

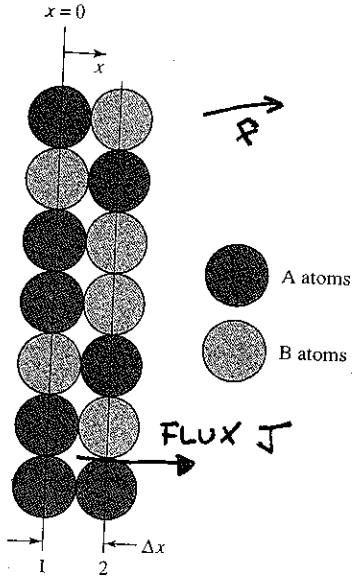
ASSIGNMENT!

STUDY ALL 4.4

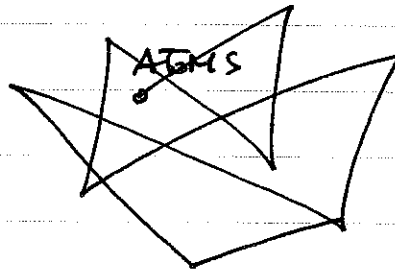
DIFFUSION

Living things MOVE \Rightarrow

ATOMS ARE VERY ~~BIG~~ SMALL THINGS, THEREFORE THEY MOVE WITH TEMPERATURE



Temperature > 0



RANDOM WALKS
JUMP AROUND
(DRUNK MAN)
EXAMPLE

$T \uparrow \Rightarrow$ MORE JUMPS

GAS $>$ CONSTANT JUMPS (PRESSURE)

LIQUIDS $>$ FREQUENT JUMPS

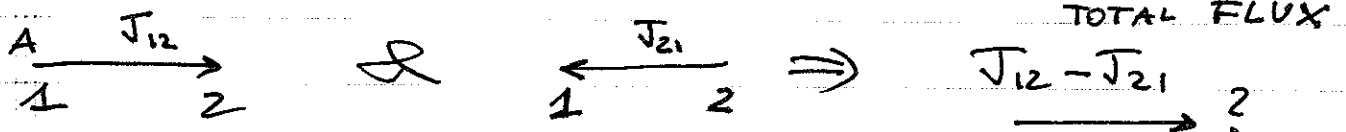
SOLIDS $=$ OCCASIONAL JUMPS

SOLID DIFFUSION

MODELING LIKE ATOMS BETWEEN TWO PLANES

- PICK 2 LAYERS AND THINK A IS SOLUTE IN AN ENVIRONMENT OF B

\Rightarrow DEFINE $C_A =$ CONCENTRATION



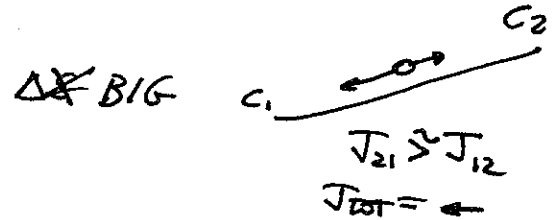
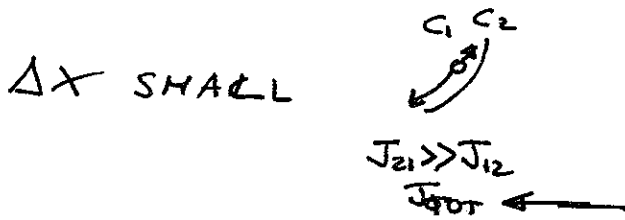
IF $C_2 > C_1 \Rightarrow J_{21} > J_{12}$ ←
IF $C_2 < C_1 \Rightarrow J_{21} < J_{12}$ →

DF1 $J_{TOTAL} \propto -(C_2 - C_1) = -\Delta C$

ASSUMPTION

2)

WHAT ABOUT Δx ?
 FURTHER THEY ARE AND LESS LIKELY
 THEY JUMP! WHY?



