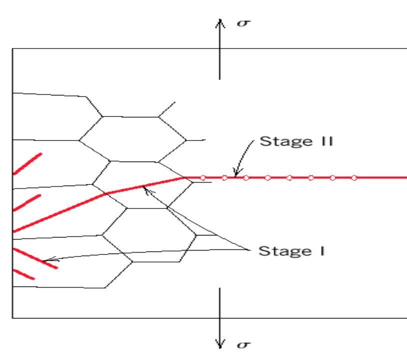
Surface Treatments

- Applications
  - Biomedical (biocompatible coatings on implants, drug coatings for sustained release…)
  - Mechanical
    - Tribological – friction and wear (tool steels, implants…)
    - Fatigue – minimize surface defects, add compressive stress
    - Hardness
  - Corrosion
    - Protective coatings for harsh environments (catalytic converters, electrochemical cells…)
  - Thermal – modify thermal coefficient of expansion to minimize stresses for thermal cycling
  - Electronic – dielectric barriers, electrical grounds
  - Optical – reflective coatings or anti-reflective coatings (tinted glass, solar cells…)
  - Many many more…

Example-- Fatigue: Crack initiation and propagation

- Crack initiation at the sites of stress concentration (microcracks, scratches, indents, interior corners, dislocation slip steps, etc.). Quality of surface is important.
- Crack propagation



- Stage I: initial slow propagation along crystal planes with high resolved shear stress. Involves just a few grains, and has flat fracture surface
- Stage II: faster propagation perpendicular to the applied stress. Crack grows by repetitive blunting and sharpening process at crack tip. Rough fracture surface.

- Crack eventually reaches critical dimension and propagates very rapidly

Factors that affect fatigue life

- Magnitude of stress (mean, amplitude...)
- Quality of the surface (scratches, sharp transitions and edges).

Solutions:

- Polishing (removes machining flaws etc.)
- **Introducing compressive stresses (compensate for applied tensile stresses) into thin surface layer by "Shot Peening"- firing small shot into surface to be treated. High-tech solution - ion implantation, laser peening.**
- **Case Hardening - create C- or N- rich outer layer in steels by atomic diffusion from the surface. Makes harder outer layer and also introduces compressive stresses**
- Optimizing geometry - avoid internal corners, notches etc.

Factors that affect fatigue life: environmental effects

- **Thermal Fatigue.** Thermal cycling causes expansion and contraction, hence thermal stress, if component is restrained.

  Solutions:

  - eliminate restraint by design
  - use materials with low thermal expansion coefficients

- **Corrosion fatigue.** Chemical reactions induce pits which act as stress raisers. Corrosion also enhances crack propagation.

  Solutions:

  - decrease corrosiveness of medium, if possible
  - **add protective surface coating**
  - **add residual compressive stresses**

Surface Hardening

- Thermochemical treatments to harden surface of part (carbon, nitrogen)
- Also called case hardening
- May or may not require quenching
- Interior remains tough and strong

Carburizing

- Low-carbon steel is heated in a carbon-rich environment
  - Pack carburizing - packing parts in charcoal or coke - makes thick layer (0.025 - 0.150 in)
  - Gas carburizing - use of propane or other gas in a closed furnace - makes thin layer (0.005 - 0.030 in)
  - Liquid carburizing - molten salt bath containing sodium cyanide, barium chloride - thickness between other two methods
- Followed by quenching, hardness about HRC 60

Nitriding

- Nitrogen diffused into surface of special alloy steels (aluminum or chromium)
- Nitride compounds precipitate out
  - Gas nitriding - heat in ammonia
  - Liquid nitriding - dip in molten cyanide bath
- Case thicknesses between 0.001 and 0.020 in. with hardness up to HRC 70

