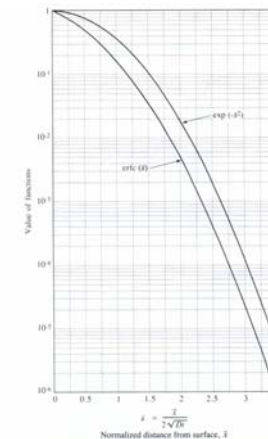


Fig. 4.4 A graph comparing the Gaussian and complementary error function (erfc) profiles. We will use this curve to evaluate the erfc and its inverse.

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Diffusion: Solving Fick's 2nd Law

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2}$$

- ✓ 1st of 2 Primary Boundary Conditions:
 - o Fixed Surface Concentration (*Infinite Source*)
 - Solution: Complimentary Error Function
 - Boundary Conditions:
 - For $t = 0, C = C_o$ at $0 \leq x \leq \infty$
 - For $t > 0, C = C_s$ at $x = 0$
 - $C = C_o$ at $x = \infty$

$$C(x,t) = C_s - (C_s - C_o) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= C_o + (C_s - C_o) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z)$$

$$= 1 - \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$$

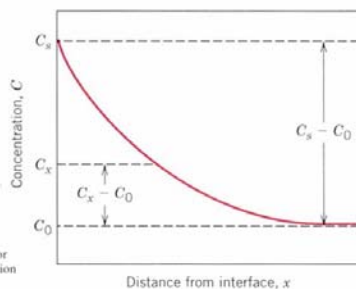


FIGURE 5.6 Concentration profile for nonsteady-state diffusion; concentration parameters relate to Equation 5.5.

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Diffusion: Solving Fick's 2nd Law

- o Fixed Surface Concentration (*Infinite Source*)
 - Solution: Complimentary Error Function

$$C(x,t) = C_s - (C_s - C_o) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= C_o + (C_s - C_o) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

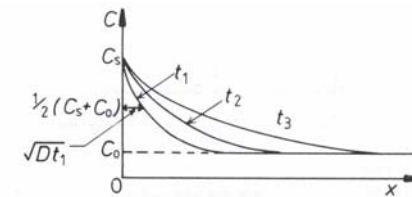


Fig. 2.11 Concentration profiles at successive times ($t_3 > t_2 > t_1$) for diffusion into a semi-infinite bar when the surface concentration C_s is maintained constant.

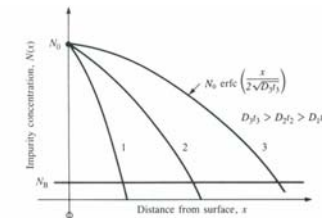


Fig. 4.2 A constant-source diffusion results in a complementary error function impurity distribution. The surface concentration N_0 remains constant and the diffusion moves deeper into the silicon wafer as the Dt product increases. Dt can change as a result of increasing diffusion time, increasing diffusion temperature, or a combination of both.

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□ Diffusion: Solving Fick's 2nd Law

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2}$$

- ✓ 2nd of 2 Primary Boundary Conditions:
 - o Redistribution of a constant total number of diffusing atoms (*Finite Source*)
 - Solution: Gaussian Function
 - Boundary Conditions:

$$C(x, t) = C(0, t) \exp\left[-\left(\frac{x}{2\sqrt{Dt}}\right)^2\right]$$

$$= C(0, t) \exp\left[-\frac{x^2}{4Dt}\right]$$

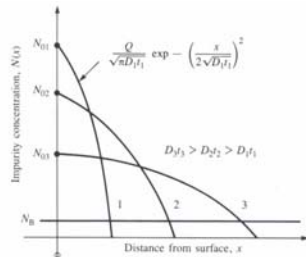


Fig. 4.3 A Gaussian distribution results from a limited-source diffusion. As the Dt product increases, the diffusion front moves more deeply into the wafer and the surface concentration decreases. The area under each of the three curves is the same.