$\Rightarrow J_{TOTAL} \propto \frac{1}{\Delta x}$

ASSUMPTION

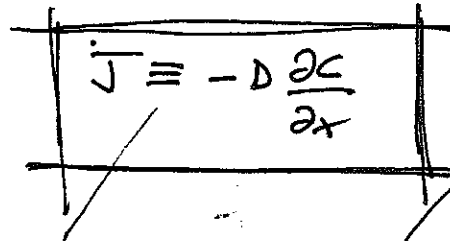
3) ~~ATOMS~~ TRY TO JUMP AT A FREQUENCY,
 THIS FREQUENCY DEPENDS ON TEMPERATURE

\Rightarrow

FICK'S LAW

$\bar{J} = D \left(-\frac{\Delta C}{\Delta x} \right)$

$J = \frac{\# \text{ particles crossing}}{\text{UNIT AREA} \times \text{SECOND}}$



$J = [m^{-2} s^{-1}]$
 $C = [1/m^3]$
 $x = [m]$

$D = \left[\frac{m^2}{s} \right]$

$C = \left[\frac{\text{FRACTION OF PARTICLES}}{\text{TOTAL NUMBER} \Rightarrow \frac{1}{(\text{VOLUME PART})^3}} \right]$
 $\Rightarrow C = \left[\frac{1}{m^3} \right]$

IDENTICAL TO HEAT
 FLUX \Rightarrow FLUX
 OF HEAT

$J_q = K \frac{T_{HOT} - T_{COLD}}{\Delta x}$
 $= -k \frac{\partial T}{\partial x} !!$

IS SAME

TEMPERATURE DEPENDENCE ?

W D !!

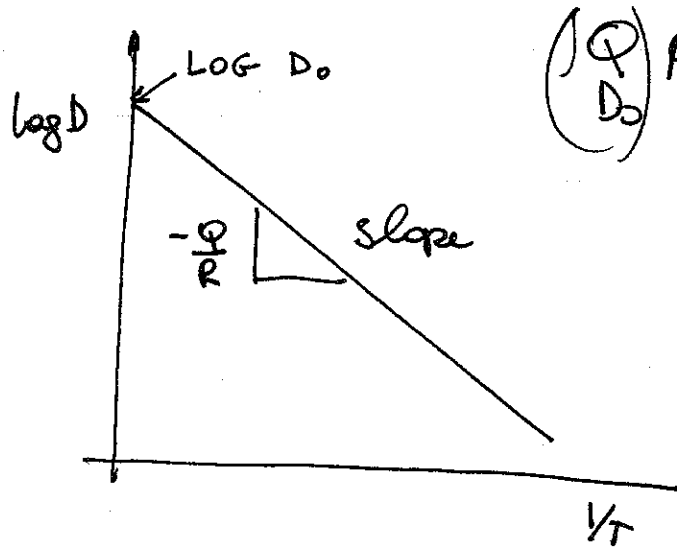
$$D(T) = D_0 \exp\left(\frac{-Q}{RT}\right)$$

kJ/MOL
ARRHENIUS

$$= D_0 \exp\left(\frac{-Q}{kT}\right)$$

JOULES

⇒ log D plot



(Q / D₀) NEED TO KNOW where do they COME FROM

BOOK IS MISLEADING

IF SOLID HOMOGENEOUS

$$\Delta C = 0 \Rightarrow \frac{\partial C}{\partial x} = 0$$

$$\Rightarrow J_{TOT} = 0 \quad \underline{\underline{CORRECT}}$$

$$BUT J_{TOT} = J_{R2} - J_{L1} = 0$$

$$J_{12} \longrightarrow = J_{21} \longleftarrow$$

Remember $J > 0$ is in same DIRECTION of \vec{x}

DF3

IF $T > 0$

YOU ALWAYS HAVE STUFF MOVING !!