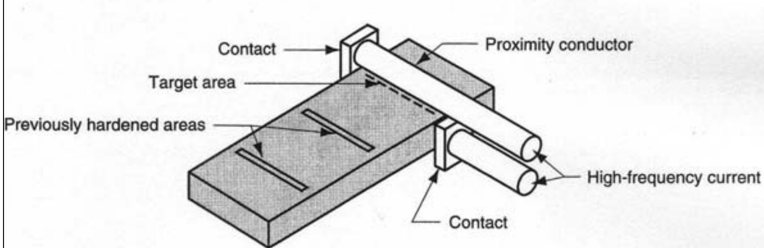
Other Case Hardening

- Carbonotriding - use both carbon and nitrogen
- Chroming - pack or dip in chromium-rich material - adds heat and wear resistance
- Boronizing - improves abrasion resistance, coefficient of friction

Heat Treatment Methods

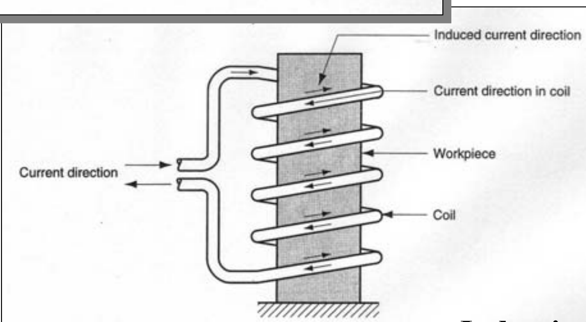
- Furnaces
  - Fuel-fired - parts exposed to combustion products
  - Electric
  - Batch or continuous
  - Vacuum - prevents oxidation of surface
  - Salt bath
  - Fluidized bed - particles suspended by gas flow - improves heat transfer

Surface Hardening Methods



HF Resistance

- Flame
- Induction heating
- High-frequency (HF) resistance heating
- Electron or laser beam heating



Induction

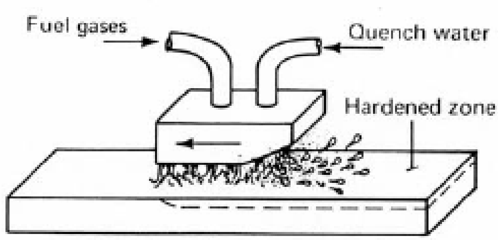
Reasons to Surface Harden

- Increase wear resistance
- Increase surface strenght for load carrying (crush resistance)
- Induce suitable residual and compressive stresses
- Improve fatigue life
- Impact resistance

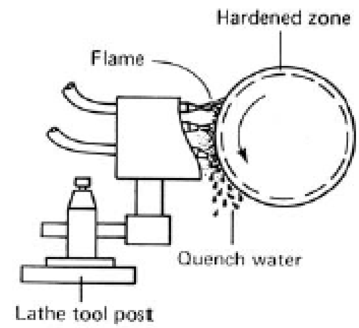
Methods to Surface Harden

- Heat Treatment
  - Induction
  - Flame
  - Laser
  - Light
  - Electron beam
- Case Hardening
  - Carburizing
  - Cyaniding
  - Carbonitriding
  - Nitriding

