Physical Chemistry (Chem 132A)

Lecture 19
Wednesday, November 17

Homework #7 is due November 18

Midterm 2

1. Second Midterm exam: Wednesday, November 22
   second midterm will cover Chapters 1—6, 19

   • there will be a seating chart
   • same procedures as midterm 1
     1 page notes allowed
     bring calculator

Diffusion and Transport

Molecules move randomly in straight paths between collisions.

FLUX

Flux (J) is the quantity of a property passing through a given area in a given time interval divided by the area and the time duration.

Flux of matter---"diffusion"
e.g. molecules/m^{2}sec

Flux doesn't have to be matter---e.g. could be energy, etc.

Fick's Law

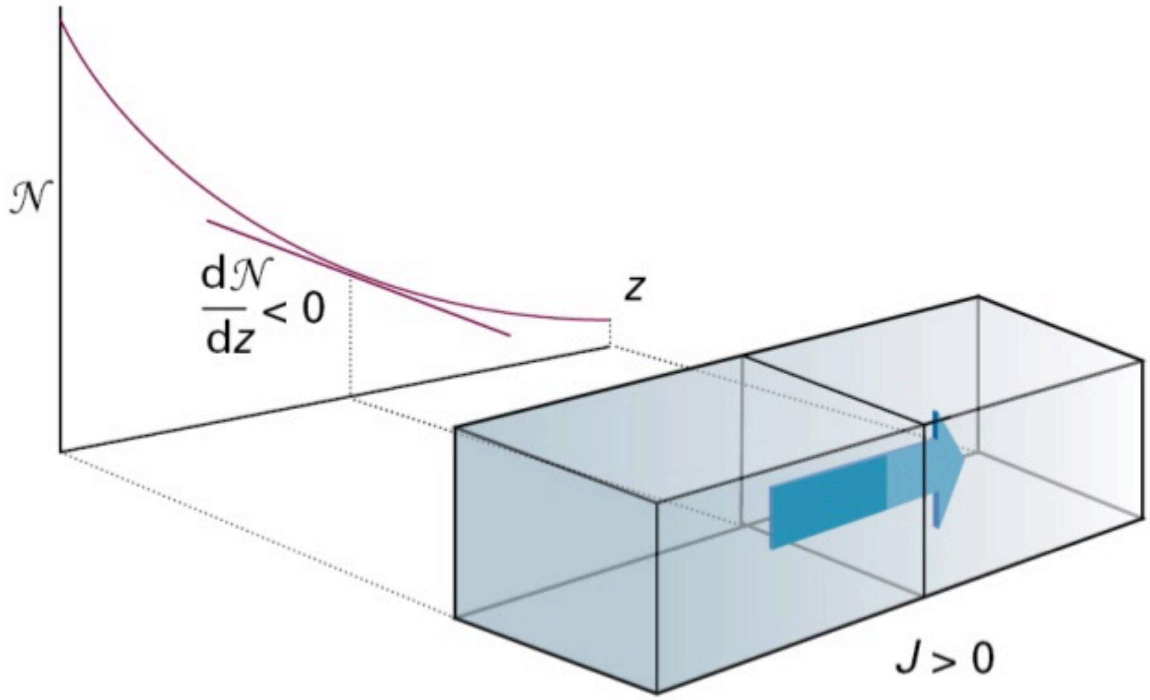
Empirically the flux is often related to the spatial first derivative of some related property.

$$J(matter) \approx \frac{dN}{dz}$$

Fick's first law

Concentration Gradient Leads to Diffusion

NET FLUX



Direction of Flux??

$$J(matter) = -D\frac{dN}{dz}$$

D = Diffusion Coeficient

UNITS?

$$J(matter) = -D\frac{dN}{dz}$$

$$\frac{dN}{dz}$$

Has units number•m^{-3}m^{-1}= number •m^{-4}

J should have units number•m^{-2}sec^{-1}

This means the units of D are: m^{2}sec^{-1}

Similar Equations for Other Properties

Thermal Energy Flux

$$J(thermalenergy) = -\kappa \frac{dT}{dz}$$

κ **Is the coeficient of thermal conductivity**

κ **Units are: $JK^{-1}m^{-1}s^{-1}$**
Js^{-1} = 1 Watt

κ **Units are often: $WK^{-1}m^{-1}$**

Since units of dT/dz are Km^{-1} the units of Thermal energy flux are: $Wm^{-2}s^{-1}$

Variation of thermal conductivity for different gases

Table 19A.1* Transport properties of gases at 1 atm

	$\kappa/(\mathrm{mW\ K^{-1}\ m^{-1}})$	$\eta/\mu\mathrm{P}^{\ddagger}$	
	273 K	273 K	293 K
Ar	16.3	210	223
CO_2	14.5	136	147
He	144.2	187	196
N_2	24.0	166	176