BUT IF $\frac{\partial C}{\partial x} = 0$ (HOMOGENEOUS)

THEN SAME AMOUNT GOES RIGHT & LEFT

⇒ OVERALL = 0

ULTRA-MEGA-IMPORTANT

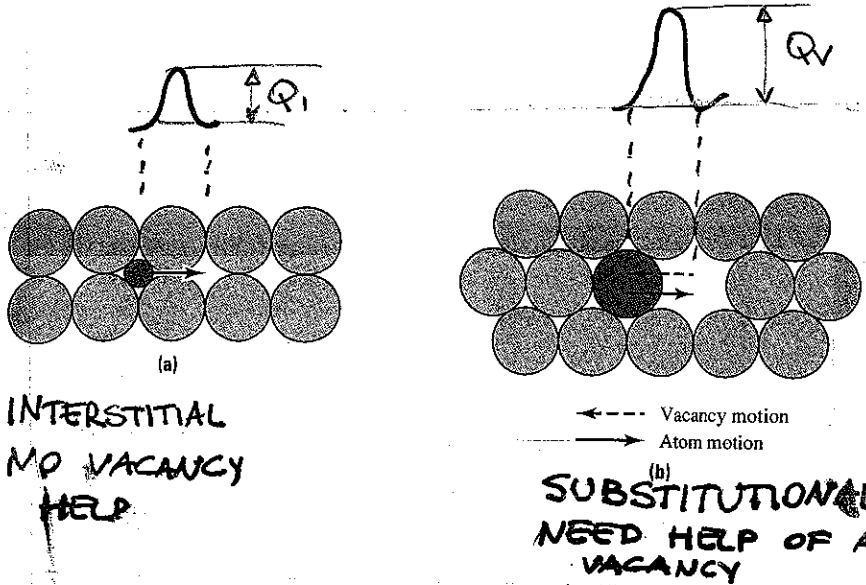
MECHANISM OF DIFFUSION

IMPURITIES

IN COVALENT AND METALLIC CRYSTALS

EXAMPLE EXTRA CARBON IN STEEL,

IMPURITY DIFFUSION!



IN SOLIDS WITH EXTRA INTERSTITIAL
 ↓
 SPACE ALWAYS AVAILABLE

INTERSTITIAL NO VACANCY HELP

SUBSTITUTIONAL NEED HELP OF A VACANCY

IN SOLID SOLUTIONS WITH DEFECTS THE DARK ATOM NEEDS HELP OF A VACANCY ⇒ PROP DEPENDS ON CONCENTR. OF VACANCIES

USUALLY ACTIV. ENERGIES

$$Q_V > Q_I$$

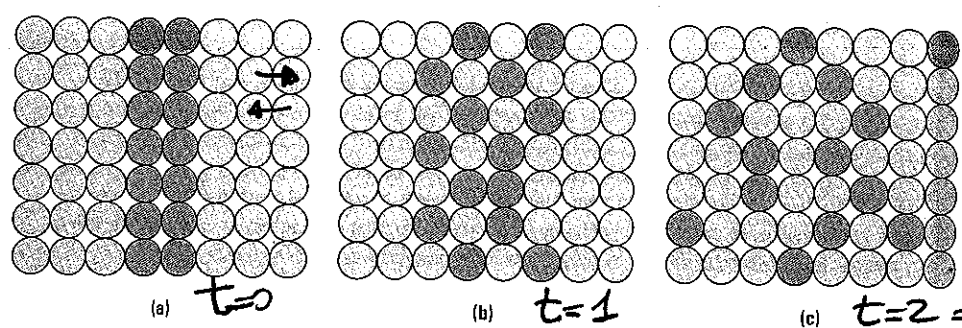
↑ NEED ENERGY TO FORM VACANCY TOO!!

$$\Rightarrow D(C)!!$$

WHAT ABOUT WITHOUT IMPURITIES

IN PURE SYSTEMS ATOMS DIFFUSE TOO!

IT'S SELF DIFFUSION



TRACER

⇒ MIX

FIGURE 4.4-5 Diffusion of radioactive isotopes in a matrix of the same atomic species. Increasing time is indicated in (a), (b), and (c). With time the radioactive species diffuse into the surrounding material. By measuring the concentration profiles at different times, the tracer diffusion constant can be determined.