Flame Hardening

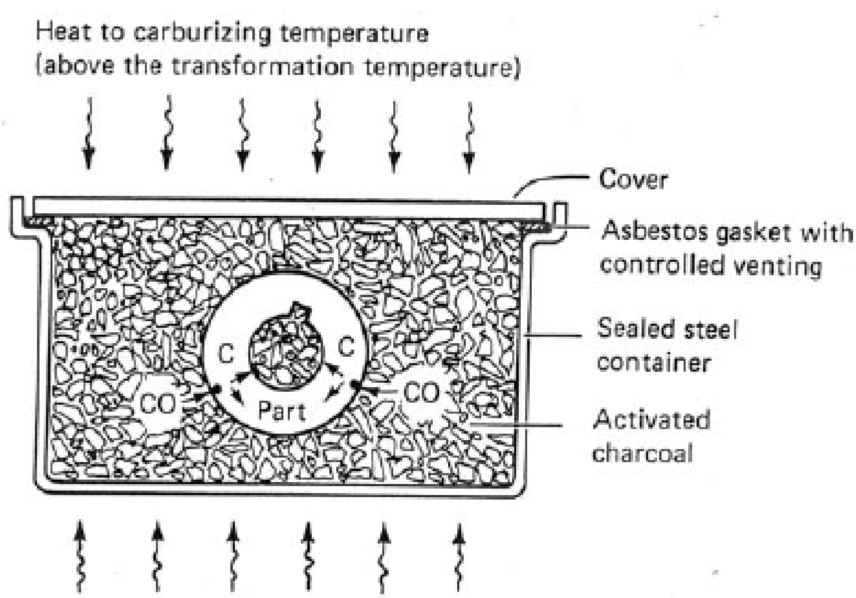


Flame hardening of flat plates



Flame hardening round bars in a lathe

Pack Carburizing



Heat Treatment

- Procedure (typically for medium to high carbon steels)
  - Heat surface to austenize (interior stays below austenite transition temperature)
  - Cool to form surface martensite
    - Interior is not modified
    - Surface is in compression
  - Subsequent tempering typically done

Heat treatment

- Characteristics
  - Hardened depth depends on
    - Frequency (for induction heating – effects the depth of the "skin"
      - Example 1,000Hz – 4.5-9mm, 1,000,000 Hz – 0.25-0.8mm
    - Heat flow (flame)
  - Surface Rc 50-60 (martensite or tempered martensite)
  - Interior – Rc 10-20 (pearlite-ferrite)

Case Hardening

- Reasons
  - Easy to control depths
  - Good for complicated parts
  - Mass production compatible
  - Can use with low carbon steels (cheaper and tougher)

Case Hardening

- Carburizing gas mixtures
  - CO, CO_2, H_2, H_2O, and N_2(carrier gas)
  - Reactions:
    - $2CO \rightarrow C(s) + CO_2$
    - $CO + H_2 \rightarrow C + H_2O$
  - Control CO/CO_2 + H_2/H_2O ratios to carburize or decarburize

Carbon Gradient

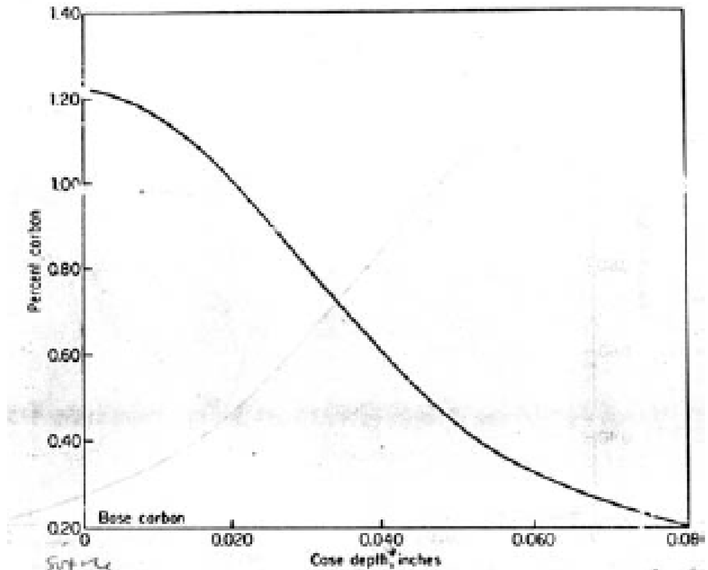
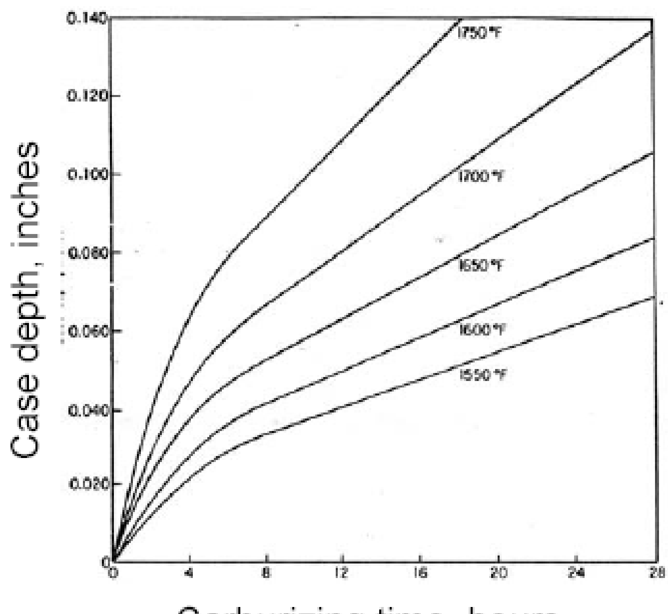