Applying Thermo: an Example of Kinetics - Diffusion

□ 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, μ , eqn. 13.

$$\mu_{\text{phase1}} \neq \mu_{\text{phase2}} \text{ i.e. } \Delta\mu \neq 0 \text{ or } \nabla\mu \neq 0$$

- ✓ HOWEVER: Temperature increases the activity of a diffusing species.
- ✓ **Diffusivity** or **Diffusion Coefficient**:

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

- ✓ 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:
 - o *entropy of formation* of the defect
 - o *attempt frequency* for jumps into available neighboring sites
 - o *lattice constant*
 - o *crystal structure* dependence

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□ Diffusion: Thermally Activated Processes

✓ Diffusivity or Diffusion Coefficient:

$$D = D_0 e^{-E_{ac}/k_B T}$$

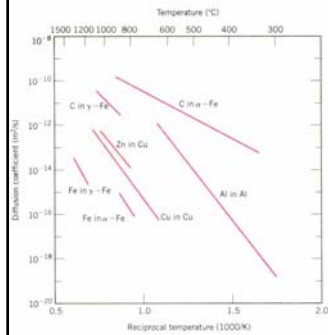


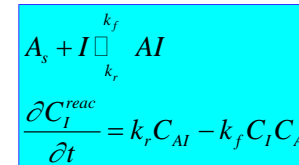
FIGURE 5.7 Plot of the logarithm of the diffusion coefficient versus the reciprocal of absolute temperature for several metals. [Data taken from E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1992.]

Applying Thermo: an Example of Kinetics - Diffusion

□ Diffusion Mechanisms = Processes = Reactions

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

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



k_r & k_f :
forward & reverse
Coefficients
of reaction

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

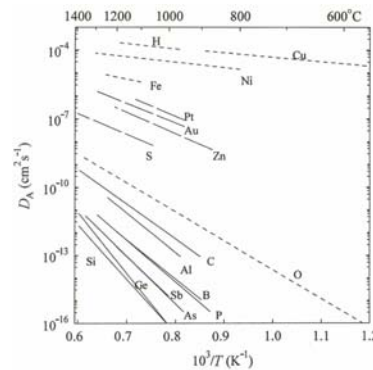
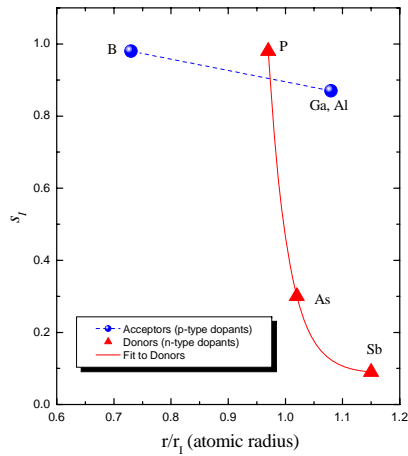


Figure 2. Temperature dependence of the diffusion coefficient of foreign atoms (A) in silicon, compared with self-diffusion. Solid lines represent diffusion data of elements that are mainly dissolved substitutionally and diffuse via the vacancy or interstitialcy mechanism. Long-dashed lines (---) illustrate 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.

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□ Diffusion Mechanisms = Processes = Reactions

- ✓ Indirect diffusion mechanisms: diffusion with the aid of point defects



$$\frac{D_{X_i}^{eff, eq}}{C_{X_i}^{eq}} = \frac{C_M^{eq} D_{MI}}{C_{X_i}^{eq}} + \frac{C_{XV}^{eq} D_{XV}}{C_{X_i}^{eq}} = \boxed{D_{MI}^{eff} + D_{XV}^{eff}} \quad \text{Equilibrium}$$

$$\frac{D_{X_i}^{eff}}{C_{X_i}^{eq}} = \frac{C_M^{eq} D_{MI}}{C_{X_i}^{eq} C_I^{eq}} + \frac{C_{XV}^{eq} D_{XV}}{C_{X_i}^{eq} C_V^{eq}} = \boxed{D_{MI}^{eff} \frac{C_I}{C_I^{eq}} + D_{XV}^{eff} \frac{C_V}{C_V^{eq}}} \quad \text{Nonequilibrium}$$

$$\frac{D_{X_i}^{eff}}{D_{X_i}^{eff, eq}} = \frac{D_{MI}^{eff}}{D_{MI}^{eff} + D_{XV}^{eff}} \frac{C_I}{C_I^{eq}} + \frac{D_{XV}^{eff}}{D_{MI}^{eff} + D_{XV}^{eff}} \frac{C_V}{C_V^{eq}} = \boxed{s_I \frac{C_I}{C_I^{eq}} + s_V \frac{C_V}{C_V^{eq}}}$$