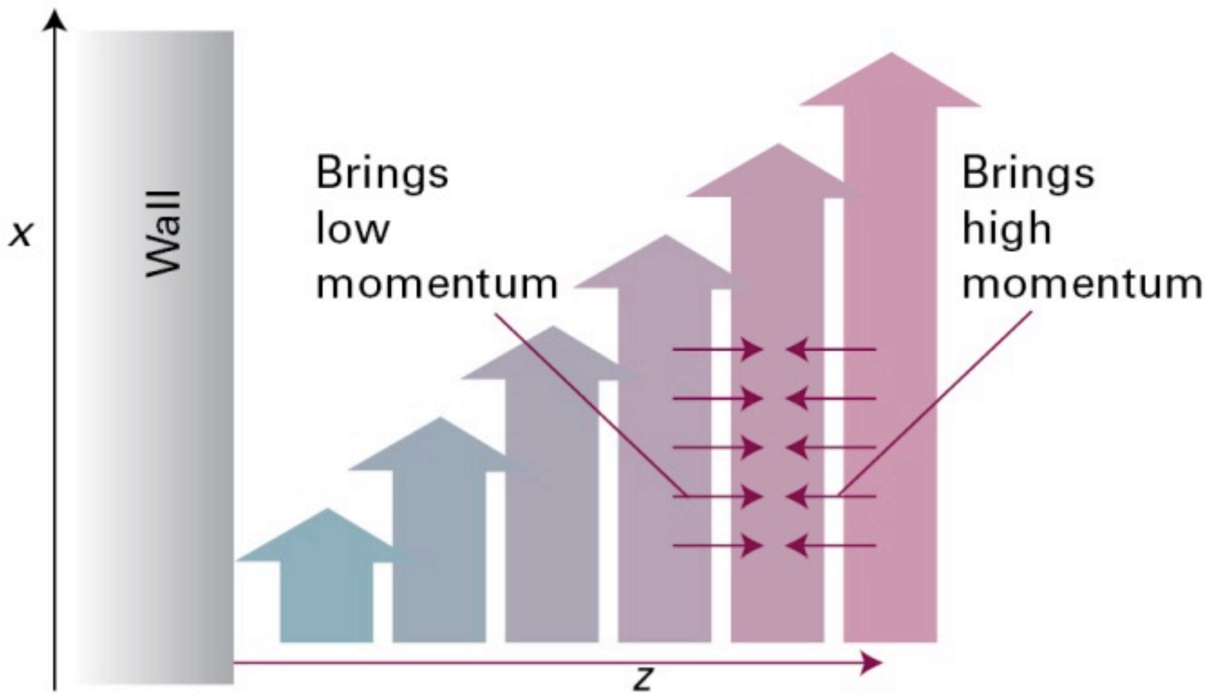
* More values are given in the *Resource section*.

‡ $1\,\mu\mathrm{P} = 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$.

$$\kappa \approx v_{\mathrm{mean}}$$

$$v_{mean} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

FLUX OF MOMENTUM AND VISCOSITY



$$J(xmomentum) = -\eta \frac{dv_x}{dz}$$

η = coeficient of viscosity

Expressions for Transport Coefficients

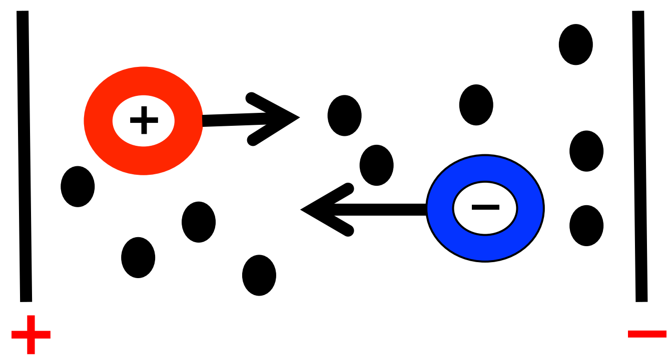
$D = (1/3)\lambda v_{mean}$ **Diffusion coefficient**

$\kappa = (1/3)\nu v_{mean}\ \lambda N k$ **Thermal conductivity**

$\eta = (1/3) v_{mean}\ \lambda m N$ **Viscosity**

These expressions provide reasonable approximations for the transport coefficients.

