Reviewing integrals

\[
\int dx = x + c
\]

\[
\int 2x \, dx = \frac{x^2}{2} + c
\]

\[
\int x^2 \, dx = \frac{x^3}{3} + c
\]

\[
\int x^n \, dx = \frac{x^{n+1}}{n+1} + c
\]

\[
\int \frac{1}{x} \, dx = \ln x + c
\]
Revisiting compound interest

\[ P = P_0 \left(1 + \frac{r}{n}\right)^{nt} \]

- \( P_0 \) is the initial amount
- \( P \) is the total amount at time \( t \)
- \( r \) is the rate of interest (e.g., 0.05 for 5\%)
- \( n \) is the number of times compounded (e.g., \( n = 2 \) times a year for \( t = 5 \) years)

We can rewrite this as

\[ P = P_0 \left(1 + \frac{r}{y}\right)^{ny} = P_0 \left(1 + \frac{2r}{y}\right)^{y} \]

where \( 2r = x \) and \( y = nt \)

We use \( \lim_{y \to \infty} (1 + \frac{x}{y})^y = e^x \)

\[ P = P_0 e^{rt} \]

when the compounding is instantaneous.
Real reactions:

Making approximations

$$\text{rate} = k[A]^m[B]^n[C]^p$$

If we start with $[A]_0$, $[B]_0$, $[C]_0$

and we use small amounts of

$[A]_0$, then $[B]_0 \Rightarrow [A]_0$

$[C]_0 \Rightarrow [A]_0$

we can assume that as $[A]_0 \rightarrow [A]$

$[B]_0 \approx [B]_0$

$[C]_0 \approx [C]_0$

$$\Rightarrow \text{rate} = k'[A]^m$$

where $k' = k[B]_0^n[C]_0^p$

e tc.
Consider

\[ \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \]

The known rate is \( k \left[ \text{NO}_2 \right]^2 \)

The reaction is not elementary.

Molecularity is the number of species that must collide to form products.

\[ \text{A} + \text{B} \rightarrow \text{products} \]

If the rate is \( k[A][B] \),

then this is an elementary reaction with a molecularity of \( 2 \).
\[ \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \]

\[ \text{rate} = k [\text{NO}_2]^2 \]

perhaps

\[ \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \]

\[ \text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \]

slow (rate limiting)

\[ \text{fast} \]

rate of overall reaction is

\[ \frac{d[\text{NO}_3]}{dt} = 6k[\text{NO}_2]^2 \]
Forward & reverse first steps

\[ 2O_3 (g) \rightarrow 3O_2 (g) \]

observed rate is \( \frac{k_1 [O_3]^2}{[O_2]} \)

note that the product \( O_2 \) enters the rate law

\[ O_3 \xrightleftharpoons[k_1=k^{-1}][k_2] O_2 + O \]

\[ O + O_3 \xrightleftharpoons[k_2=2][k_1=k^{-1}][k_2=2] 2O_2 \]

overall rate = \( k_2 [O_2] (O_3) \)

if the second reaction is rate limiting then \( \frac{[O_3]}{[O_2]} = \frac{k_1 [O_2]}{k^{-1} [O_2]} \) (\( k_1 [O_2] = k_2 [O_2] (O_2) \))
rate = \( k_2 (O_3) = k_2 \frac{k_1 (O_{3})}{k_1 \frac{[O_{3}]}{[O_2]}} \)

\( = k \frac{[O_{3}]}{[O_2]}^2 \left( k = \frac{k_2 k_1}{k_1} \right) \)

\[ \frac{C_\text{l}_2(\text{g}) + C\text{H}_3(\text{g})}{\text{g}} \rightarrow \text{HCl}(\text{g}) + \text{C}(\text{g}) \]

from exp. rate = \( k \left| \frac{[C_\text{l}_2]^{1/2}}{[C\text{H}_3]} \right| \)

proposed reaction:

\[ \frac{C_\text{l}_2(\text{g})}{\text{g}} \rightarrow 2\text{C}(\text{g}) \]

\[ \frac{\text{C}(\text{g}) + \text{C}(\text{g})}{\text{g}} \rightarrow \text{HCl}(\text{g}) + \text{C}(\text{g}) \]

\[ \frac{\text{C}(\text{g}) + \text{C}(\text{g})}{\text{g}} \rightarrow \text{C}(\text{g}) \]

\[ \frac{\text{C}(\text{g}) + \text{C}(\text{g})}{\text{g}} \rightarrow \text{C}(\text{g}) \]

\[ \frac{\text{C}(\text{g}) + \text{C}(\text{g})}{\text{g}} \rightarrow \text{C}(\text{g}) \]
\[
\text{rate} = k_2 ([O_3]) = k_2 \frac{k_1 [O_1] [O_3]}{k_1 [O_2]}
\]
\[
= k \frac{[O_3]^2}{[O_2]}
\]
\[
\left( k = \frac{k_2 k_1}{k_{-1}} \right)
\]

\[
\text{Cl}_2(g) + \text{CH}_2(g) \rightarrow \text{HCl}(g) + \text{C}_2(g)
\]

