KINETICS: RATES OF CHEMICAL REACTIONS

[MH5; Chapter 11]

- **Kinetics** is a study of how quickly a chemical reaction proceeds (the **rate** of the reaction) and the factors that affect that rate.
- What are the factors that affect the rate of a reaction?

1) Nature of Reactants.
Some reactions are faster than others....

<u>EXAMPLES:</u>

$H_2 (g) + F_2 (g) \rightarrow 2HF (g)$	explosively fast
$2 Fe (s) + 3/2\ O_2 (g) \rightarrow Fe_2O_3 (s)$	months; this is rusting..
$C\ (graphite) \rightarrow C\ (diamond)$	undetectably slow

2) Concentration of Reactants. Increasing reactant concentrations usually speeds up the rate of reaction.

3) Temperature. Reactions generally go faster as the temperature is increased.

4) Presence of a catalyst; a catalyst increases the rate of a reaction without being consumed in the reaction.

- The **rate** of reaction is a **positive** quantity that describes how the concentration of a reactant or a product varies with time.

- Consider the reaction: $N_2 + 3H_2 \rightarrow 2NH_3$

- We could define rate in terms of $[N_2]$, $[H_2]$ or $[NH_3]$.

$$\left.\begin{aligned} \text{Rate} &= \frac{\Delta[N_2]}{\Delta t} \\ &= \frac{\Delta[H_2]}{\Delta t} \\ &= \frac{\Delta[NH_3]}{\Delta t} \end{aligned}\right\}$$

3 different rates, depending on which species we use.

- But $[H_2]$ will decrease three times as fast as that of N_2 while $[NH_3]$ will increase twice as fast as that of N_2 decreases...

- We express the rate of concentration change:

$$\overset{\text{disappearing}}{-\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t}} = \overset{\text{appearing}}{+\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}}$$

- By defining rate of reaction in this way, it is independent of the species we are using to track the reaction.

- put rate of reaction of each species in terms of all the others

Concentration Effects [MH5; 11.2]

- The effects of concentration on the rate of a reaction are described by **Rate Laws**.
- For the general reaction:

$$\mathbf{A + B + C \ldots \rightarrow products}$$

the Rate Law is:

$$\mathbf{Rate = k\ [A]^a\ [B]^b\ [C]^c \ldots}$$

- Rate may be measured by the rate of production of products, or the rate of disappearance of reactants.
- **[A], [B]** etc. are the concentrations of components **A**, **B** etc., in units of **mol L**$^{-1}$
- **a, b, c**.... are the exponents of each reactant in the Rate Law. They are **NOT** the coefficients of **A**, **B**, **C** in the balanced equation.
- **k** is the **Specific Rate Constant** of that reaction at a particular temperature.

- The exponents a, b, c can **only** be found by experiment.
- The exponent is called the **order** of the reaction; it relates changes in reactant concentration the changes in rate.
- They are often whole numbers, but not always......

- If: a = 1, the reaction is **First Order** in [A]
  a = 2, the reaction is **Second Order** in [A]
  a = 0, the reaction is **Zero Order** in [A]; that is, the rate of reaction is independent of the concentration of component A
- Exponent values higher than 2 are seldom seen; sometimes you will see an order of $\frac{1}{2}$, or even of $-\frac{1}{2}$......

EXAMPLE: For the gas phase reaction;

$$2\ H_2 + 2\ NO \rightarrow 2\ H_2O + N_2$$

the rate law is Rate = $k\ [H_2]^1\ [NO]^2$

- The reaction is first order in $[H_2]$ and second order in $[NO]$.
- The overall order of this reaction is three; (the sum of all the individual orders).
- Note that the products **do not** (usually) appear in the rate law.

- How do we find the exponents from an experiment?

EXAMPLE:

Consider some data for the reaction:

$$A + B \rightarrow \text{products}$$

Run	[A] mol L^{-1}	[B] mol L^{-1}	Rate, mol L^{-1} s^{-1}
i)	0.001	0.002	5×10^{-4}
ii)	0.002	0.002	10×10^{-4}
iii)	0.001	0.004	20×10^{-4}

- Determine: i) The Rate Law
  ii) The Specific Rate Constant, k

- The strategy is:
  a) vary one concentration at a time
  b) evaluate the exponents separately
  c) combine the exponents into a rate law
  d) substitute one data set to find k

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

For [A]: - vary [A]; keep [B] constant

∴ runs i) and ii)

$$\frac{\text{Rate ii)}}{\text{Rate i)}} = \frac{\cancel{k}\,[A]_{ii)}^{x}\,\cancel{[B]_{ii)}}^{y}}{\cancel{k}\,[A]_{i)}^{x}\,\cancel{[B]_{i)}}^{y}}$$

$$\therefore \frac{\text{Rate ii)}}{\text{Rate i)}} \propto \frac{[A]_{ii)}^{x}}{[A]_{i)}^{x}} \Rightarrow \underline{\frac{10 \times 10^{-4}}{5 \times 10^{-4}}} \propto \left(\frac{.002}{\underline{.001}}\right)^{x}$$

$$\underline{2} = \underline{2}^{x} \qquad \therefore \underline{\underline{x = 1}}$$

