$R = k[A]^x$

[2]

CONC.	RATE
1.45×10^{-3}	2.17×10^{-5}
2.90×10^{-3}	2.17×10^{-5}

↑ ↑

Reaction is zero order in that reactant

1.36×10^{-3}	1.07×10^{-5}
2.72×10^{-3}	4.28×10^{-5}

↑ ↑

2X increase 4X increase

The reaction is second order in that reactant

CONC	RATE
2.06×10^{-3}	1.20×10^{-5}
6.18×10^{-3}	3.60×10^{-5}
↑ 3 x increase in conc.	↑ 3 x increase in rate

CONC. FACTOR	ORDER	RATE FACTOR
2	0	1
3	0	1
4	0	1
2	1	2
3	1	3
4	1	4
2	2	4
3	2	9
4	2	16

INTEGRATED RATE LAWS

$$aA \longrightarrow \text{prod(s)}$$

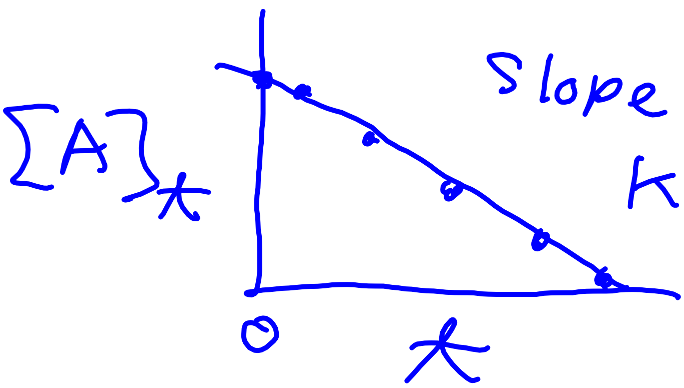
ZERO ORDER

$$R = k[A]^0 = k(1) = k$$

$$R = k$$

$$[A]_t = [A]_0 - kt$$

$$y = b + m \cdot x$$



slope = −k

k = −slope

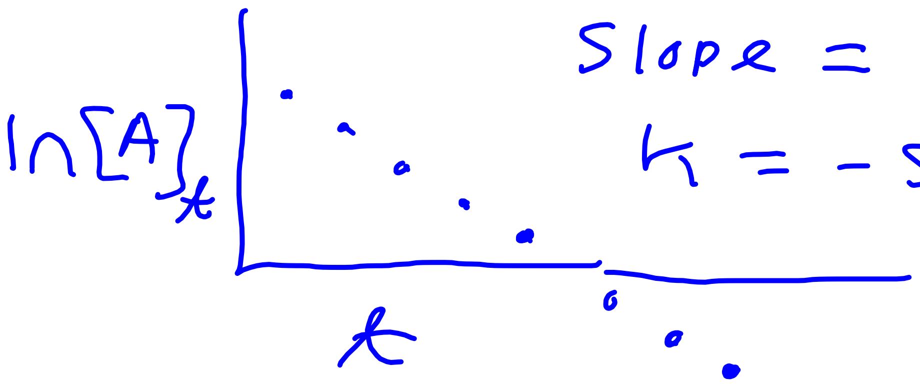
FIRST ORDER

$aA \rightarrow prod(s)$

$R = k[A]^1 = k[A]$

$\ln[A]_t = \ln[A]_0 - kt$

$y = b + m \cdot x$



slope = −k

k = −slope

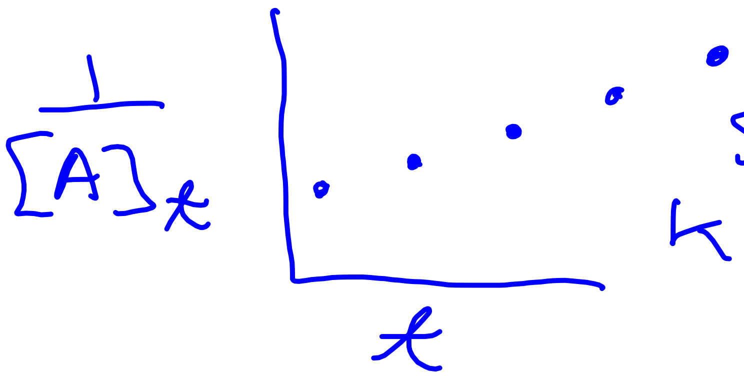
SECOND ORDER

$2A \longrightarrow \text{prod(s)}$

$R = k[A]^2$

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

$$y = b + m \cdot x$$



slope = k

k = slope

HALF LIFE

when $t = t_{\frac{1}{2}}$

then $[A]_t = \frac{1}{2}[A]_0 = \frac{[A]_0}{2}$

ZERO ORDER

$$[A]_t = [A]_0 - kt$$

$$\frac{1}{2}[A]_0 = [A]_0 - kt_{\frac{1}{2}}$$

$$\frac{1}{2}[A]_0 - [A]_0 = \cancel{[A]_0} - \cancel{[A]_0} - kt_{\frac{1}{2}}$$

