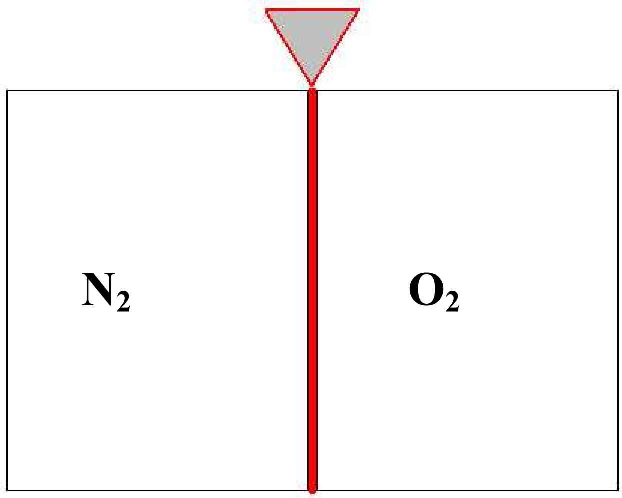
Materials Engineering 272-C
Fall 2001, Lecture 7 & 8

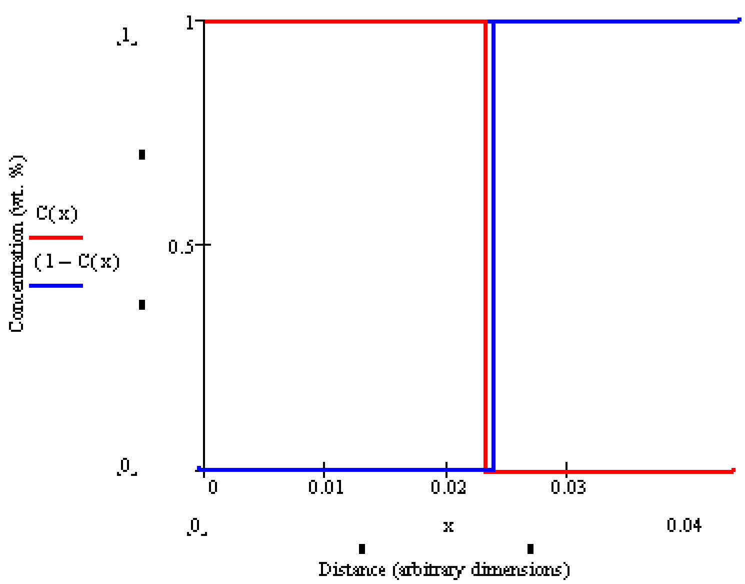
Fundamentals of Diffusion

Diffusion: Transport in a solid, liquid, or gas driven by a concentration gradient (or, in the case of mass transport, a chemical potential gradient). Diffusion does not necessarily apply to transport of mass. Consider, for example, thermal diffusion, or transport of phonons – heat quanta.

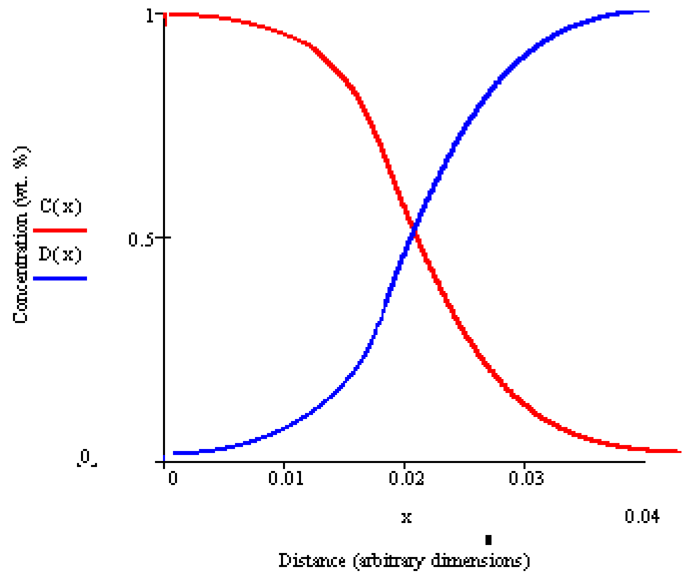
Example: Two chambers, each containing a different gas, separated by a removable barrier; when the barrier is pulled away, *interdiffusion* occurs