For B: - vary [B]; keep [A] constant

∴ use runs i) and iii)

$$\frac{\text{Rate iii)}}{\text{Rate i)}} \propto \frac{[B]_{iii)}^{y}}{[B]_{i)}^{y}} \Rightarrow \underline{\frac{20 \times 10^{-4}}{5 \times 10^{-4}}} \propto \left(\frac{.004}{\underline{.002}}\right)^{y}$$

$$\therefore \underline{4} = \underline{2}^{y} \qquad \Rightarrow \underline{\underline{y = 2}}$$

- The Rate Law is: $\text{Rate} = k\,[A]\,[B]^{2}$

- Now find a numerical value for k:

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

*Use data from <u>ONE</u> run

$$= \frac{5 \times 10^{-4}}{(0.001)(0.002)^2} = \underline{\underline{1.25 \times 10^{5}}}$$

- Units for k:

$$k = \frac{mol\,L^{-1}s^{-1}}{(mol\,L^{-1})(mol\,L^{-1})^2} = \frac{\cancel{mol\,L^{-1}}\,s^{-1}}{(\cancel{mol\,L^{-1}})(mol^2L^{-2})}$$

$$= \frac{s^{-1}}{mol^2L^{-2}} = s^{-1}mol^{-2}L^{2} \Rightarrow \underline{\underline{mol^{-2}L^{2}s^{-1}}}$$

- Once the rate law is known, we can predict the rate of reaction under other concentration conditions at the same temperature.

- Suppose [A] = 0.03 and [B] = 0.05 mol L^{-1}

Rate = $k[A][B]^2$

$$= 1.25 \times 10^{5}(0.03)(0.05)^2$$

$$= \underline{\underline{9.375}}$$

UNITS : $= mol^{-2}L^{2}s^{-1}(mol\,L^{-1})(mol\,L^{-1})^2$

$$= \underbrace{\cancel{mol^{-2}L^{2}}}\,s^{-1}(mol\,L^{-1})\underbrace{(\cancel{mol^{2}L^{-2}})}$$

$$= \underline{mol\,L^{-1}s^{-1}}$$

- What if the data are not easily interpreted to find the order ??
- As it is almost impossible to prepare reaction mixtures with concentrations that are exact multiples, we end up with data such as....

$$\text{Rate} = k\,[A]^{x}$$

Run	[A] mol L^{-1}	Rate
i)	1.78×10^{-2}	6.00×10^{-5}
ii)	2.85×10^{-2}	7.59×10^{-5}

What is the exponent of [A] in the rate law ?

$$\frac{\text{Rate ii)}}{\text{Rate i)}} = \frac{\cancel{k}\,[A]_{ii)}^{x}}{\cancel{k}\,[A]_{i)}^{x}}$$

$$\underbrace{\frac{7.59 \times 10^{-5}}{6.00 \times 10^{-5}}} = \underbrace{\left(\frac{2.85 \times 10^{-2}}{1.78 \times 10^{-2}}\right)}^{x}$$

Let the exponent of [A] be 'x' ;

$$\underline{1.265} = \underline{1.60}^{x}$$

use logs to solve :