$$\cancel{-}kt_{\frac{1}{2}} = \cancel{-}\frac{1}{2}[A]_0$$

$$\boxed{t_{\frac{1}{2}} = \frac{[A]_0}{2k}}$$

ZERO ORDER HALF LIFE

↓ algebra

$$k = \frac{[A]_0}{2t_{1/2}}$$

HALF-LIFE

FIRST ORDER

when $t = t_{\frac{1}{2}}$

then $[A]_t = \frac{1}{2}[A]_0 = \frac{[A]_0}{2}$

$$\ln[A]_t = \ln[A]_0 - kt$$

$$\ln\left(\frac{1}{2}[A]_0\right) = \ln[A]_0 - kt_{\frac{1}{2}}$$

$$\ln\frac{1}{2} + \ln[A]_0 = \ln[A]_0 - kt_{\frac{1}{2}}$$

$$-kt_{\frac{1}{2}} = \ln\frac{1}{2}$$

$$-kt_{\frac{1}{2}} = \ln 2^{-1}$$

$$-kt_{\frac{1}{2}} = -1 \cdot \ln 2$$

$$kt_{\frac{1}{2}} = \ln 2$$

$$\boxed{t_{\frac{1}{2}} = \frac{\ln 2}{k}}$$

FIRST ORDER HALF LIFE

↓ algebra

$$k = \frac{\ln 2}{t_{\frac{1}{2}}}$$

SECOND ORDER

when $t = t_{\frac{1}{2}}$

then $[A]_t = \frac{1}{2}[A]_0 = \dfrac{[A]_0}{2}$

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

$$\frac{1}{\frac{1}{2}[A]_0} = \frac{1}{[A]_0} + kt_{\frac{1}{2}}$$

$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + kt_{\frac{1}{2}}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0} - \frac{1}{[A]_0} + kt_{\frac{1}{2}}$$

$$kt_{\frac{1}{2}} = \frac{1}{[A]_0}$$

$$\boxed{t_{\frac{1}{2}} = \frac{1}{k[A]_0}}$$

SECOND ORDER HALF LIFE

↓ algebra

$$k = \frac{1}{t_{\frac{1}{2}}[A]_0}$$

TEMPERATURE DEPENDENCE OF THE RATE CONSTANT

$aA \longrightarrow prod(s)$

$R = k[A]^x$

Arrhenius Equation

$k = A \cdot e^{-\frac{E_a}{RT}}$ $R = 8.314 \frac{J}{K\,mol}$

A ← frequency factor

$e^{-\frac{E_a}{RT}}$ ← energy factor

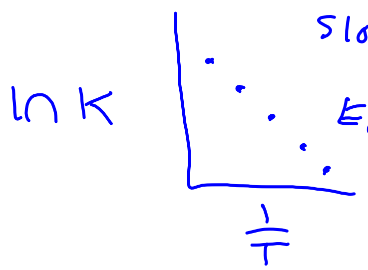
$\ln k = \ln\left(A \cdot e^{-\frac{E_a}{RT}}\right)$

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

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

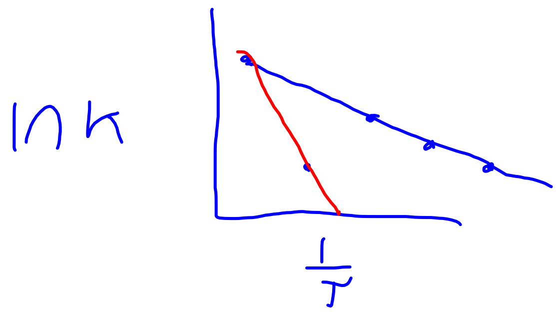
$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$

$y = b + m \cdot x$



$\text{slope} = -\frac{E_a}{R}$

$E_a = -R \cdot \text{slope}$



$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$

(T_1, k_1), (T_2, k_2)

$$\ln k_2 = \cancel{\ln A} - \left(\frac{E_a}{R}\right)\left(\frac{1}{T_2}\right)$$

$$-\left[\ln k_1 = \cancel{\ln A} - \left(\frac{E_a}{R}\right)\left(\frac{1}{T_1}\right)\right]$$

$$\ln k_2 - \ln k_1 = \left(\frac{E_a}{R}\right)\left(\frac{1}{T_1}\right) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T_2}\right)$$

$$\boxed{\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

2-point Arrhenius Equation

Remember Clausius-Clapeyron?

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$ab - ac = a(b - c)$$

REACTION MECHANISMS

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

Experimentally Determined

Rate Law: $R = k[NO_2][F_2]$

Proposed Mechanism:

Step 1 $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$

Step 2 $NO_2(g) + F(g) \rightarrow NO_2F(g)$