DF4

SINCE ATOMS ARE IDENTICAL YOU CANNOT RECOGNIZE ⇒ NEED FOR COLOR!! ⇒ TAKE ISOTOPE

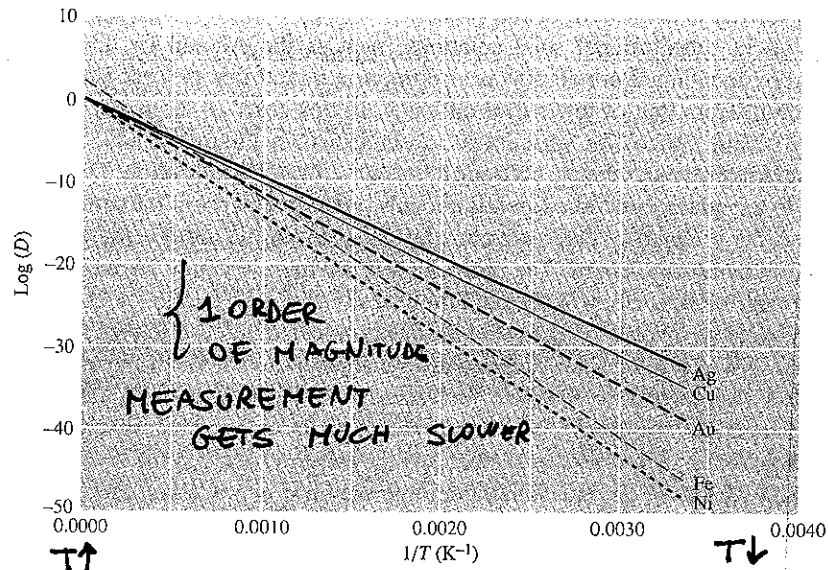


FIGURE 4.4-6 Self-diffusion coefficients for selected metals. The data were extrapolated to "infinite" temperature to demonstrate D_0 . Data obtained from several sources.

TABLE 4.4-1 Diffusion coefficients for selected systems.

Material	D_0 (m ² /s)	Q (kJ/mol)
Self-diffusion coefficients		
Ni	1.30×10^{-4}	279
Cu	2.00×10^{-5}	197
Ag	4.00×10^{-5}	184
Au	9.10×10^{-6}	174
Fe	1.18×10^{-2}	281
Si	1.80×10^{-1}	460
PE in melt	1.20×10^{-11}	28
Impurity diffusion coefficients		
Cu in Ag	1.20×10^{-4}	193
Cu in Al	1.50×10^{-3}	126
Zn in Ag	5.40×10^{-5}	174
Zn in Cu	3.40×10^{-5}	191
Ni in Cu	2.70×10^{-4}	236
Ni in Fe	7.70×10^{-5}	280
C in BCC Fe	2.00×10^{-6}	84
C in FCC Fe	2.00×10^{-5}	142
N in Fe	3.00×10^{-7}	76
Al in Al ₂ O ₃	2.3×10^{-3}	477
O in Al ₂ O ₃	1.9×10^{-1}	636
Mg in MgO	2.49×10^{-5}	330
O in MgO	4.3×10^{-2}	344
Ni in MgO	1.8×10^{-3}	202
O in SiO ₂	2.7×10^{-5}	111
CO ₂ in polyester (PET)	6.0×10^{-15}	51
CO ₂ in PE	2.0×10^{-4}	38
CO ₂ in PVC	4.2×10^{-2}	64
O ₂ in PET	5.2×10^{-5}	47
O ₂ in PE	6.2×10^{-4}	41
O ₂ in PVC	4.1×10^{-3}	54

DFS

EXAMPLE 4.4-4

Explain each of these observations:

- a. The activation energy for the diffusion of H in FCC iron is less than that for self-diffusion in FCC iron.
- b. The activation energy for the diffusion of H in BCC iron is less than that for the diffusion of H in FCC iron.

a) H SMALL ! FE BIG

b) BCC OPEN , FCC IS CLOSED PACKED

MECHANISM IN IONICS

YOU HAVE BOTH IONS JUMPING AROUND !



IONS \Rightarrow COULOMB BONDED , NO FREE CHARGE

\Rightarrow ELECTRICAL CONDUCTIVITY IS ALL GIVEN

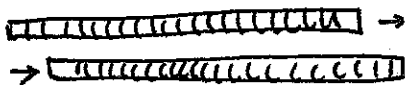
BY IONIC DIFFUSION

\Rightarrow SMALL CONDUCTIVITY, BUT I CAN GET DIFFUSION MEASURING CONDUCTIVITY !