$$\log(1.265) = x \log(1.60)$$

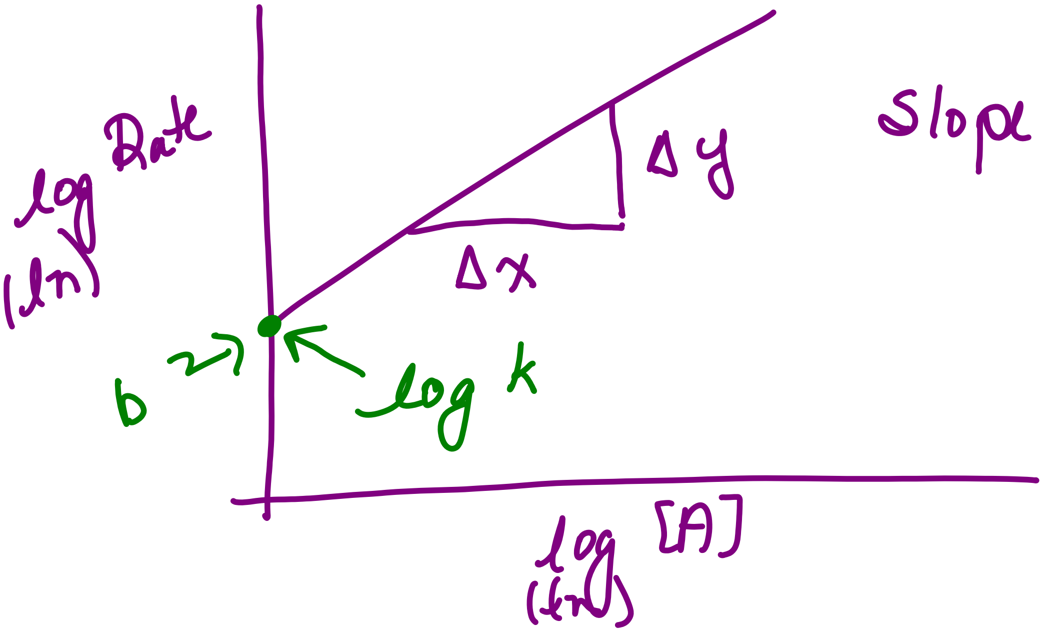
$$0.102 = x\,(0.204)$$

$$x = \frac{0.102}{0.204} = \underline{\underline{0.5}}$$

$\therefore$ RATE LAW:

$$\text{Rate} = k\,[A]^{0.5}$$

- If several data points are available (as in an experiment), plotting a graph is often a more accurate method of determining reaction order: $A \rightarrow \text{products}$ $\therefore \text{Rate} = k[A]^a$



$$\text{Slope} = \frac{\Delta y}{\Delta x} = m = a$$

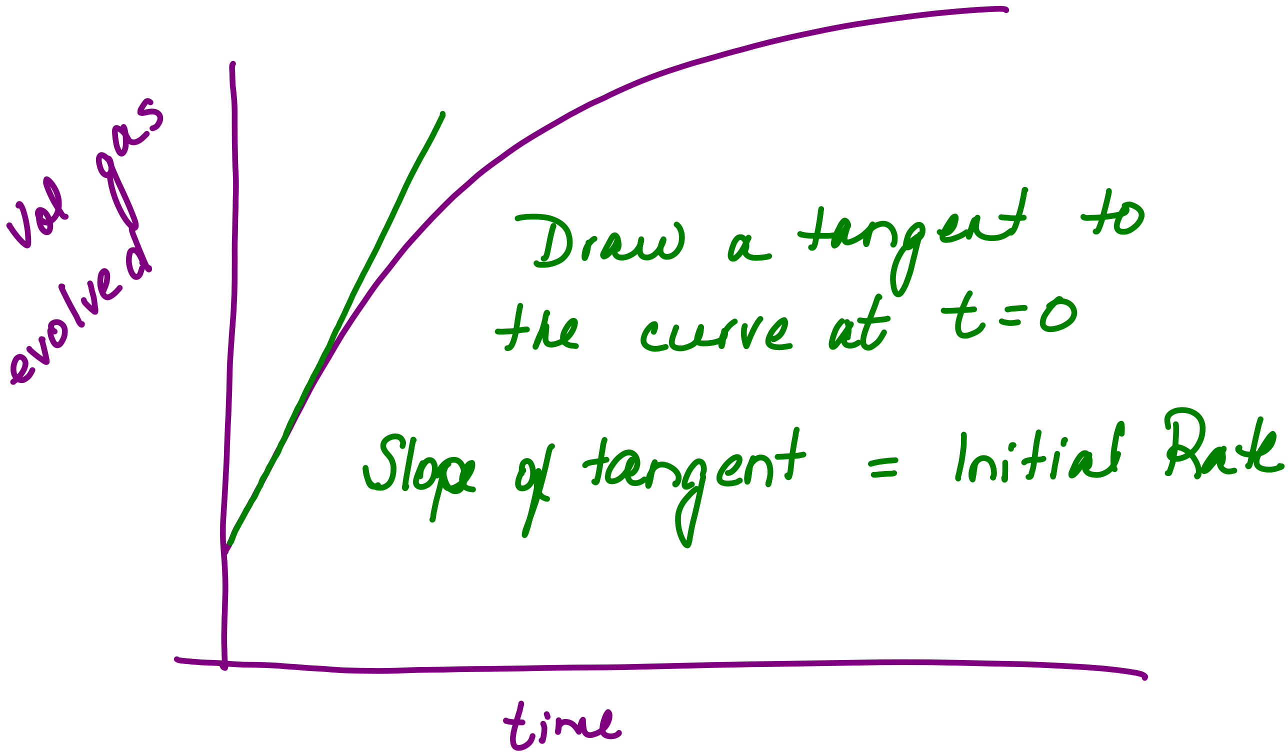
$$\text{Rate} = k[A]^a \Rightarrow \log \text{Rate} = \log k + a \log [A]$$

$$\log \text{Rate} = \underline{a} \log [A] + \log k$$

$$y = m x + b$$

- Does the rate of reaction change as a function of time, t ?
- Yes, the rate decreases as the reactants are consumed.
- Eventually all the reactants are consumed, and the reaction stops - or appears to stop.
- The rate we use in calculations is always the **initial rate**.

- How could we measure initial rate ?
- Consider a reaction in which a gas is evolved; we are measuring the volume of gas produced as a function of time.



