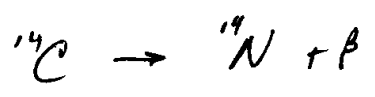


①

# KINETICS



$$\frac{\# \beta}{t} \Rightarrow \text{RATE} = \frac{\Delta N}{\Delta t} = \frac{-\Delta [C]}{\Delta t} \Rightarrow -\frac{\partial [C]}{\partial t}$$

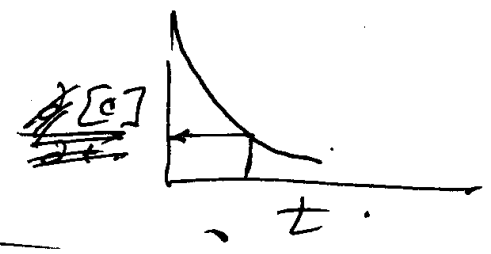
↑ POSITIVE #.

$$\text{RATE} \Rightarrow -\frac{\partial [C]}{\partial t} \propto [C]$$

RATE  $-\frac{\partial [C]}{\partial t} = k [C]$  RATE LAW.

$\frac{\text{mol}}{\text{L} \cdot \text{s}}$

$\frac{\text{mol}}{\text{L}}$   
 $\frac{1}{\text{s}}$  or  $\text{s}^{-1}$



$$-\frac{\partial [C]}{\partial t} = k [C]$$

$$\int_{[C]_0}^{[C]} \frac{\partial [C]}{[C]} = \int_0^t -k dt$$

$$\ln [C] \Big|_{[C]_0}^{[C]} = -kt \Big|_0^t$$

$$\ln [C] - \ln [C]_0 = -kt$$

$$\ln \frac{[C]}{[C]_0} = -kt$$

$$\frac{[C]}{[C]_0} = e^{-kt}$$

$[C] = [C]_0 e^{-kt}$

integrated rate law.

(2)

half life

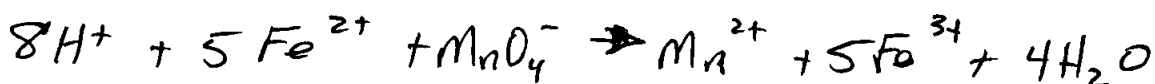
$$t_{1/2} \quad [C]_t = \frac{1}{2} [C]_0$$

$$\ln \frac{[C]}{[C]_0} = -kt$$

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

$$-\ln\left(\frac{1}{2}\right) = +kt_{1/2}$$

$$\ln 2 = kt_{1/2} \Rightarrow t_{1/2} = \frac{\ln 2}{k}$$



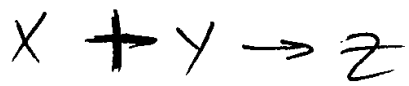
overall reaction

made of elementary reaction steps.  
reaction mechanism.

Stoichiometry does not allow prediction of reaction mechanism!



$$RATE = \frac{\partial [C]}{c \partial t} = \frac{\partial [D]}{d \partial t} = \frac{-\partial [A]}{a \partial t} = \frac{-\partial [B]}{b \partial t}$$



$$\text{Rate} = k \cdot [X]^m [Y]^n$$

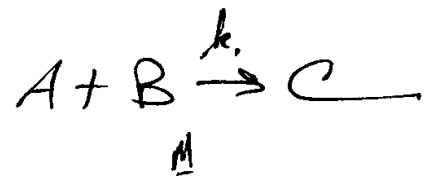
← order of react.

↑  
rate const.  
RATE LAW.

$m+n \equiv$  overall order of reaction.

We can have zero order. ("pseudo-zero order")  
" " " fractional "

How to determine order of reaction!



Method of initial rates:

expts	[A]	[B]	Rate. (m/l-s.)
①	$1 \times 10^{-5}$	$1 \times 10^{-5}$	$7.6 \times 10^{-7}$
②	$2 \times 10^{-5}$	$1 \times 10^{-5}$	$1.5 \times 10^{-6}$
③	$2 \times 10^{-5}$	$2 \times 10^{-5}$	$6.1 \times 10^{-6}$

$$\text{rate}_2 = 1.5 \times 10^{-6} = k [A]_2^m [B]_2^n$$

$$\text{rate}_1 = 7.6 \times 10^{-7} = k [A]_1^m [B]_1^n$$

$$= 2 = \left(\frac{2 \times 10^{-5}}{1 \times 10^{-5}}\right)^m = (2)^m \rightarrow m = 1$$

for  $\Sigma A$  held constant: expt (2) & (3)

(4)

$$\frac{(3)}{(2)} = \frac{6.1 \times 10^{-6}}{1.5 \times 10^{-6}} = \left( \frac{2 \times 10^{-5}}{1 \times 10^{-5}} \right)^n = (2)^n$$

↑  
4  $\Rightarrow$   $n=2$

$$\text{Rate} = k[A][B]^2$$

$$\frac{\text{rate (3)}}{\text{rate (2)}} = \left( \frac{[B]_3}{[B]_2} \right)^m$$

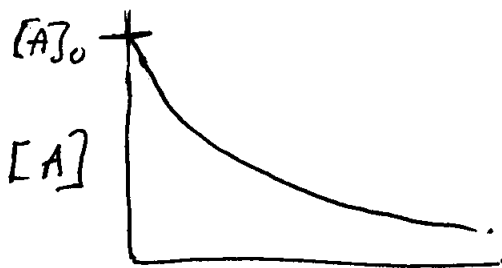
$$\ln \left( \frac{\text{rate (3)}}{\text{rate (2)}} \right) = m \ln \left( \frac{[B]_3}{[B]_2} \right)$$

↑ solve for m!