Fig. 8-71 Carbon-concentration gradient in a carburized steel with 0.080 in. total case.

Carburizing Time/Temperature Plots



Case Hardened Gear Tooth

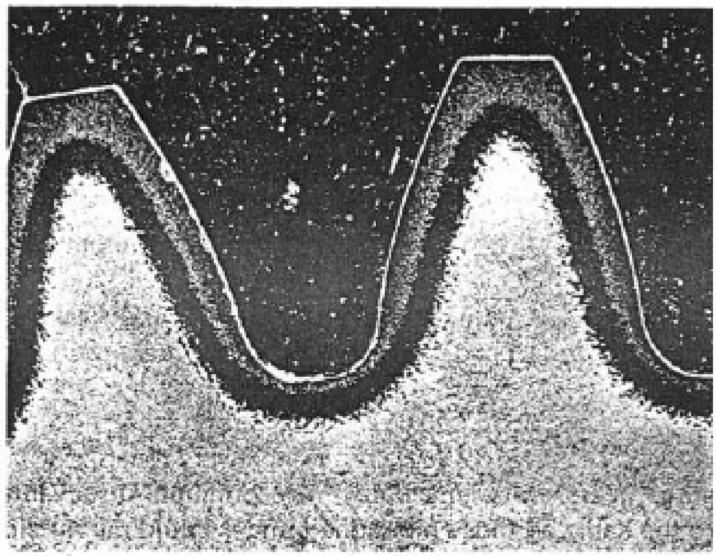


Fig. 8-75 A properly carburized, hardened, and tempered gear. Etched in 2 percent nital, 7X.

Microstructure Through Carburized Surface

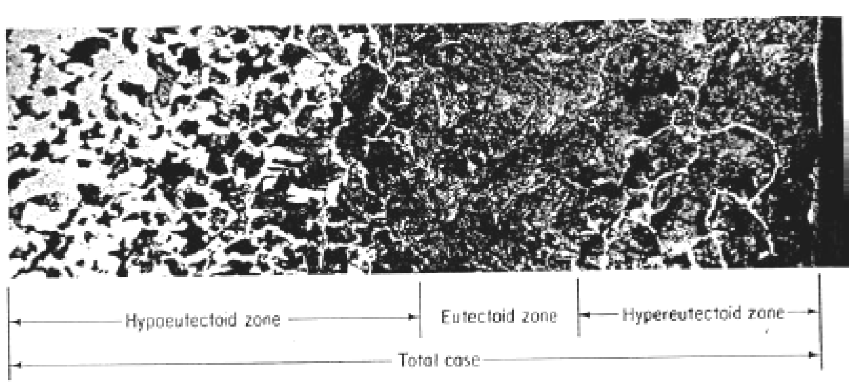


Fig. 8-70 0.20 percent carbon steel, pack-carburized at 1700°F for 6 h and furnace-cooled. Etched in 2 percent nital, 30X.