Draw a tangent to the curve at $t=0$

Slope of tangent = Initial Rate

- The initial rate of gas evolution will be the slope of this line at $t = 0$.

- This corresponds to the initial reactant concentrations.
- The slope of the line is calculated from the tangent slope [MH5; Figure 11.2]

First Order Reactions [MH5; 11.3]

- Consider the reaction: **$A \rightarrow$ products**

- This reaction is found to be first order in [A]; the Rate Law is: **Rate = k [A]**

- As the reaction proceeds, the [A] decreases......
- At the beginning of the reaction t (time) = t_0 .
- At t_0 , $[A] = [A]_0$

- After some amount of time (t) has passed, $[A] = [A]_t$.
- So, Rate = k $[A]_t$ at some time t.

- Because Rate of Reaction is really the Rate of Change of [A];

$$Rate = \frac{\Delta [A]}{\Delta t} = \frac{d[A]}{dt} = k[A]$$

- If we integrate this, we get:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \quad \underline{OR} \quad \frac{[A]_t}{[A]_0} = e^{-kt}$$

- This is the **Integrated Rate Law** for a first-order reaction; it relates reactant concentration to time.
- The example on p. 287 showed how to determine the Rate Law

(which tells you the order of the reaction with respect to a certain reactant) using the initial Rate of Reaction.

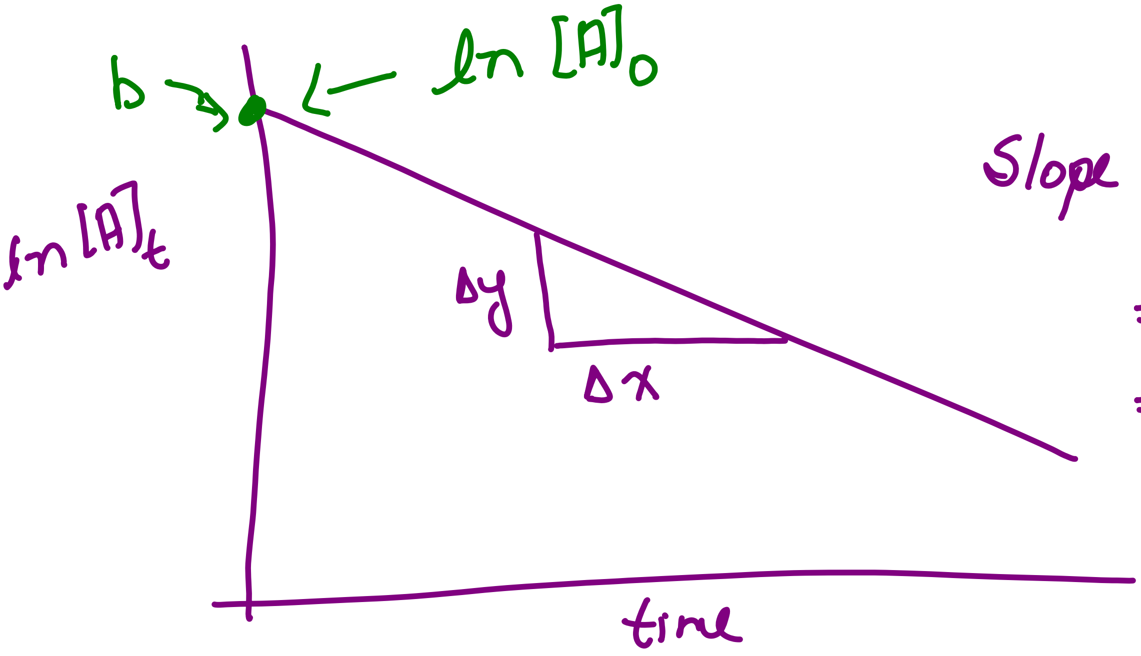
- What if you don't know the initial rate ? Is there another way to determine the order of the reaction ?
- We can experimentally measure the [A] at various times.....then we can plot the data.
- Integrated Rate Laws can be rearranged into the form of an equation for a straight line: **y = m x + b**
- **m** is the slope of the line and **b** is the y - intercept.

- For a first order reaction:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \Rightarrow \ln[A]_t - \ln[A]_0 = -kt$$

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

$$y = mx + b$$



$$\text{Slope} = \frac{\Delta y}{\Delta x} = \underline{m} = -\underline{k}$$

For a First Order Reaction, plotting $\ln[A]_t$ vs time → straight line

slope $= -k$

EXAMPLE 1:

The reaction: **M → products** is known to be first order in [M].
The initial [M] is 0.625 M. After 10.5 minutes, [M] = 0.426 M.
What will [M] be after one hour?

