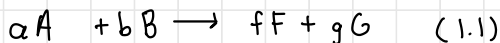


Chemical Kinetics I: Rate Laws

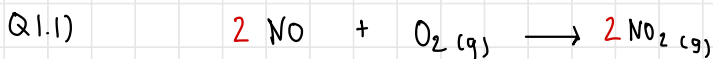
Suppose you have



The rate of rxn  $v(t)$  can be written as

$$v(t) = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{f} \frac{d[F]}{dt} = \frac{1}{g} \frac{d[G]}{dt}$$

Note the  $\ominus$  sign if reactant and  $\oplus$  sign if product



$$v(t) = -\frac{1}{2} \frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2} \frac{d[NO_2]}{dt}$$

Relationship b/w  $v(t)$  and concentrations is expressed thru a rate law:  $v(t) = k[NO]^2[O_2]$  for the rxn.

In general (looking at Eqn. 1.1):  $v(t) = k[A]^a[B]^b$

the units of  $k$  are required so that the rate is expressed in units of  $\frac{\text{mol}}{\text{L} \cdot \text{s}} = \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} = \frac{\text{M}}{\text{s}}$

book pref.

Q1.2)

Rate Law	Order	Units
$v = k$	0th	$\text{mol}/\text{dm}^3 \cdot \text{s}$
$v = k[A]$	1st	$1/\text{s}$
$v = k[A]^2$	2nd	$\frac{\text{dm}^3}{\text{mol} \cdot \text{s}} = \frac{1}{\text{M} \cdot \text{s}}$
$v = k[A][B]$	2nd	$\frac{\text{dm}^3}{\text{mol} \cdot \text{s}} = \frac{1}{\text{M} \cdot \text{s}}$
$v = k[A]^n$	n+th	$\text{M}^{-n+1} \cdot \frac{1}{\text{s}}$

$M = \text{molarity here so}$   
 $\frac{\text{mol}}{\text{L}} = \frac{\text{mol}}{\text{dm}^3}$

Suppose we have



and we wish to find  $[A](t)$ ? Well, start w/

$$v(t) = - \frac{d[A]}{dt} = k[A]$$

separate!

integrate!

$$\frac{d[A]}{[A]} = -k dt \longrightarrow \int_{A_0}^A \frac{d[A]}{[A]} = - \int_0^t k dt$$

$A_0$ :  $[A]$  when  $t=0$

always 0 to  $t$

$A$ :  $[A]$  when  $t=t$

$$\ln([A]) - \ln([A]_0) = -(kt - k(0))$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \longrightarrow \frac{[A]}{[A]_0} = e^{-kt} \longrightarrow [A] = [A]_0 e^{-kt}$$

Q1.3) Too lazy to write Q:

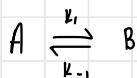
$$\text{Find } k: \ln \frac{[A]}{[A]_0} = -k(19.7 \text{ min}) \longrightarrow k = 1.39 \times 10^{-2} \text{ min}^{-1}$$

$$\frac{[A]}{[A]_0} = 0.76 \text{ since } 100\% \text{ conc. at } [A]_0 \text{ and } 76\% \text{ at } [A]$$

$$t_{85.5\%} = \frac{[A]}{[A]_0} = 0.145 \longrightarrow \ln(0.145) = -(1.39 \times 10^{-2} \text{ min}) t$$

$$t_{85.5\%} = 139 \text{ min}$$

Reversible Rxns:



$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \text{ if at equilibrium}$$

if we wish to see how  $[A]$  changes over time:

$$\frac{d[A]}{dt} = \underbrace{k_{-1}[B]}_{\substack{\text{rev. rxn} \\ \uparrow [A]}} - \underbrace{k_1[A]}_{\substack{\text{fwd. rxn} \\ \downarrow [A]}}$$

consequently:

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$$

Q1.4)

$$\frac{d[A]}{dt} = \underbrace{-k_1[A]}_{\substack{\text{both} \\ \ominus \text{ signs}}} - \underbrace{k_2[A]}_{\substack{\text{both} \\ \ominus \text{ signs}}} \longrightarrow \frac{d[A]}{[A]} = -(k_1 + k_2) dt$$

$$\longrightarrow \int_{A_0}^A \frac{d[A]}{[A]} = - \int_0^t (k_1 + k_2) dt \longrightarrow \ln\left(\frac{[A]}{[A]_0}\right) = -(k_1 + k_2)t$$

$$[A] = [A]_0 e^{-(k_1 + k_2)t}$$

$$\text{when } t = t_{1/2}, [A] = \frac{[A]_0}{2} \quad \text{so} \quad \ln\left(\frac{[A]}{[A]_0}\right) = -(k_1 + k_2)t_{1/2}$$

$$\ln\left(\frac{[A]_{0/2}}{[A]_0}\right) = -(k_1 + k_2)t_{1/2} \longrightarrow \frac{\ln(0.5)}{k_1 + k_2} = t_{1/2}$$

## Chemical Kinetics II: Rxn. Mech.

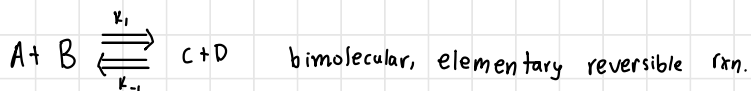
" $\Rightarrow$ " : elementary rxn.

molecularity  $\equiv$  # reactant molecules in rxn.

