CHEM 3420: Final Review — May 3rd, 2024

Chemical Kinetics I: Rate Laws

Suppose you have

$$aA + bB \longrightarrow fF + gG \qquad (1.1)$$

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

Q1.1) $$2\,NO + O_{2\,(g)} \longrightarrow 2\,NO_{2\,(g)}$$

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

Relationship b/t $v(t)$ 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 $\frac{mol}{L \cdot s} = \underbrace{\frac{mol}{dm^3 \cdot s}}_{\text{book pref.}} = \frac{M}{s}$

Q1.2)

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

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

Suppose we have

$$A + B \longrightarrow C$$

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 $t:t$

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

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

Q1.3) Too lazy to write Q:

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

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

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

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

Reversible Rxns:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

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

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

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

consequently:

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

Q1.4)

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

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

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

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

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

Chemical Kinetics II: Rxn. Mechs.

"$\Longrightarrow$" : elementary rxn.

"$\longrightarrow$" : complex rxn.

molecularity $\equiv$ # reactant molecules in rxn.

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

27-2: Detailed Balance

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$ bimolecular, elementary reversible rxn.

so $v_1 = k_1[A][B]$ & $v_{-1} = k_{-1}[C][D]$

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

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:

$$A \xrightarrow{k_{obs}} P$$

w/ two elementary rxns.

$$A \overset{k_1}{\Longrightarrow} I \qquad I \overset{k_2}{\Longrightarrow} P$$

$$\left.\begin{aligned} \frac{d[A]}{dt} &= -k_1[A] \\ \frac{d[I]}{dt} &= k_1[A] - k_2[I] \\ \frac{d[P]}{dt} &= k_2[I] \end{aligned}\right.$$

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

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

sus

$$[O] = \frac{k_1[O_3][M]}{k_{-1}[O_2][M] + k_2[O_3]} \longrightarrow \frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2[M]}{k_{-1}[O_2][M] + k_2[O_3]}$$

Q2.2) 29-43 recall $v(t) = -\frac{1}{a}\frac{d[A]}{dt}$

$$\frac{d[Br]}{dt} = -2k_1[Br]^2 + 2k_{-1}[Br_2^*]$$

and $\frac{d[Br_2^*]}{dt} = k_1[Br]^2 - k_{-1}[Br_2^*] - k_2[Br_2^*][M]$

s.s. approx. : $[Br_2^*] = \frac{k_1[Br]^2}{k_{-1} + k_2[M]} \longrightarrow \frac{d[Br]}{dt} = -2k_1[Br]^2 + \frac{2k_1k_{-1}[Br]^2}{k_{-1} + k_2[M]}$

$$\frac{d[Br]}{dt} = \frac{-2k_1k_{-1}[Br]^2 - 2k_1[Br]^2k_2[M] + 2k_{-1}k_1[Br]^2}{k_{-1} + k_2[M]} = \boxed{-\frac{2k_1k_2[Br]^2[M]}{k_{-1} + k_2[M]}}$$

if $V_2 >> V_{-1}$, then $k_2[Br_2^*][M] >> k_{-1}[Br_2^*]$ so $k_2[M] >> k_{-1}$

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

if $V_2 << V_{-1}$, then $k_2[M] << k_{-1}$ so

$$\frac{d[Br]}{dt} = -\frac{2k_1k_2}{k_{-1}}[Br]^2[M]$$

Can also express as

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

$$k_{obs} = \frac{-k_1k_2[M]}{k_{-1} + k_2[M]} \quad \begin{cases} \text{small } [M], & k_{obs} = -\dfrac{k_1k_2[M]}{k_{-1}} \\ \text{large } [M], & k_{obs} = -k_1 \end{cases}$$

* additive terms get affected, not multiplicative *