$$\ln \frac{[M]_t}{[M]_0} = -kt \qquad \underline{\text{OR}} \qquad \frac{[M]_t}{[M]_0} = e^{-kt}$$

$$\ln \left[\frac{(0.426\cancel{M})}{(0.625\cancel{M})} \right] = -k\,(10.5\ \text{min})$$

$$-0.3833 = -k\,(10.5\ \text{min})$$

$$\therefore\ k = 0.0365\ \text{min}^{-1}$$

now use k . . .

$$\frac{[M]_{60}}{0.625\,M} = e^{-(0.0365\,\cancel{\text{min}^{-1}})(60\,\cancel{\text{min}})}$$

$$= 0.112$$

$$[M]_{60} = 0.112 \times 0.625M$$

$$= \underline{\underline{0.0699\ M}}$$

The Concept of Half - Life for First Order Reactions

[MH5; page 292]

- A Half-Life is the **time** taken for half the initial concentration of the reactant, A, to be consumed. "$t_{1/2}$"
- At this stage in the reaction:

$$[A]_t = \frac{[A]_0}{2} \quad \underline{\underline{\text{OR}}} \quad \frac{[A]_t}{[A]_0} = 0.5$$

$$* \ \frac{[A]_t}{[A]_0} = \text{Fraction Remaining} \ *$$

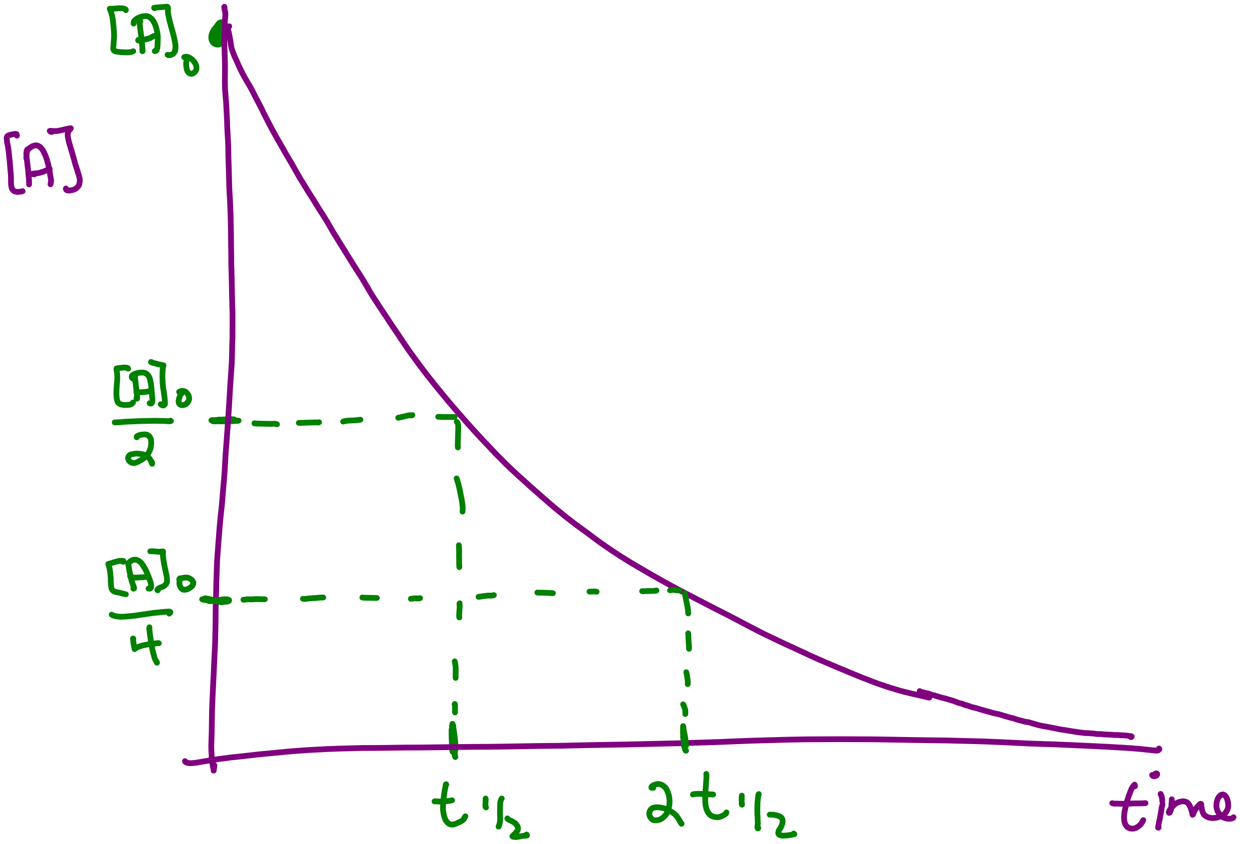
$$\Rightarrow \ln\left(\frac{[A]_t}{[A]_0}\right) = -kt_{1/2}$$

$$\ln(0.5) = -kt_{1/2}$$

$$-0.693 = -kt_{1/2}$$

$$\therefore t_{1/2} = \frac{0.693}{k} \quad \underline{\underline{\text{OR}}} \quad k = \frac{0.693}{t_{1/2}}$$

- This process is called **Exponential Decay**.



