[Class Notes] 2/20

Exam covers: ch 14, ch 15, lab
Thursday 2/

CHEMICAL KINETICS III

integrated rate law

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-d[A]}{dt} = k[A]$$

step 1. Rearrange $\frac{d[A]}{[A]} = -k\,dt$

step 2A. integrate $\int_{A_0}^{A_t} \frac{dA}{[A]} = \int_0^t -k\,dt$

step 2B. solve integral: $\ln[A]_t - \ln[A]_0 = -kt$

step 3. rearrange: $\ln[A]_t = -kt + \ln[A]_0$

$$y = mx + b$$

Alternate form $\ln\left[\frac{[A]_t}{[A]_0}\right] = -kt$

EX) $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ $k = 0.17/h$

$[A]_0 = 1.25 \times 10^{-3} M$

$[A]_t = 0.31 \times 10^{-3} M$

$$\ln(0.31 \times 10^{-3} M / 1.25 \times 10^{-3} M) = (0.17/h)t$$

$t = 8.2h$

Ex) Ce(IV) + Fe(II) ⇄ Fe(III) + Ce(III)

"clock reaction"

Second order differential rate law

- decomposition of nitrogen dioxide

$NO_2(g) \rightarrow NO(g) + \frac{1}{2} O_2(g)$

$$\text{rate} = K[NO_2]^2 = \frac{-\Delta[NO_2]}{\Delta t} = \frac{-d[NO_2]}{dt}$$

integrated rate law

$$\frac{1}{[NO_2]_t} = Kt + \frac{1}{[NO_2]_0}$$

→ plotting $1/[NO_2]_t$ vs time should yield a line with slope K and intercept $1/[NO_2]_0$

$$\frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}$$

Zero order differential rate law

- decomposition of nitrogen dioxide

$2N_2O(g) + \rightarrow 2N_2(g) + O_2(g)$

rate = K (constant) ☆ Pt catalyst

rate is constant over time (concentration / time)

$$\text{rate} = \frac{-\Delta[N_2O]}{\Delta t} = K$$

$[N_2O]_t = -Kt + [N_2O]_0$

→ plotting $[N_2O]$ vs time should yield a line w/ slope -K and intercept $[N_2O]_0$

summary of rate law

	zero order	first order	second order
rate law	rate = K	rate = K[A]	rate = K[A]^2
integrated rate law	$[A]_t = -Kt + [A]_0$	$\ln[A] = -Kt + \ln[A]_0$	$\frac{1}{[A]} = Kt + \frac{1}{[A]_0}$
plot that produces straight line	[A] vs. t	ln[A] vs. t	$\frac{1}{[A]}$ vs. t
relationship of rate constant to slope of straight line	slope = -K	slope = -K	slope = K

units of K

- ∅ order: rate = K

$\left(\frac{M}{s}\right) = \left(\frac{M}{s}\right)$ K units = $\left(\frac{M}{s}\right)$

-1[st] order: rate = K[A]

$\left(\frac{M}{s}\right) = K\ M$ K units = $\left(\frac{1}{s}\right)$

-2[nd] order: rate = K[A]^2

$\left(\frac{M}{s}\right) = K\,(M)^2$

$\left(\frac{M}{M^2 s}\right) = K$ K unit = $\left(\frac{1}{M s}\right)$