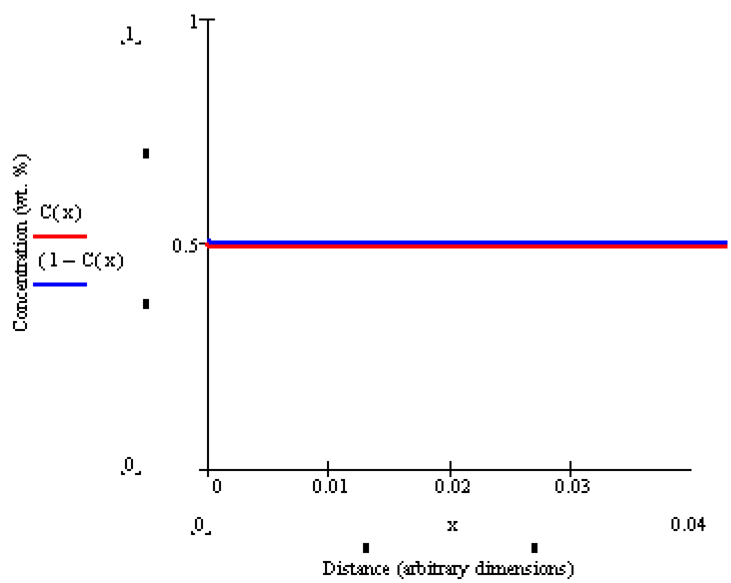
Initially, a plot of concentration of each species would look like the following:



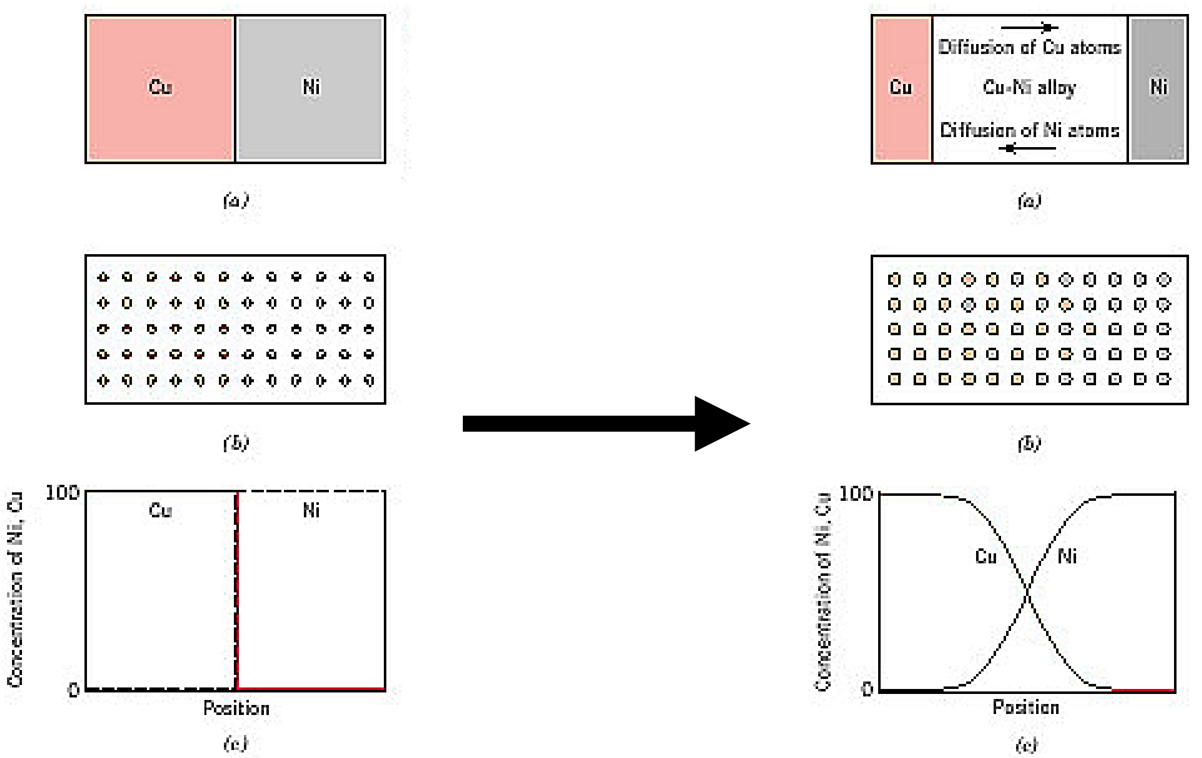
After a time, the concentration profiles would look like this:



And after a *long* time, the concentration of the two gasses would be everywhere the same:

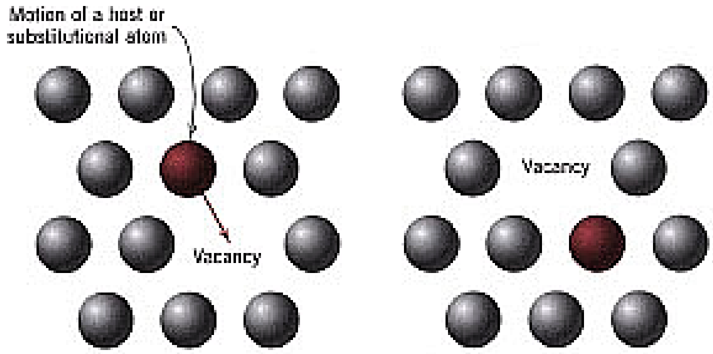


We see essentially the same process in solids, as seen in the case of Cu and Ni: (note, diffusion in the gaseous state does not require an activation energy as it does in solids)

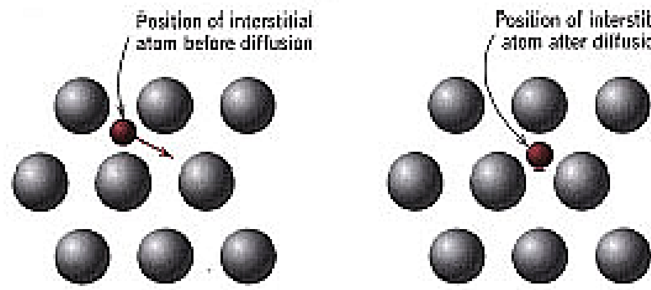


The process of substitutional diffusion requires the presence of *vacancies*

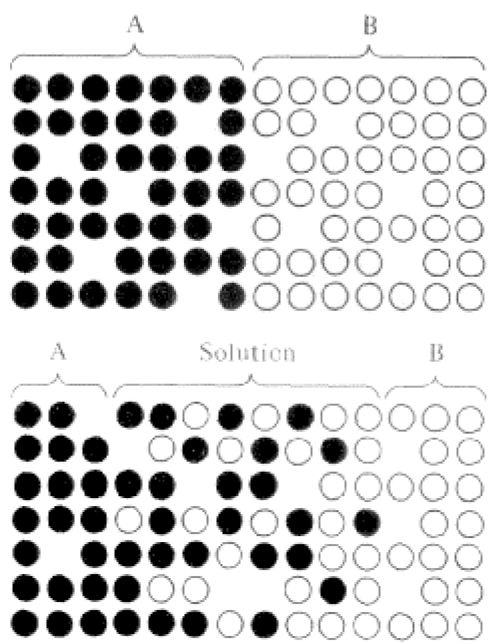
(Vacancies give the atoms a place to move)