Microhardness Through Case zone

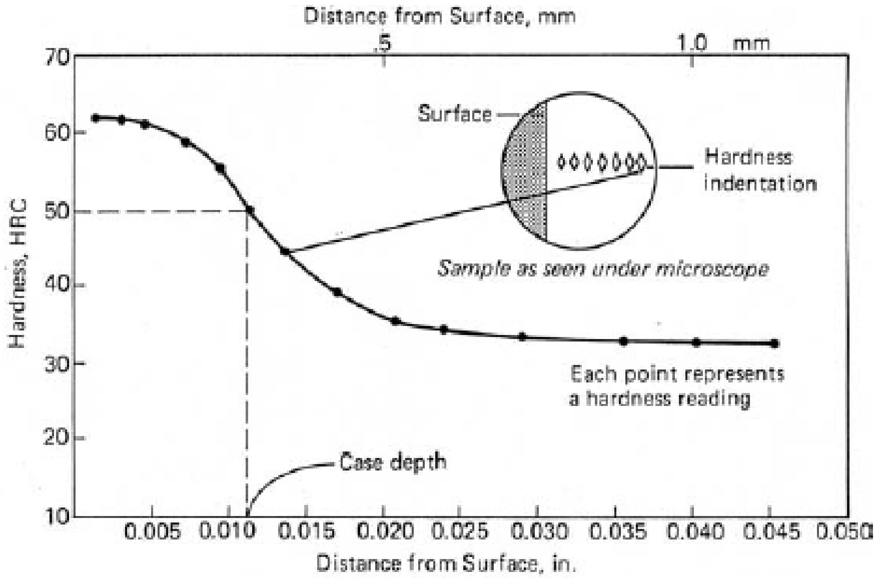
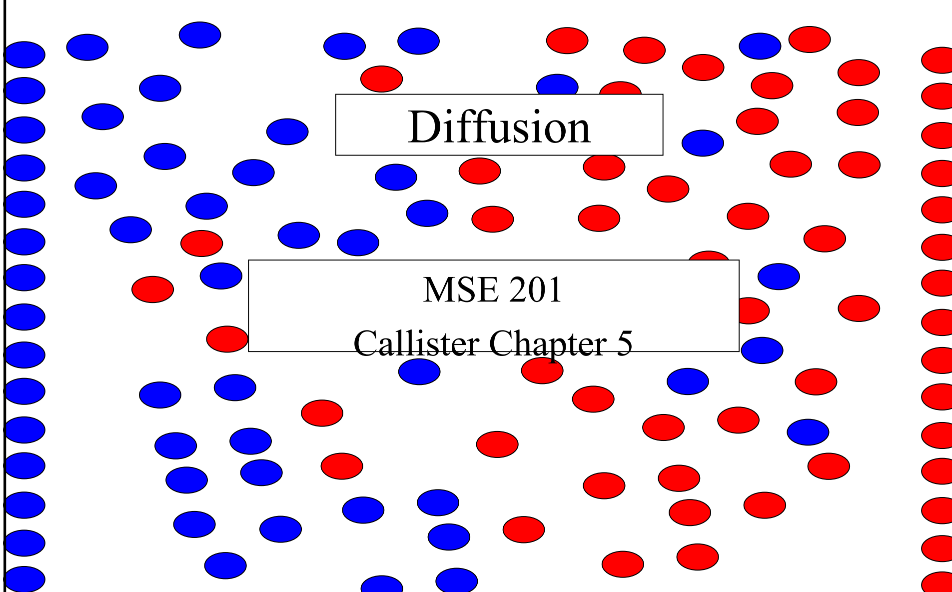


Figure 8-6 Determination of case depth by microhardness survey.