Ion Mobilities



Text: Chapter 19B

$S = uE$
E = applied field
u is the mobility

Table 19B.2* Ionic mobilities in water at 298 K, $u/(10^{-8}\,m^2\,s^{-1}\,V^{-1})$

	$u/(10^{-8}\,m^2\,s^{-1}\,V^{-1})$		$u/(10^{-8}\,m^2\,s^{-1}\,V^{-1})$
H^+	36.23	OH^-	20.64
Na^+	5.19	Cl^-	7.91
K^+	7.62	Br^-	8.09
Zn^{2+}	5.47	SO_4^{2-}	8.29

Diffusion

Driving force for diffusion is a concentration gradient

The concentration gradient causes a spatial dependence to the chemical potential (μ)

Define a "Force"

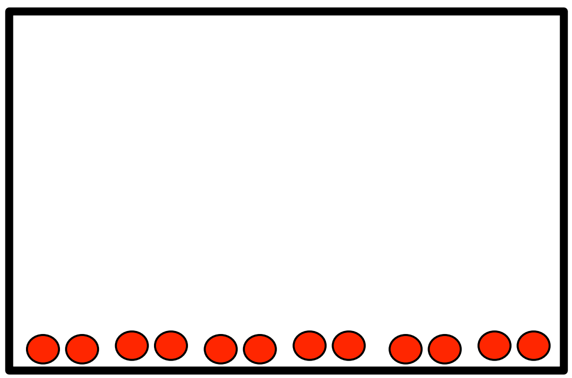
$$F = -\left(\frac{\partial \mu}{\partial x}\right)_{T,p}$$

$$F = -RT\left(\frac{\partial \ln a}{\partial x}\right)_{T,p} = -RT\left(\frac{\partial \ln c}{\partial x}\right)_{T,p} = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{T,p}$$

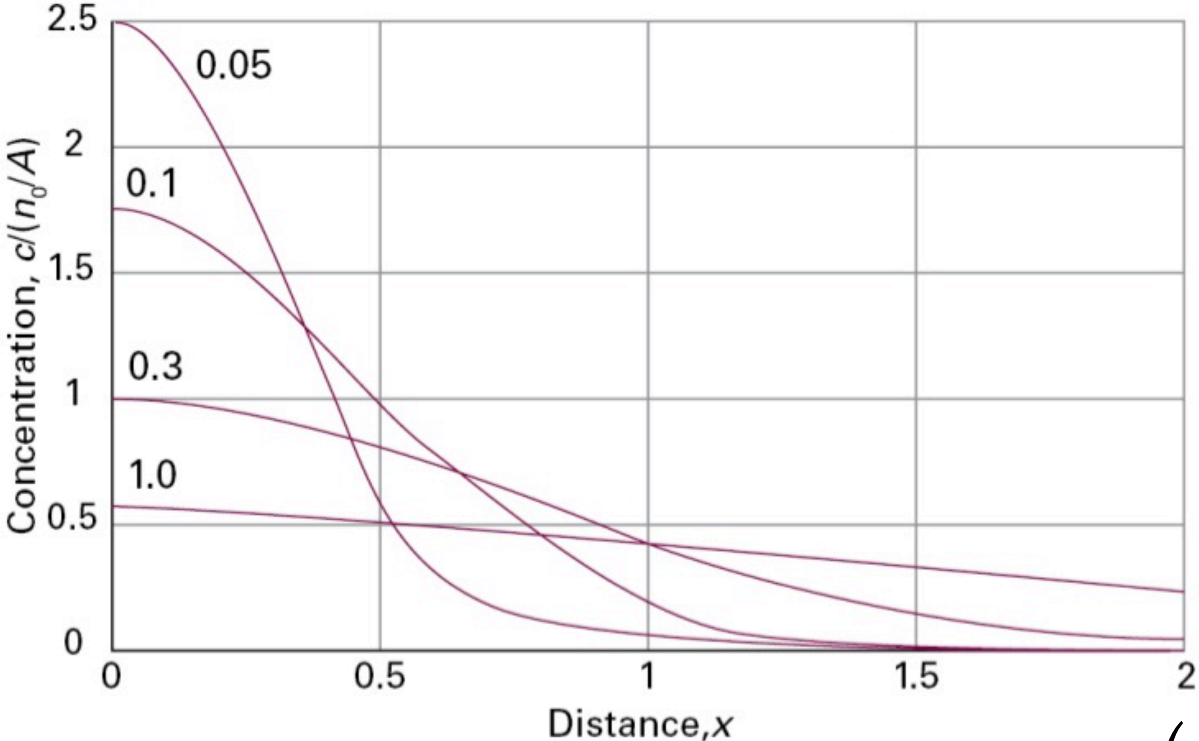
Diffusion Equation

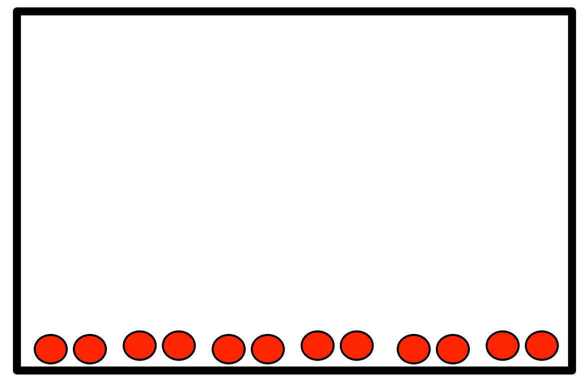
$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial^2 x}$$

