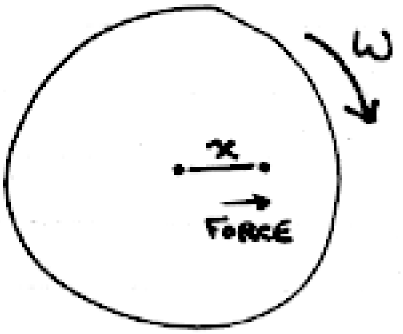
11/2/01 ①

$$U_t : \text{terminal velocity} = \frac{m(1-\bar{v}_2\rho)}{f}\, g \qquad \text{GRAVITY}$$

$$= \frac{m(1-\bar{v}_2\rho)}{f}\, \omega^2 x \qquad \text{CENTRIFUGE}$$

ω = angular velocity
(radians/sec)



Define:

$$S = \frac{U_t}{\omega^2 x} = \frac{m(1-\bar{v}_2\rho)}{f} \qquad \text{(Svedberg)}$$

$\uparrow$ $\frac{\text{velocity}}{\text{acceleration}}$

UNITS = sec

$\nwarrow$ Property of a specific particle in a specific medium!

Properties in S

Particle: m = mass
$\bar{v}_2$ = partial specific volume

Medium: ρ = density of medium

Both: $f = 6\pi \overset{\text{medium}}{\eta}\, r \leftarrow \text{particle}$

$$S = \frac{\overset{\substack{\text{per molecule}\\ \downarrow}}{m}(1-\bar{v}_2\rho)}{\underset{\substack{\uparrow\\ \text{? per molecule}}}{kT/D}} = \frac{\overset{\substack{\text{per mole}\\ \downarrow}}{M}(1-\bar{v}_2\rho)}{\underset{\substack{\uparrow\\ \text{per mole}}}{RT}}\,D$$

$$M = \frac{R\overset{\substack{\text{measure}\\ \downarrow}}{T}\,\overset{\swarrow\,\text{measure}}{s}}{\underset{\substack{\nearrow\\ \text{measure}}}{D}\,(1-\underset{\substack{\nearrow\\ \text{measure}}}{\bar{v}_2}\underset{\substack{\nwarrow\\ \text{measure}}}{\rho})} = \text{Molecular Weight!}$$

<u>Practical Aside:</u>

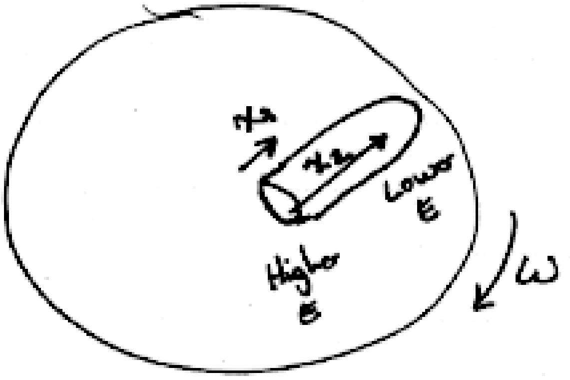
"Standard" s ⇒ $S_{20,w}$ ↙ "standard" Conditions

$$\underset{\substack{\nearrow\ \ \uparrow\\ 20^\circ\text{C}\ \ \text{water}}}{S_{20,w}} = \left[\left(\frac{\eta}{\eta_{20,w}}\right)\frac{(1-\bar{v}_2\rho)_{20,w}}{(1-\bar{v}_2\rho)}\right]\underset{\substack{\uparrow\\ \text{other temp}\\ \text{other medium}}}{s}$$

Sedimentation Equilibrium

$$E_1 = \overbrace{M(1-\bar{v}_2\rho)}^{m}\,\overset{\cdot\, g\cdot h}{g\,x_1}$$

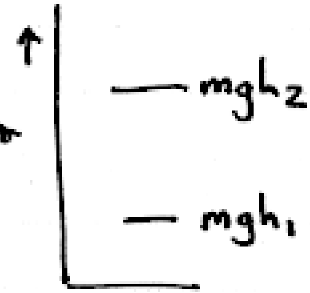
per <u>mole</u> grams per <u>mole</u>



Boltzmann says

AT EQU<u>ILIBR</u>IUM

Remember Gravity



$$\frac{C_j}{C_i} = e^{-(E_j-E_i)/RT}$$

$$\frac{C_2}{C_1} = e^{-\frac{M(1-\bar{v}_2\rho)(x_2-x_1)g}{RT}}$$

<u>GRAVITY</u>

$$= \cancel{e^{-\frac{M(1-\bar{v}_2\rho)(x_2\omega^2 x_2 - x_1\omega^2 x_1)}{RT}}}$$