MECHANISM IN POLYMERS

POLYMERS \Rightarrow LIKE SPAGHETTI (MOVING WORMS) ENTANGLED

COMPLETELY DIFFERENT MECHANISM



ALL MUST MOVE

$\Rightarrow D = D_0 e^{-Q/RT}$
 $\hookrightarrow D_0 \propto \frac{1}{N^2}$

DFG

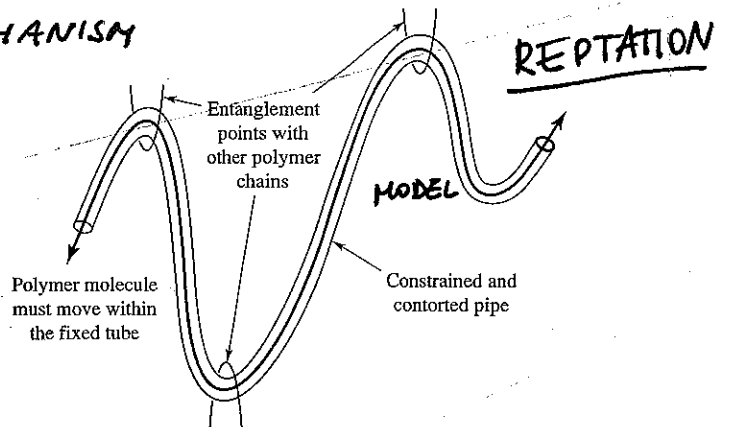
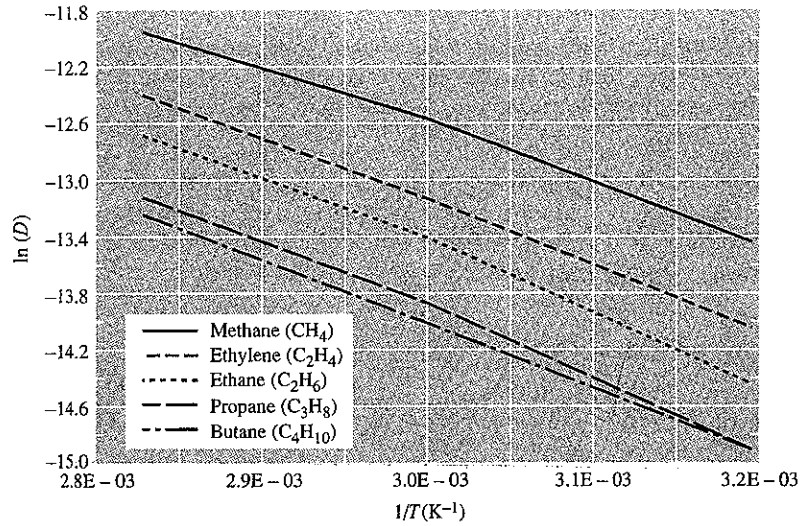


FIGURE 4.4-8

Diffusion coefficients of various organic molecules in natural rubber as a function of temperature. Note that at any given temperature, the smaller species diffuse more rapidly than the larger species.



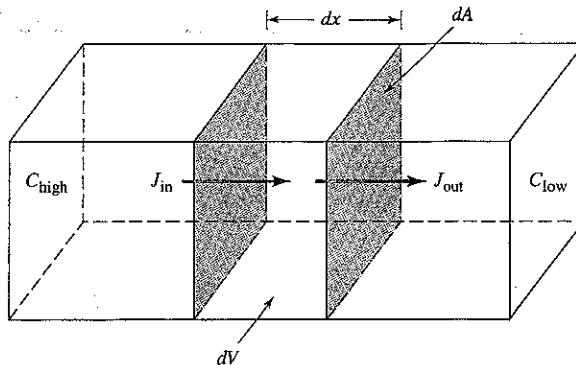
BUT VERY FAST FOR IMPURITIES !