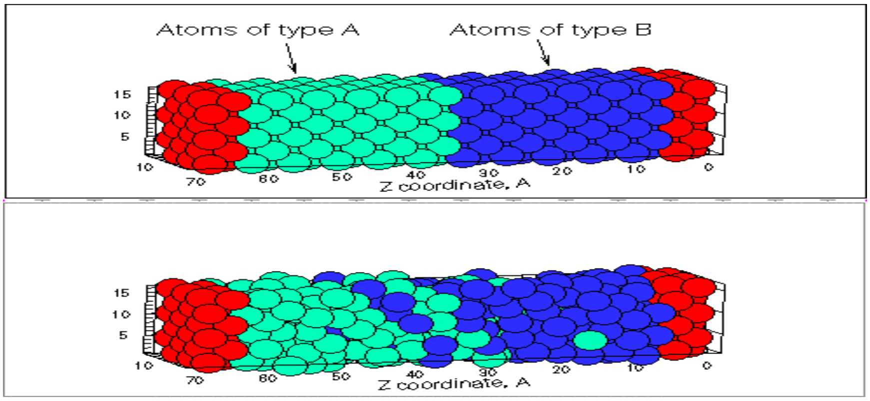
Diffusion

MSE 201

Callister Chapter 5

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 ~ 10^{13} Hz
- Average atomic / electronic energy due to thermal excitation is of order kT [*with a distribution around this average energy, P(E) ~ exp(-E/kT)*]

k : Boltzmann's constant

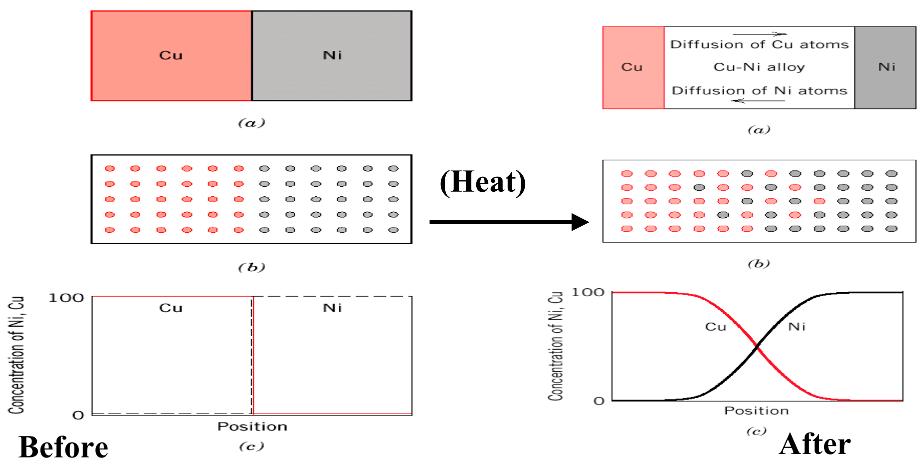
(1.38×10^{-23} J/K or 8.62×10^{-5} eV/K)

T: Absolute temperature (Kelvin)

What is diffusion?