Simple diffusion in one dimension with no convection



$$c(x,t) = \frac{n_0}{A(\pi Dt)^{1/2}} e^{\frac{-x^2}{4Dt}}$$





$$c\left(x,t\right)=\frac{n_0}{A\left(\pi Dt\right)^{1/2}}e^{\frac{-x^2}{4Dt}}$$

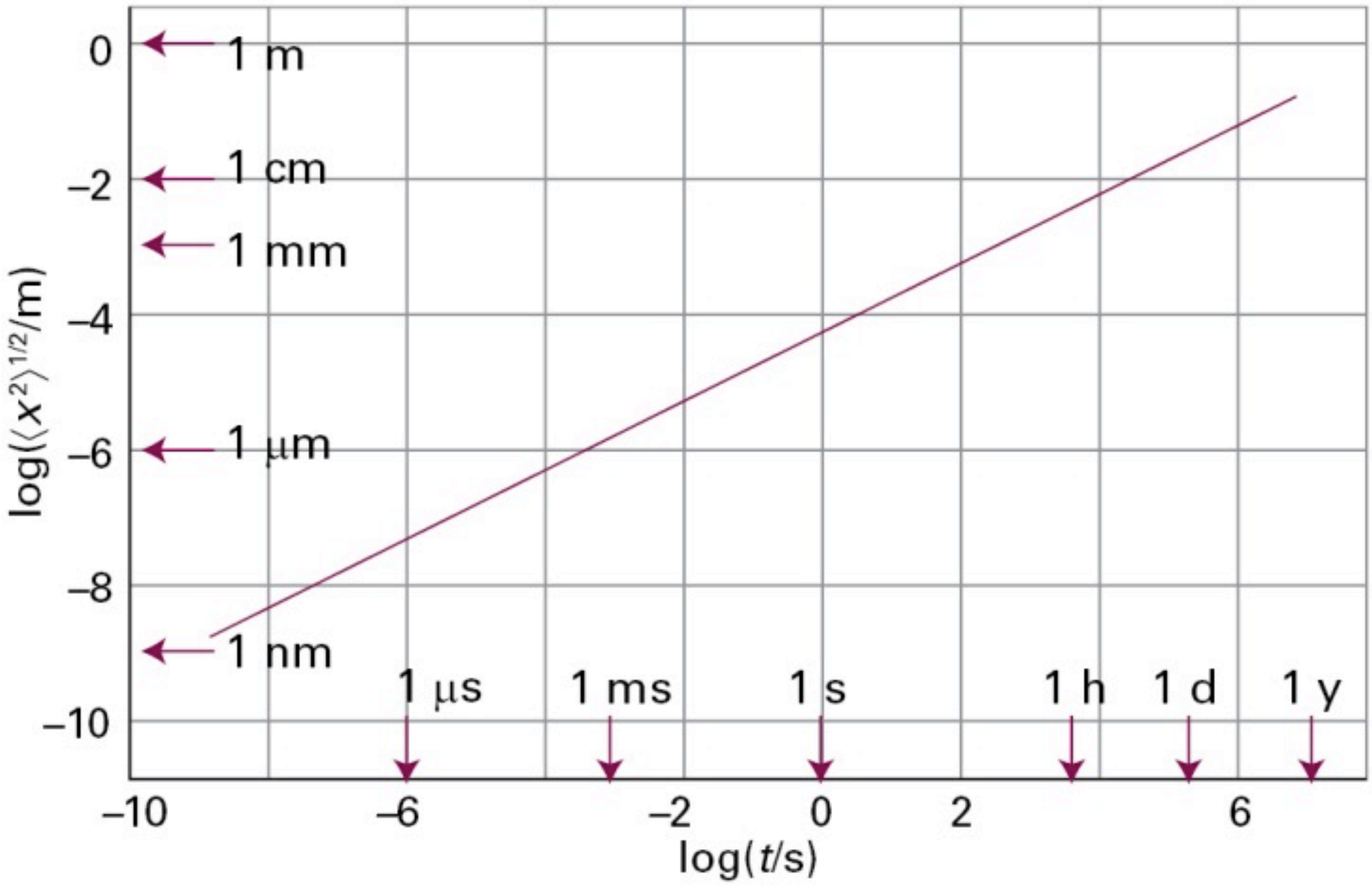


Figure 19C.5 The root-mean-square distance covered by particles with $D = 5 \times 10^{-10}$ m^2 s^{-1}. Note the great slowness of diffusion.

THE END

SEE YOU MONDAY