- When is reaction “complete” ? Never !!
- The decay graph approaches to axis x = 0, but never reaches it.
- **Radioactive** decay always proceeds according to first-order kinetics.

A Different Approach to Half Life.......

- We have said that the **half life** (or $\mathbf{t_{1/2}}$) is the time required to reduce the reactant concentration to half of its original value.
- For a first order reaction, the half life is constant; it only depends on the rate constant, k, and not on the concentration of the reactant.

- **We will follow a reaction for a few half lives...**

- After 1 half life, the fraction of the reactant remaining will be $0.50 = (0.5)^1$
- After 2 half lives, the fraction of the reactant remaining will be $0.25 = (0.5)^2$
- After 3 half lives, the fraction of the reactant remaining will be $0.125 = (0.5)^3$

- So......we can make a general statement that says:

- The fraction of the reactant remaining after $\underline{n}$ half lives = $(0.5)^n$, where "$\underline{n}$" is the number of half lives.

- In order to use this statement effectively, we need to know how many half lives have elapsed at any given time in a reaction.

- $$\text{The \# of half lives} = \frac{\text{The time elapsed}}{\text{The length of the half life}}$$

EXAMPLE 2:

A first order reaction has a half life of 11 minutes.

i) What fraction of the reactant remains after one hour? (60 min)

$t_{1/2} = 11 \text{ min}$

half lives in 60 minutes

$= \frac{60 \cancel{\text{min}}}{11 \cancel{\text{min}}} = 5.45$

$\therefore$ Fraction Remaining $= (0.5)^{5.45}$

→ use y^x function $= \underline{\underline{0.0229}}$

ii) What fraction has decomposed?

Fraction decomposed

$= 1 -$ Fraction remaining

$= 1 - 0.0229$

$= \underline{0.9771}$

- The fraction of the reactant remaining can be applied to an actual starting amount of reactant to determine the actual amount remaining (or the amount that has been used up).

EXAMPLE 3:

The half life of the first order reaction:

$$\mathbf{N_2O_5\ (g) \rightarrow 2\ NO_2\ (g) + \tfrac{1}{2}\ O_2\ (g)}$$

has been found to be 120 sec at 67 ° C.

If the initial concentration of N_2O_5 is 0.850 M, calculate the concentration of N_2O_5 after 5 minutes have elapsed.

Also calculate the concentration of NO_2 at this time.

1st approach : $t_{1/2} = 120$ sec

time elapsed = 5 min = 300 sec

$\therefore$ # of half lives $= \dfrac{300\ \cancel{\text{sec}}}{120\ \cancel{\text{sec}}} = 2.5$

Fraction of N_2O_5 remaining $= (0.5)^{2.5}$

$= \underline{0.177}$

$[N_2O_5]_{\text{remaining}} = 0.850\text{ M} \times 0.177$

$= 0.150\text{ M}$

$\therefore [N_2O_5]_{\text{reacted}} = 0.850\text{ M} - 0.150\text{ M}$

$= 0.700\text{ M}$

$[NO_2]_{\text{formed}} = 2\ [N_2O_5]_{\text{reacted}}$

$= 2\ (0.700\text{ M})$

$= \underline{1.40}\text{ M}$

2nd Approach

$$t_{1/2} = 120 \text{ sec} \Rightarrow k = \frac{0.693}{t_{1/2}}$$

$$\therefore \quad k = \frac{0.693}{120 \text{ sec}} = 5.775 \times 10^{-3} \text{ sec}^{-1}$$

$$\frac{[N_2O_5]_t}{[N_2O_5]_0} = e^{-kt}$$

$$\frac{[N_2O_5]_t}{0.850\text{ M}} = e^{-(5.775 \times 10^{-3} \cancel{\text{sec}}^{-1})(300 \cancel{\text{sec}})}$$

$$= e^{-1.7325}$$

$$\frac{[N_2O_5]_t}{0.850\text{ M}} = 0.1768 \quad \text{(Fraction remaining)}$$

$$[N_2O_5]_t = 0.1768 \times 0.850\text{ M}$$

$$= \underline{\underline{0.150\text{ M}}}$$

EXAMPLE 4:

The 0.012% naturally abundant potassium isotope ^{40}K is radioactive with $t_{\frac{1}{2}} = 1.26 \times 10^9$ years.

i) What is the rate constant for decay of ^{40}K ?

$$t_{1/2} = 1.26 \times 10^9 \text{ yrs}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.26 \times 10^9 \text{ yrs}} = 5.5 \times 10^{-10} \text{ yrs}^{-1}$$

ii) Out of an initial 10 g of ^{40}K, how much will remain after $\underline{10^{10} \text{ years}}$?