(look at def of x)

In a centrifuge: $E_1 = -\frac{M(1-\bar{v}_2\rho)(\omega^2 x_1)x_1}{2}$

$$\therefore \quad \frac{C_2}{C_1} = e^{-\left[-\frac{M(1-\bar{v}_2\rho)\omega^2(x_2^2-x_1^2)}{2RT}\right]}$$

$$\ln\frac{C_2}{C_1} = \frac{M(1-\bar{v}_2\rho)\,\omega^2(x_2^2-x_1^2)}{2RT}$$

Plot $\ln c$ vs x^2 gives
straight line
with slope $= \dfrac{M(1-\bar{v}_2\rho)\omega^2}{2RT}$

$$\therefore \quad M = \frac{2RT}{\text{[redacted]}(1-\bar{v}_2\rho)\,\omega^2}\,(\text{slope})$$

Good way for accurately determining molecular weight in the native state.

Very often used to assess dimerization, etc.

Chapter 7 – Rates of Chemical Reactions

v = rate of reaction $= \dfrac{dc}{dt}$ (also velocity)

Rate Law:

Express $v = f(c_i)$ function of conc's

Reaction/Kinetic Mechanism

Allows one to discern the rate law

(But we usually go in reverse!)

Kinetic Order

$$v = k[A]^{1}$$

$$v = k[A]^{2}$$

$$v = k[A]^{1}[B]^{2}$$

Kinetic Order

Simplifications

If a rate law is: $v = k[A][B]$

but $[A]$ doesn't change signif over course of reaction (e.g. it's in large excess)

THEN can write $v = k'[B]$

$$(k' = k[A])$$

ZERO-ORDER RXN

$$\frac{dC}{dt} = k$$ (independent of all components)

Approach $dc = k_0 dt$ k_0 units ⇒ $M s^{-1}$

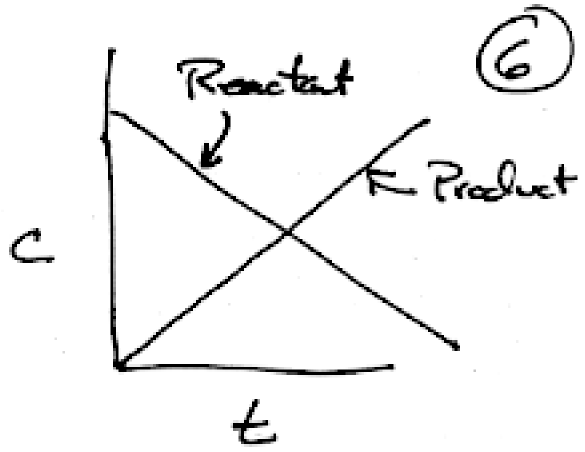
$$\int_{c_1}^{c_2} dc = k_0 \int_{t_1}^{t_2} dt \Rightarrow c_2 - c_1 = k(t_2 - t_1)$$

ADH in liver

⑥

Zero ORDER (CONT.)

$$\frac{dP}{dt} = -\frac{dR}{dt} = k_0$$



FIRST ORDER (VERY COMMON)

$$\frac{dc}{dt} = k_1 C$$

k_1 units ⇒ s^{-1}

~~$\frac{dC}{C} = k_1 dt$~~

e.g. $A \rightarrow B$

$$\frac{dB}{dt} = -\frac{dA}{dt} = k_1 A$$

$$-\frac{dA}{A} = k_1 dt$$

$$-\int \frac{dA}{A} = k_1 \int dt$$

$$-(\ln A_2 - \ln A_1) = k_1 (t_2 - t_1)$$

$$\boxed{\begin{array}{l} A_1 = A_0 \\ t_1 = 0 \end{array}}$$

$$\ln \frac{A_2}{A_1} = -k_1 (t_2 - t_1)$$

$$\frac{A_2}{A_1} = e^{-k_1 (t_2 - t_1)}$$

$$\boxed{A = A_0 e^{-k_1 t}}$$

Classic