" $\longrightarrow$ " : complex rxn.

$A + B \Rightarrow C$  is a bimolecular elementary rxn.

### 27-2: Detailed Balance



$$\text{so } v_1 = k_1 [A][B] \quad ; \quad v_{-1} = k_{-1} [C][D]$$

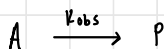
at equilibrium,  $v_1 = v_{-1}$  so  $k_1 [A]_{eq} [B]_{eq} = k_{-1} [C]_{eq} [D]_{eq}$

$$\text{and } K_c = \frac{k_1}{k_{-1}} = \frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}}$$

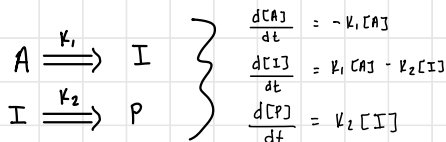
Principle of Detailed Balance:

Rate of fwd. & rev. process are equal for each step of rxn. mech at equilibrium for each elementary step

consider a general, complex rxn:



w/ two elementary rxns.



Steady-state approx. assumes  $\frac{d[I]}{dt} = 0$

$$\text{so } [I]_{ss} = \frac{k_1[A]}{k_2}$$

Q2.1) Example 27-5

Question hints you'll need  $\frac{d[O]}{dt}$  b/c of steady-state approx

$$\frac{d[O_3]}{dt} = -k_1[O_3][M] + k_1[O_2][O][M] - k_2[O][O_3]$$

$$\frac{d[O]}{dt} = k_1[O_3][M] - k_1[O_2][O][M] - k_2[O][O_3]$$

using s.s. approx we get

$$[O] = \frac{k_1[O_3][M]}{k_1[O_2][M] + k_2[O_3]} \longrightarrow \frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2[M]}{k_1[O_2][M] + k_2[O_3]}$$

Q2.2) 29-43

recall  $V(t) = -\frac{1}{2} \frac{d[A]}{dt}$

$$\frac{d[Br]}{dt} = -2k_1[Br]^2 + 2k_1[Br_2^*]$$

$$\text{and } \frac{d[Br_2^*]}{dt} = k_1[Br]^2 - k_1[Br_2^*] - k_2[Br_2^*][M]$$

$$\text{s.s. approx. : } [Br_2^*] = \frac{k_1[Br]^2}{k_1 + k_2[M]} \longrightarrow \frac{d[Br]}{dt} = -2k_1[Br]^2 + \frac{2k_1k_1[Br]^2}{k_1 + k_2[M]}$$

$$\frac{d[Br]}{dt} = \frac{-2k_1k_1[Br]^2 - 2k_1[Br]^2k_2[M] + 2k_1k_1[Br]^2}{k_1 + k_2[M]} = \boxed{-\frac{2k_1k_2[Br]^2[M]}{k_1 + k_2[M]}}$$

if  $v_2 \gg v_{-1}$ , then  $k_2 [\text{Br}_2^*] [\text{M}] \gg k_{-1} [\text{Br}_2^*]$  so  $k_2 [\text{M}] \gg k_{-1}$

$$\text{so } \frac{d[\text{Br}]}{dt} = -k_1 [\text{Br}]^2$$

if  $v_2 \ll v_{-1}$ , then  $k_2 [\text{M}] \ll k_{-1}$  so

$$\frac{d[\text{Br}]}{dt} = -\frac{2k_1 k_2}{k_{-1}} [\text{Br}]^2 [\text{M}]$$

Can also express as

$$\frac{d[\text{Br}]}{dt} = k_{\text{obs}} [\text{Br}]^2 \quad \text{where } k_{\text{obs}} \text{ is a function of } [\text{M}]$$

$$k_{\text{obs}} = \frac{-k_1 k_2 [\text{M}]}{k_{-1} + k_2 [\text{M}]} \quad \begin{cases} \text{small } [\text{M}], & k_{\text{obs}} = -\frac{k_1 k_2 [\text{M}]}{k_{-1}} \\ \text{large } [\text{M}], & k_{\text{obs}} = -k_1 \end{cases}$$

\* additive terms get affected, not multiplicative \*