t

$$[A]_0 = 10.0 g$$

$$\frac{[A]_t}{[A]_0} = e^{-kt} \Rightarrow \frac{[A]_t}{10.0g} = e^{-(5.5 \times 10^{-10} \cancel{yr^{-1}})(10^{10} \cancel{yr})}$$

$$\frac{[A]_t}{10.0g} = e^{-5.5} = 4.087 \times 10^{-3} \text{ (Fraction Remaining)}$$

$$\therefore [A]_t = 4.087 \times 10^{-3} \times 10.0g = \underline{0.041} g$$

iii) After what time would 1% of a sample of ^{40}K remain ?

$$\text{If } \frac{[A]_t}{[A]_0} \times 100 = 1\%$$

$$\text{then } \frac{[A]_t}{[A]_0} = 0.01 = e^{-k\underline{t}}$$

$$\Rightarrow 0.01 = e^{-(5.5 \times 10^{-10} yr^{-1})(t)}$$

$$\ln 0.01 = -(5.5 \times 10^{-10} yr^{-1})(t)$$

$$-4.605 = -5.5 \times 10^{-10} yr^{-1} \times t$$

$$\therefore t = \underline{8.37 \times 10^9} yr$$

Zero Order Reactions [MH5; p. 293]

- For zero - order reactions: $A \longrightarrow \text{products}$

$$\text{Rate} = k\,[A]^0 \Rightarrow \text{Rate} = k$$

$$\text{Rate} = \frac{\Delta[A]}{\Delta t} = \frac{d[A]}{dt} = k[A]^0$$

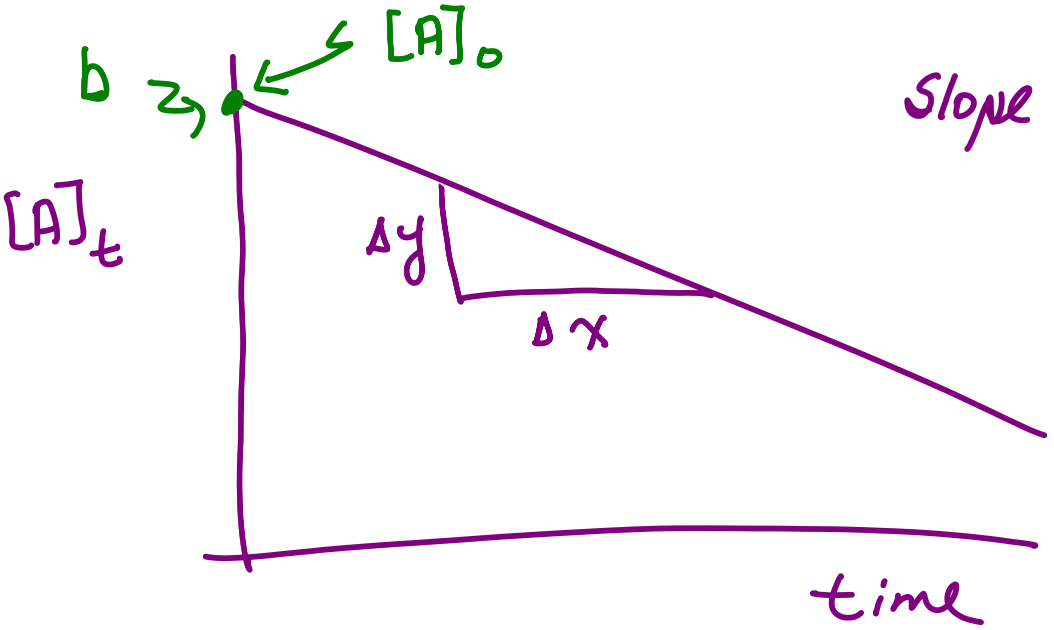
$$\therefore\ [A]_t - [A]_0 = -kt$$

- Rearrange the integrated rate law into the form of the equation for a straight line.......

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

$$y = mx + b$$

- A plot of $[A]_t$ vs time yields a straight line with a slope of -k.



$$\text{Slope} = \frac{\Delta y}{\Delta x} = m = -\underline{k}$$

Second-Order Reactions [MH5; page 293 - 294]