(a)

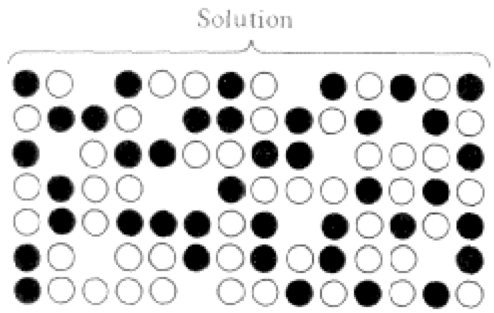


(b)



Diffusion tends to equalize concentration gradients.

Note the presence of vacancies in the material


Solution

Recall, the fraction of vacancies is temperature dependent:

- $$\frac{Nv}{N_o} = e^{-\frac{Q_v}{kT}}$$
- $\therefore$ diffusion is a temperature-dependent process

In the example of a Cu-Ni diffusion couple, diffusion of Ni into Cu occurs at a faster rate than Cu in Ni.

Why is this?

T_m(Ni) = 1451°C, T_m(Cu) = 1083°C $\Rightarrow$ larger fraction of vacancies in Cu at a given temperature than in Ni.

Mathematically, we would write

$$\left(\frac{N_v}{N_o}\right)_{Cu} \rangle \left(\frac{N_v}{N_o}\right)_{Ni}$$

(We say that Cu is at a higher *homologous* temperature than Ni)

Diffusion tends to equalize compositional gradients (if all other factors are equal - sometimes "kinetics" do not favor diffusional equilibration. That is, some diffusional processes occur so slowly as to be imperceptible.)

Factors that affect solid state diffusion:

Diffusion occurs at a higher rate…

- at higher temperatures
  atoms have more energy to overcome "barrier" to diffusion
  greater probability of activation over the energy barriers

- with smaller atoms
  smaller atoms can "squeeze" in between host atoms more easily

- in lower melting point host material
  lower $T_m \Rightarrow$ weaker bonds (easier to push apart)

- in lower packing density host material
  easier to migrate with fewer bonds to expand

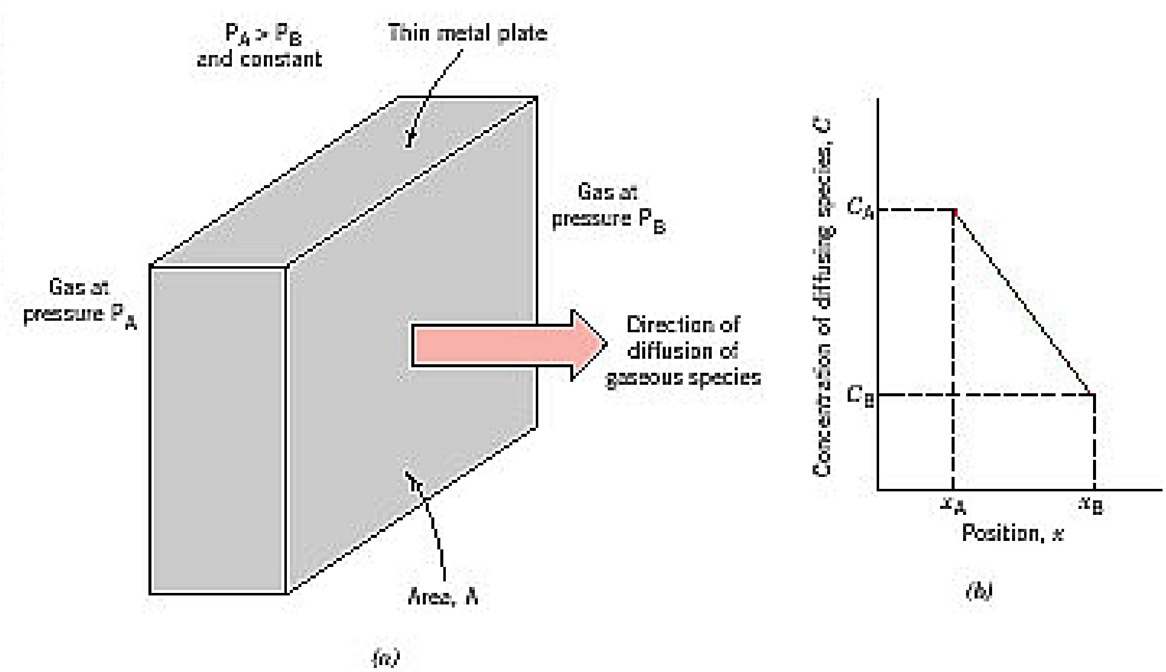
- in grain boundaries
  more disordered than bulk material (lower bond density)