NEED TO TAYLOR PROPER LENGTH WHERE THE FIRST GOES THROUGH & THE SECOND DOES NOT!

NEED TO SEPARATE TWO ORGANIC SPECIES?

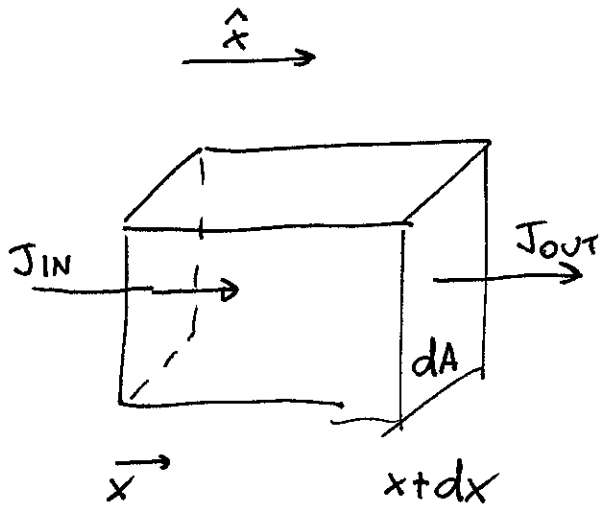
WHAT ABOUT TIME EVOLUTION ?

$J = -D \frac{\partial C}{\partial x}$, but $J = \text{STUFF per unit second} \Rightarrow \bar{J}$ changes $C \Rightarrow \frac{\partial C}{\partial t} ??$



TAKE THE BOX!

DF 7



IF $J_{OUT} \neq J_{IN}$
SOMETHING
CHANGES INSIDE!!

PARTICLES DO NOT
GET DESTROYED \Rightarrow CONC
CHANGES

$$J_{OUT}(x+dx) \approx J(x+dx) = J(x) + \frac{\partial J}{\partial x} dx \quad \text{TAYLOR}$$

$$J_{IN}(x) = J(x)$$

$J = \text{FLUX} \Rightarrow$ # PARTICLES FLOWING PER UNIT AREA PER UNIT SECOND

$\Rightarrow J_{IN} dA \Rightarrow$ # PART getting IN / UNIT SECOND

$J_{OUT} dA \Rightarrow$ # PART getting OUT / UNIT SECOND

~~$\Rightarrow (J_{OUT} - J_{IN}) dA =$ # PART DISAPPEARING INSIDE / UNIT SECONDS~~

$(J_{IN} - J_{OUT}) dA =$ # PART INCREASING PER UNIT SECOND!!

$$\Rightarrow (J(x) - J(x) - \frac{\partial J}{\partial x} dx) dA = \frac{d}{dt} (c dA dx) = \frac{\partial c}{\partial t} dA dx \Delta t$$

VOLUME DOES NOT
CHANGE IN TIME

\Rightarrow

$$\Rightarrow \frac{d(c dA dx)}{dt} = dA dx \frac{dc}{dt}$$

$$\Rightarrow \boxed{-\frac{\partial J}{\partial x} = \frac{dc}{dt} \quad !!}$$

~~SECONDS
BY SECONDS~~

CONSERVATION
OF PARTICLES

DF 8

BUT

$$J = -D \frac{\partial c}{\partial x}$$

$$\Rightarrow -\frac{\partial J}{\partial x} = D \frac{\partial^2 c}{\partial x^2} = \frac{dc}{dt}$$

$$\frac{dc}{dt} = D \frac{\partial^2 c}{\partial x^2}$$

CONST D(T) NOT D(C)!!

FOURIER LAW!!