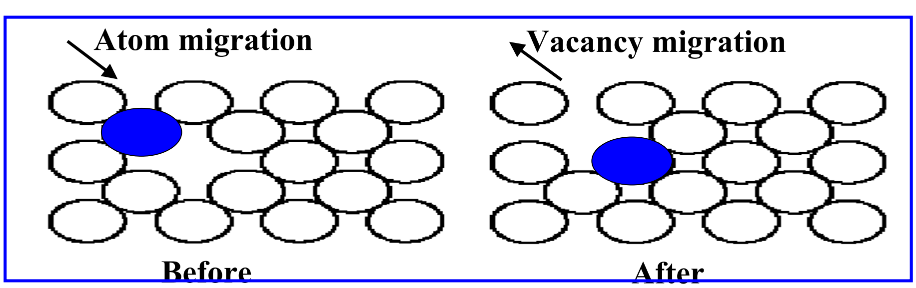
Interdiffusion and Self-diffusion

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



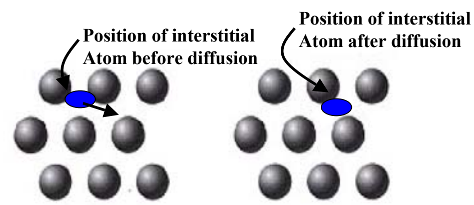
Diffusion Mechanisms

- 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.**

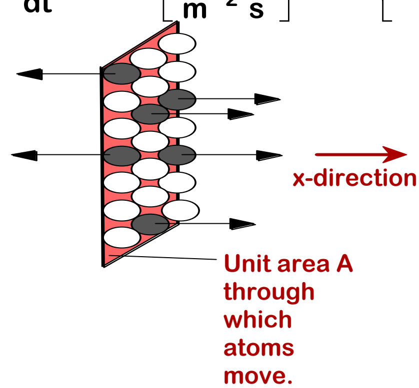


Self diffusion (motion of atoms within a pure host) also occurs. Predominantly vacancy in nature (difficult for atoms to "fit" into interstitial sites because of size.

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^2-second) or in terms of the mass flux - mass of atoms diffusing through unit area per unit time, (e.g., kg/m^2-second).

$$J = \frac{1}{A}\frac{dM}{dt} \Rightarrow \left[\frac{kg}{m^2 s}\right] \text{ or } \left[\frac{atoms}{m^2 s}\right]$$



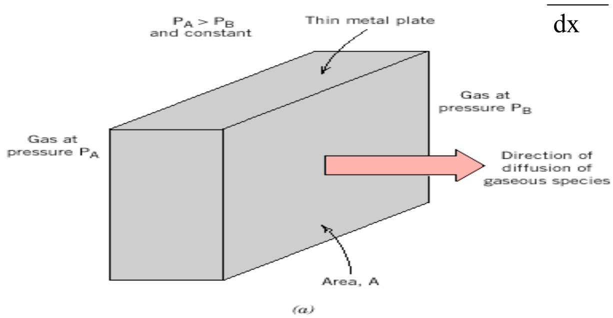
Steady-State Diffusion

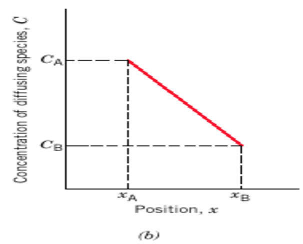
Steady state diffusion: the diffusion flux does not change with time.

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

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

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

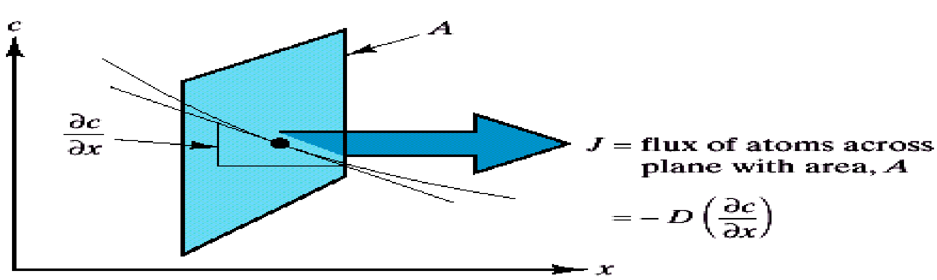




Steady-State Diffusion: Fick's first law

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

$$J = -D \frac{dC}{dx}$$ where **D 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.

$$D = D_0 \exp\left(-Q_d / RT\right)$$

D_0 – temperature-independent preexponential (m^2/s)

Q_d – the activation energy for diffusion (J/mol or eV/atom)