Steady state diffusion is described in terms of a **flux** and a **concentration gradient**:

(steady state means the concentration gradient does not change with time, or that the flux into a unit area is equal to the flux leaving the area – no accumulation or loss)

Flux = number (or mass) of atoms passing through an area per unit time

Units: $\frac{atoms}{cm^2 \cdot \sec}$ **or** $\frac{grams}{cm^2 \cdot \sec}$ ('could also be moles, Kg; the main thing is to just be consistent)



Flux is usually denoted by the letter "J"

flux $\propto$ concentration gradient

$$J \propto \frac{\Delta C}{\Delta x}$$

-or –

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

Fick's first law…

in words

and mathematically

where the constant of proportionality (D) is called the diffusion coefficient

units of the diffusion coefficient: length^2/time (cm^2/s or m^2/s)

Diffusion coefficient is a measure of the **mobility** of atoms

the diffusion coefficient is a "thermally activated" quantity:

$$D = D_o e^{-\frac{Q_d}{RT}}$$

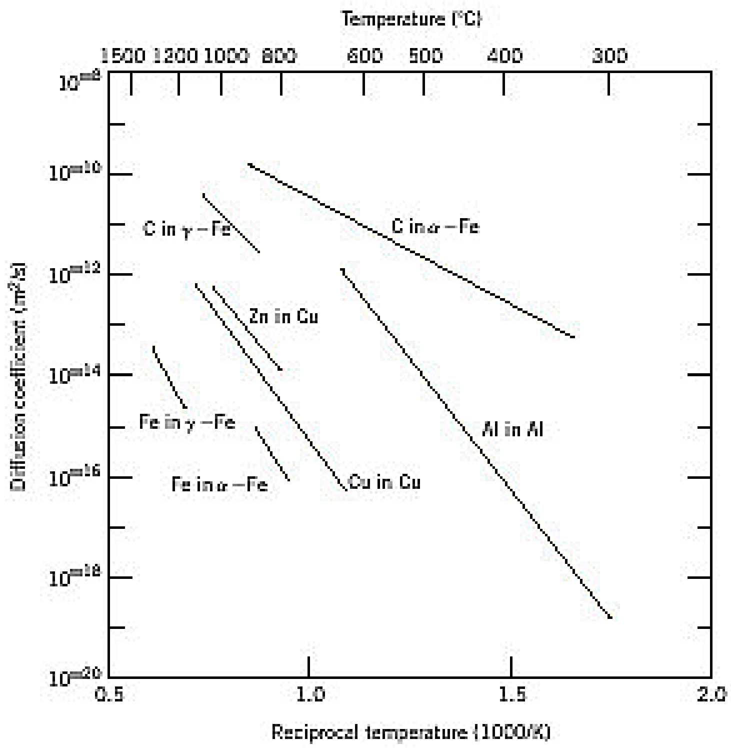
-or-

$$D = D_o e^{-\frac{q_d}{kT}}$$

where Q_d and q_d are activation energies for diffusion

per mole **per atom**

Since D increases exponentially with temperature, diffusion <u>rates</u> increase with temperature:



Typical values for preexponential (D_o) and activation energy:
(after Kittel, "Solid State Physics" 5th ed.)
note: $D=D_o\exp\{-q/k_BT\}$

Host crystal	Atom	D_o (cm^2/s)	q_d (eV/atom)
Cu	Cu	0.20	2.04
Cu	Zn	0.34	1.98
Ag	Ag	0.40	1.91
Ag	Au	0.26	1.98
Ag	Cu	1.2	2.00
Ag	Pb	0.22	1.65
U	U	0.002	1.20
Si	Al	8.0	3.47
Si	Ga	3.6	3.51
Si	In	16.0	3.90

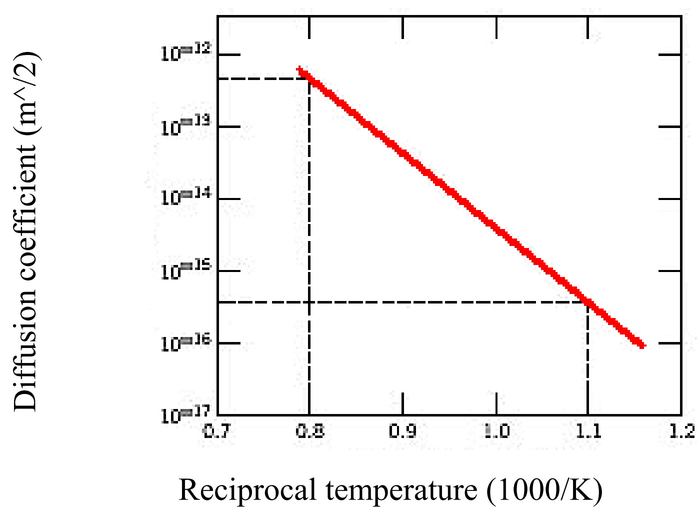
2 primary mechanisms that affect flux:
- Diffusion coefficient (temperature)
- Slope of concentration gradient

D_o and Q_d (or q_d) can be found by plotting ln(D) vs. $\dfrac{1}{T}$

Then,

Slope = -Q/R (or $-q/k_B$)

Intercept = $\ln(D_o)$:



We usually don't have steady state; more often, the concentration versus position curve changes with time (non-steady state)

In this case, we must use another relationship → Fick's second law:

(we are interested in the **time rate of change of the concentration**…)

$$\delta C = \frac{\Delta(\# atoms)}{volume} = \frac{(J_1 - J_2)A\delta t}{A\delta x}$$, simplifying, we have $\frac{\delta C}{\delta t} = \frac{\Delta J}{\Delta x}$

- or $-\frac{dC}{dt} = \frac{dJ}{dx} = \frac{d\left(D\frac{dC}{dx}\right)}{dx} \cong D\frac{d^2C}{dx^2}$, assuming D is independent of position!
-