$A \rightarrow B$

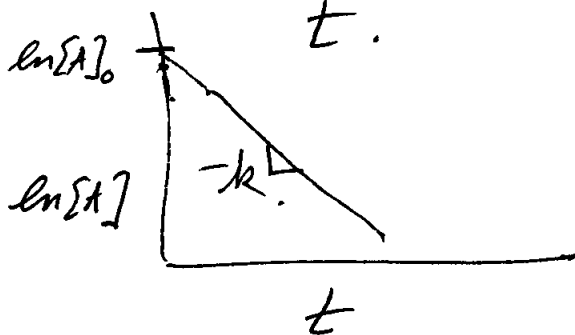
$$\text{Rate} = \frac{-\partial[A]}{\partial t} = k[A]$$

$$[A] = A_0 e^{-kt}$$



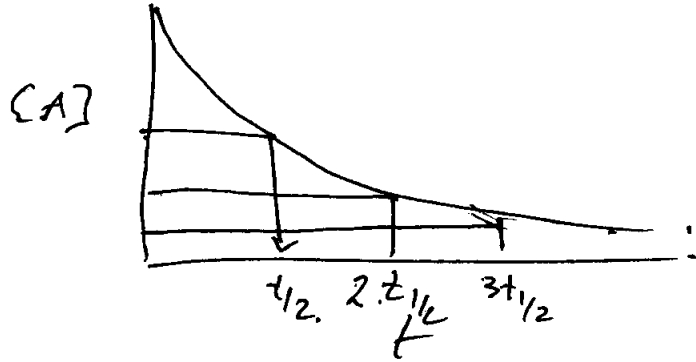
$$\ln[A] = \ln[A]_0 - kt$$

$$y = b + mx$$

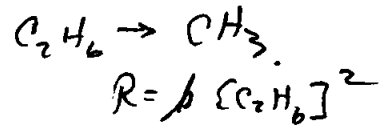


HALF LIFE

$$t_{1/2} = \frac{\ln 2}{k} \quad (\text{1<sup>ST</sup> order reaction})$$



2<sup>ND</sup> ORDER.  
~~P~~W → Q



Rate =  $k [W]^2$

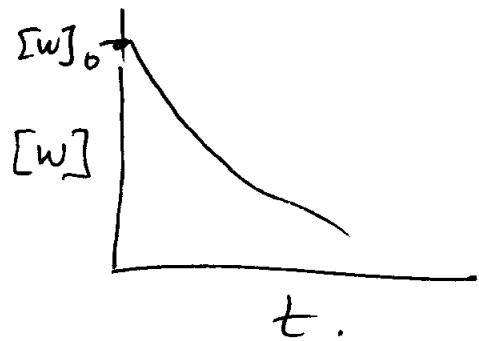
$k: \frac{l}{mol \cdot s}$

$$-\frac{d[W]}{dt} = k [W]^2$$

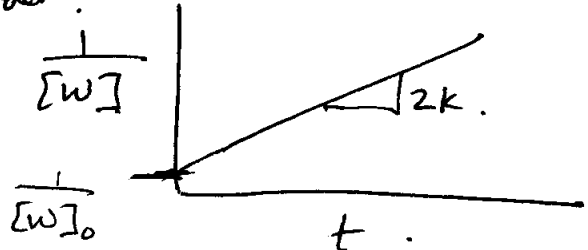
$$-\frac{d[W]}{[W]^2} = k dt$$

$$+\frac{1}{2[W]} \Big|_{[W]_0}^{[W]} = kt \Big|_0^t$$

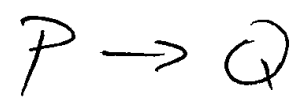
$$\boxed{\frac{1}{[W]} - \frac{1}{[W]_0} = 2kt}$$



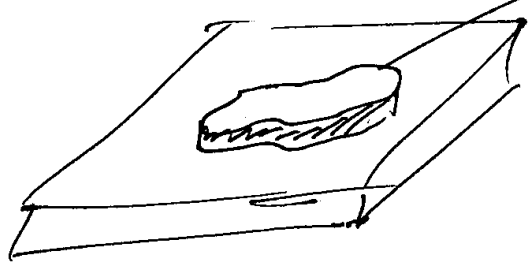
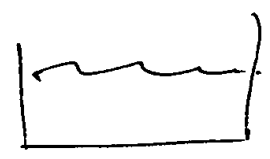
2<sup>nd</sup> order



zero order



$$\text{Rate} = k$$



islands  
(multi-layer)