HEAT

$$\frac{dT}{dt} = D_{TH} \frac{\partial^2 T}{\partial x^2}$$

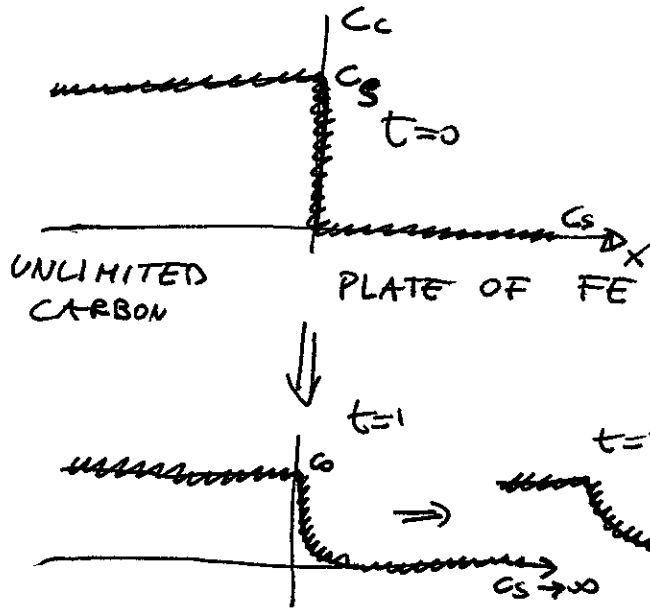
Thermal diffusivity

DIFFERENTIAL EQUATION

NEED BOUNDARY CONDITIONS

EXAMPLE C & FE

INFINITELY FEEDING SURFACE



$$C_s = C_{\text{surface}}$$

$$C_0 = C_{\text{BULK FE BEFORE } t=0}$$

$$C_s > C_0 \Rightarrow$$

Carbon enters

$$C(x,t) = C_0 + [C_s - C_0] \left[1 - \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \right]$$

erfc function!

$$x_{\text{eff}} = 2\sqrt{Dt}$$

CARBURIZATION OF STEEL

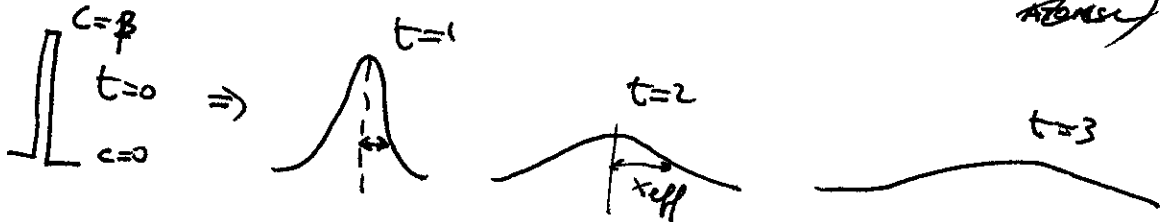
TO MAKE IT WEAR RESISTANT!

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy$$

is space/time relation 1/10 to get ~~erfc~~ CONCENTRATION!

DF9

DEPLETING SOURCE ~~(CONCENTRATION DECREASES OVER TIME)~~



$$C(x,t) = \left(\frac{\beta}{2\sqrt{\pi Dt}} \right) \exp\left(-\frac{x^2}{4Dt}\right)$$

x_{eff} is where ~~slope~~ SHAPE IS $\approx 1/3$ OF ORIGINAL ^{e^{-1}}

$$x_{eff} \approx 2\sqrt{Dt}$$

EFFECTIVE PENETRATION DISTANCE

Place x_{eff} where ~~slope~~ where $C(x_{eff}, t) = \frac{C_0 + C_s}{2}$

$$\Rightarrow \text{FOR PLATE} \Rightarrow \frac{1}{2} = \text{erf}\left(\frac{x_{eff}}{2\sqrt{Dt}}\right) \quad \text{erf}(0.5) \approx 0.5$$

$$\Rightarrow x_{eff} \approx \sqrt{Dt}!$$

$$x_{eff} \approx 2\sqrt{Dt} \quad \text{for cylinders}$$

ERF(z)

$$\text{erf}(z) \equiv \frac{2}{\sqrt{\pi}} \int_0^z e^{-x^2} dx$$

$$\text{erf}(-z) = -\text{erf}(z)$$

$$\lim_{z \rightarrow \infty} \text{erf}(z) \rightarrow 1$$

$$\text{erf}(z) \sim \frac{2}{\sqrt{\pi}} z \quad \text{for } z \approx 0$$

$$\text{erf}\left(\frac{1}{2}\right) \sim \frac{1}{2}$$