Fick's 2nd law is: $\boxed{\frac{dC}{dt} = D\frac{d^2C}{dx^2}}$

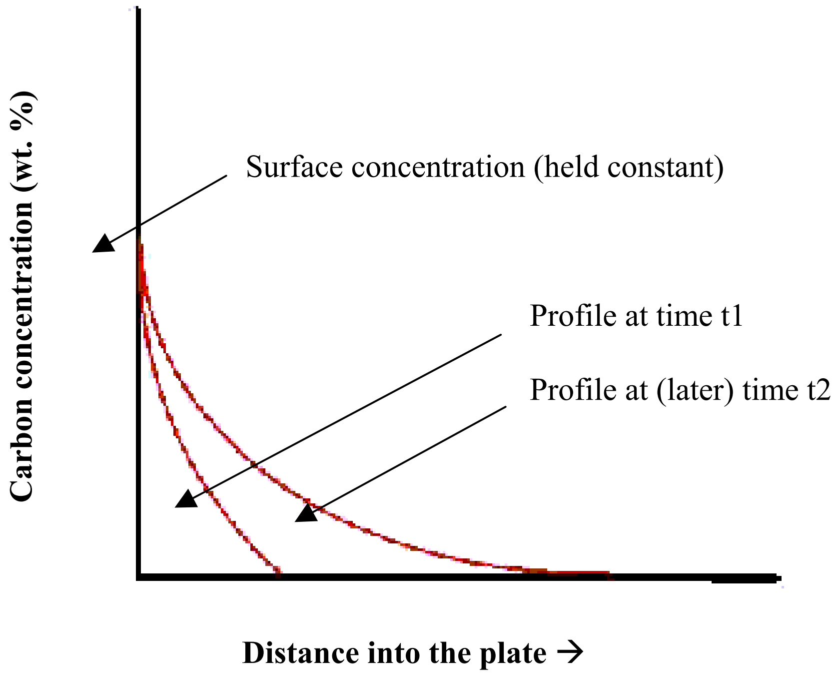
Which describes diffusion in cases where the concentration profile changes with time

Think of as the **curvature** of the concentration profile

Example:

Consider diffusion of C into γ-Fe (this is one example of **carburization**)

In carburization, we diffuse C atoms into the surface of low C steels, heated to ~ 1000°C (FCC structure)



(The profile above is consistent with an initial carbon concentration of ~ 0. Steels, by definition, always have a non-zero carbon content, w_o.

Solution to Fick's 2nd law:

Employing appropriate boundary conditions, Fick's 2nd law can be solved, with the solution written in a useful form for metallurgical applications:

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

where C_x = carbon concentration at any point "x" in the steel during diffusion,
C_o = initial (uniform) carbon concentration in the steel (at t = 0),
C_s = surface concentration of carbon during diffusion (we can control this)

erf{} = "error" function (a mathematical expression: -1 < erf(x) < 1)
While not strictly true, for this class we will assume erf{x} ≅ x.

(The assumption that erf(x) ≅ x isn't too bad for x < 0.7. In situations where x > 0.7 or where erf(x) > 0.65, you should really use the correct value. The following table may be of help. Remember to interpolate to obtain values between those listed.)

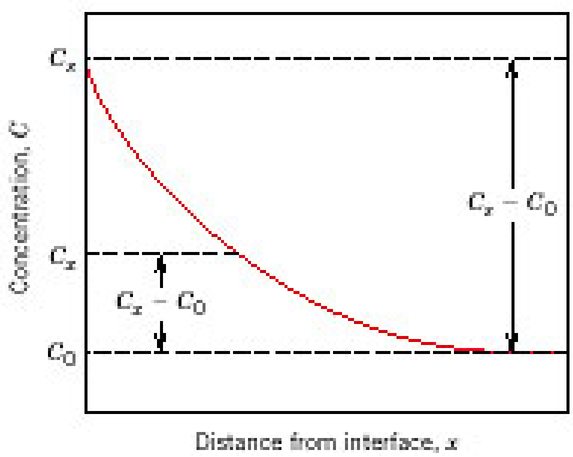
Table 5.1 Tabulation of Error Function Values

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

Then, the (somewhat oversimplified) solution becomes:

$$\boxed{C(x) \cong C_o + (C_s - C_o)\left[1 - \frac{x}{2\sqrt{Dt}}\right]}$$

(x in cm, t in sec, D in cm^2/s, C1, Co, Cx all in wt. %)



Next, some example problems…

I. Callister: 5.6

The purification of H_2 (gas) by diffusion through a Pd sheet was discussed in Section 5.3. Compute the number of <u>kilograms</u> of hydrogen that pass per hour through a 5-mm thick sheet of Pd having an area of 0.20 m^2 at 500°C. Assume a diffusion coefficient of 1.0×10^{-8} m^2/s, that the concentrations at the high- and low-pressure sides of the plate are 2.4 and 0.6 kg of H_2 per m^3 of Pd, and that steady state conditions have been attained.