From exp. rate = \( k \frac{[\text{Cl}_2]^2}{[\text{CH}_2]} \)

Proposed reaction:
\[
\text{Cl}_2(g) \xrightarrow{k_{-1}} 2\text{Cl}(g)
\]

\[
\text{Cl}(g) + \text{CH}_2(g) \xrightarrow{k_2} \text{HCl} + \text{C}_2(g)
\]

\[
\text{Cl}_2(g) + \text{Cl}(g) \xrightarrow{k_1} \text{CCl}_4
\]
1. check: overall reaction is balanced

2. Let's assume the first reaction is very rapid, and at equilibrium:

\[ k_1 [Cl_2] = k_{-1} [Cl]^2 \]

\[ [Cl] = \left( \frac{k_1 [Cl_2]}{k_{-1}} \right)^{1/2} \]

rate = \[ k_2 [Cl] / [CHCl_3] \]

\[ k = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} \]

\[ = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} \left[ Cl \right]^{1/2} \left[ CHCl_3 \right]^{1/2} \]
The steady state approximation.

Concentration of an intermediate, M is constant during the reaction.

\[ \frac{d[M]}{dt} = 0 \]

\[ \text{eq.} \quad 2\text{NO} \quad \underset{k_1}{\stackrel{k_2}{\rightleftharpoons}} \quad \text{N}_2\text{O}_2 \]

\[ \text{N}_2\text{O}_2 + \text{H}_2 \quad \underset{k_3}{\longrightarrow} \quad \text{N}_2\text{O} + \text{H}_2\text{O} \]

\[ 2\text{NO}_3 + \text{H}_2\text{O} \quad \longrightarrow \quad \text{N}_2\text{O}_2\text{O}_5 + \text{H}_2\text{O} \]

\( \text{N}_2\text{O}_2 \) is the intermediate.
\( \text{N}_2\text{O}_2 \) is produced and lost

Production: \( \frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}^2] \)

Loss: \( \frac{d[\text{N}_2\text{O}_2]}{dt} = k_{-1}[\text{N}_2\text{O}_2] + k_2[\text{N}_2\text{O}_2][\text{H}_2] \)

No net production or loss

\[ k_1[\text{NO}^2] = k_{-1}[\text{N}_2\text{O}_2] + k_2[\text{N}_2\text{O}_2][\text{H}_2] \]

Production: \[ k_1[\text{NO}^2] \]
Consumption: \[ k_{-1}[\text{N}_2\text{O}_2] + k_2[\text{N}_2\text{O}_2][\text{H}_2] \]

\[ k_1[\text{NO}^2] = [\text{N}_2\text{O}_2](k_{-1} + k_2[\text{H}_2]) \]

\[ [\text{N}_2\text{O}_2] = k_1[\text{NO}^2] / (k_{-1} + k_2[\text{H}_2]) \]
rate of reaction = \( k_2 \left[ \text{H}_2\text{O} \right] \left[ \text{H}_2 \right] \)

\[
= \frac{k_2 k_1 \left[ \text{H}_2\text{O} \right]^2}{k_{-1} + k_2 \left[ \text{H}_2 \right]}
\]

Approximations: if \( k_2 \left[ \text{H}_2 \right] \) is very large because \( \left[ \text{H}_2 \right] \) is large then the rate is \( \tilde{\frac{k_2 k_1 \left[ \text{H}_2\text{O} \right]^2}{k_{-1} \left[ \text{H}_2 \right]}} \)

If \( \left[ \text{H}_2 \right] \) is very small then

\[
k_{-1} + k_2 \left[ \text{H}_2 \right] = k_{-1} \implies \text{rate} \approx \frac{k_2 k_1 \left[ \text{H}_2\text{O} \right]^2}{k_{-1}}
\]
Temperature dependence of the rate constant $k$

$$k = A e^{-\frac{E_a}{RT}}$$

$\ln k = \ln A - \frac{E_a}{RT}$

$\frac{\ln k}{T} \quad \text{slope} = -\frac{E_a}{R}$