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

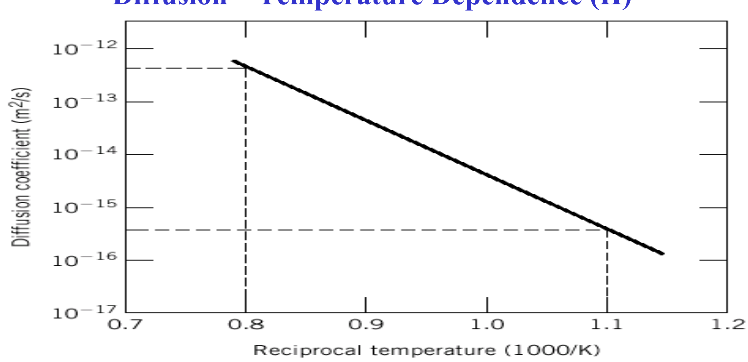
T – absolute temperature (K)

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 lnD versus 1/T or logD versus 1/T. Such plots are Arrhenius plots.

Diffusion – Temperature Dependence (II)

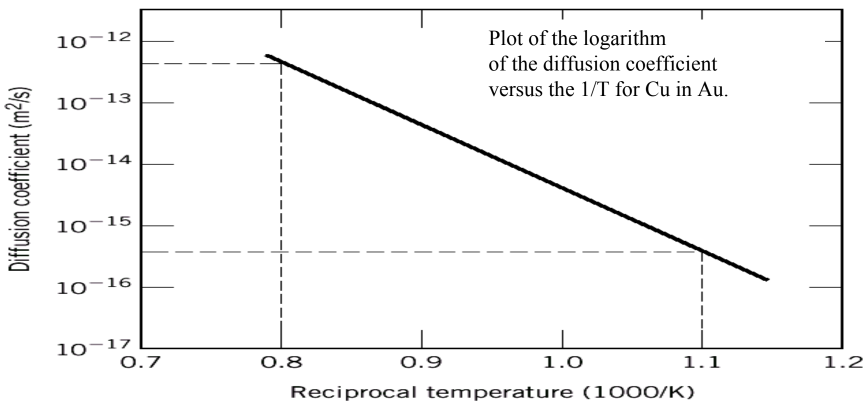


Graph of log D vs. 1/T has slop of $-Q_d/2.3R$, intercept of ln D_o

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

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

Diffusion Coefficient



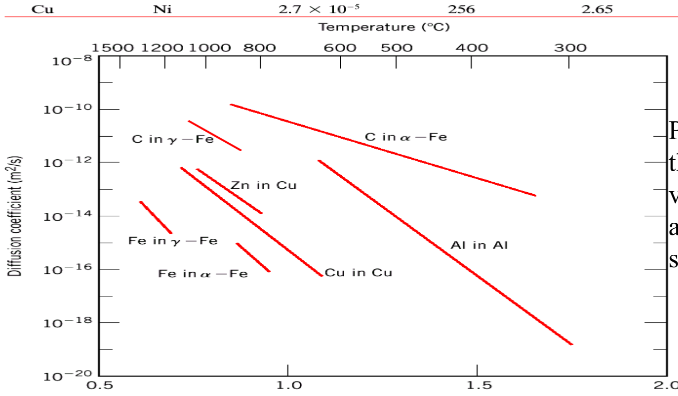
Determine activation energy, Q_d:

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

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

Diffusion Properties for Several Materials

Diffusing Species	*Host Metal*	$D_0 (m^2/s)$	*Activation Energy Q_d* *kJ/mol*	*eV/atom*	*Calculated Values* *T(°C)*	*D(m²/s)*
Fe	α-Fe (BCC)	2.8×10^{-4}	251	2.60	500 900	3.0×10^{-21} 1.8×10^{-15}
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94	900 1100	1.1×10^{-17} 7.8×10^{-16}
C	α-Fe	6.2×10^{-7}	80	0.83	500 900	2.4×10^{-12} 1.7×10^{-10}
C	γ-Fe	2.3×10^{-5}	148	1.53	900 1100	5.9×10^{-12} 5.3×10^{-11}
Cu	Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-5}	189	1.96	500	4.0×10^{-18}
Al	Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Cu	Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Mg	Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-13}
Cu	Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}



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