This problem calls for the mass of hydrogen per hour that diffuses through a Pd sheet. It first becomes necessary to employ both Equations (5.1a) and (5.3). Combining these expressions and <u>solving for the mass</u> yields

$$M = JAt = -DAt\frac{DC}{Dx}$$

Recall, flux is mass per unit time per unit area. Thus, multiplying J by area and time will give total mass.

$$= -(1.0 \times 10^{-8}\ m^2/s)(0.2\ m^2)(3600\ s/h)\left[\frac{0.6 - 2.4\ kg/m^3}{5 \times 10^{-3}\ m}\right]$$

$$= 2.6 \times 10^{-3}\ kg/h$$

II. Callister 5.12 (*decarburization*)

An FCC Fe-C alloy initially containing 0.35 wt. % C is exposed to an oxygen-rich (and carbon-free) atmosphere at 1400 K (1127°C). Under these conditions the carbon in the alloy diffuses toward the surface and reacts with the oxygen in the atmosphere; that is, the carbon concentration at the surface is maintained essentially at 0 wt. % C. (This process of carbon depletion is termed decarburization.) At what <u>position</u> will the carbon concentration be 0.15 wt. % after a 10-hour treatment. The value of D at 1400 K is 6.9×10^{-11} m^2/s.

This problem asks that we determine the position at which the carbon concentration is 0.15 wt% after a 10-h heat treatment at 1400 K when $\mathbf{C_o}$ = 0.35 wt% C. From Equation (5.5)

$$\frac{C_x - C_o}{C_s - C_o} = \frac{0.15 - 0.35}{0 - 0.35} = 0.5714 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Thus,

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4286$$

Since we are assuming erf(z) ≅ z, we will simply let z = 0.4:

Which means that

$$\frac{x}{2\sqrt{Dt}} = 0.4$$

And, finally

$$x = 2(0.4)\sqrt{Dt} = (0.8004)\sqrt{(6.9 \text{ x } 10^{-11} \text{ m}^2/\text{s})(3.6 \text{ x } 10^4 \text{ s})}$$

$$= 1.3 \text{ x } 10^{-3} \text{ m} = 1.3 \text{ mm}$$

III. Callister 5. 26.

At approximately what temperature would a specimen of γ-Fe have to be carburized for 2 hours to produce the same diffusion result as at 900°C for 15-hours?

To solve this problem it is necessary to employ Equation (5.7) (Dt = constant) which takes on the form

$$(Dt)_{900} = (Dt)_T$$

(the hint is that the problem stated "*the same diffusion result*," meaning that we want the same specific carbon concentration in both cases)

At 900°C, and using the data from Table 5.2

$$D_{900} = (2.3 \text{ x } 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{148000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(900 + 273 \text{ K})}\right]$$

$$= 5.9 \text{ x } 10^{-12} \text{ m}^2/\text{s}$$

Thus,

$$(5.9 \text{ x } 10^{-12} \text{ m}^2/\text{s})(15 \text{ h}) = D_T(2 \text{ h})$$

And

$$D_T = 4.43 \text{ x } 10^{-11} \text{ m}^2/\text{s}$$

Solving for **T** from Equation (5.9a)

$$T = -\frac{Q_d}{R(\ln D_T - \ln D_o)}$$

$$= -\frac{148000 \text{ J/mol}}{(8.31 \text{ J/mol-K})[\ln(4.43 \text{ x } 10^{-11}) - \ln(2.3 \text{ x } 10^{-5})]}$$

$$= 1353 \text{ K} = 1080°\text{C}$$

Next topic: mechanical properties of materials