$A \longrightarrow \text{products}$

- For second-order reactions: $\text{Rate} = k[A]^2$

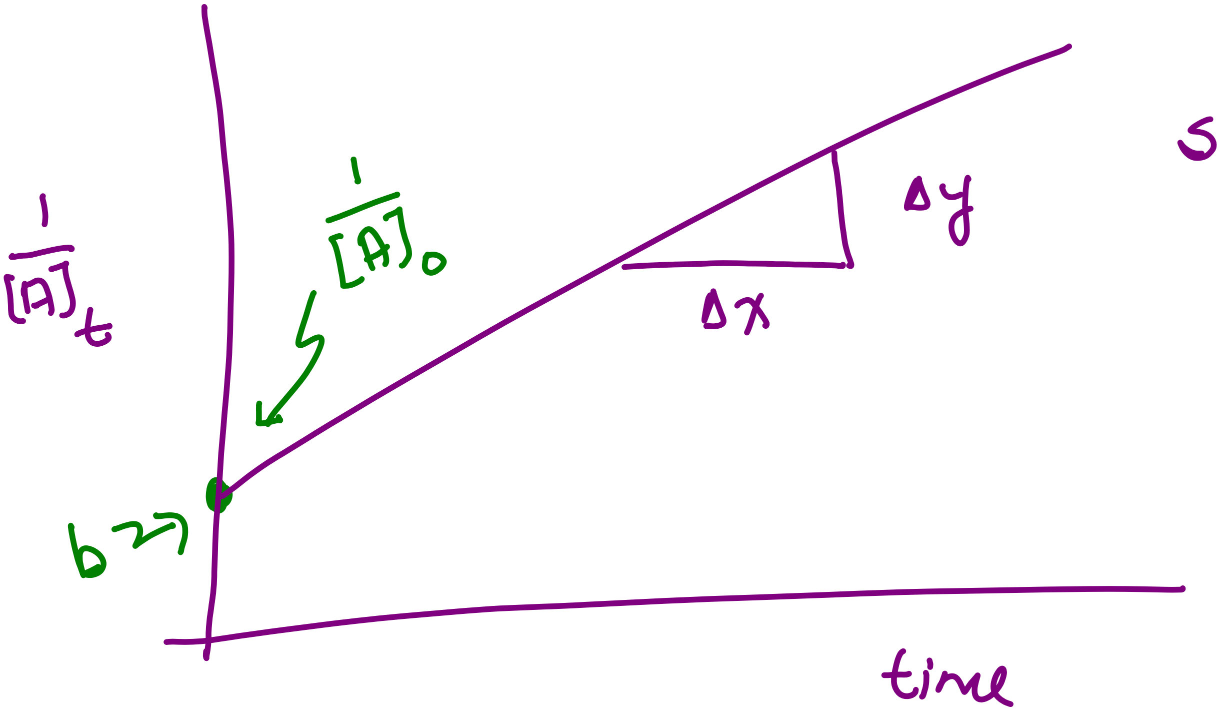
$$\text{Rate} = \frac{\Delta [A]}{\Delta t} = k[A]^2$$

Integrate: $$kt = \frac{1}{[A]_t} - \frac{1}{[A]_0}$$

- This is the **Integrated Rate Law** for a second-order reaction.
- This can also be rearranged into the form of the equation of straight line.....

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

$$y = mx + b$$



$$\text{Slope} = \frac{\Delta y}{\Delta x} = m = \underline{k}$$

- What is the half life ? at $t_{\frac{1}{2}}$: $[A]_t = \frac{[A]_0}{2} \Rightarrow \frac{1}{[A]_t} = \frac{1}{\frac{[A]_0}{2}}$

$$k\,t_{\frac{1}{2}} = \frac{2}{[A]_0} - \frac{1}{[A]_0} \qquad \text{so } t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

- $t_{\frac{1}{2}}$ depends on the initial concentration $[A]_0$
- No half-life can be calculated using "k" for second-order reactions as it could for first-order reactions.

EXAMPLE 1:

For the reaction: **D → products**, the Rate Law is: Rate = k $[D]^2$. 2nd order

If the concentration of D falls from 0.890 M to 0.560 M in 12 minutes, what is the half life of the reaction?

$$t_{1/2} = \frac{1}{k[A]_0} \quad \text{and} \quad kt = \frac{1}{[A]_t} - \frac{1}{[A]_0}$$

Substitute: $k\,(12\,min) = \frac{1}{0.560\,M} - \frac{1}{0.890\,M}$

$$= 0.662\ M^{-1}$$

$$k = \frac{0.662\ mol^{-1}L}{12\ min}$$

$$= \underline{0.0552\ mol^{-1}L\ min^{-1}}$$

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(0.0552)(0.890)\,(\cancel{mol^{-1}L}\,min^{-1})(\cancel{mol\,L^{-1}})}$$

$$= \underline{20.4\ min}$$

EXAMPLE 2:

Ammonium cyanate, NH_4NCO, in water rearranges to produce urea, a common fertilizer, $(NH_2)_2CO$:

$$NH_4NCO \rightarrow (NH_2)_2CO$$

The rearrangement is a second order reaction. It takes 11.6 hours for the concentration of NH_4NCO to go from 0.250M to 0.0841 M.

a) What is k for the reaction ? $kt = \frac{1}{[A]_t} - \frac{1}{[A]_0}$

$$k(11.6\ hr) = \frac{1}{0.0841\ M} - \frac{1}{0.250\ M}$$

$$k(11.6\ hr) = 7.89\ mol^{-1}L$$

$$\therefore\ k = \underline{\underline{0.680\ mol}}^{-1}L\ hr^{-1}$$

b) What is the half life of the reaction when NH_4NCO is 0.100 M ?

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

$$= \frac{1}{\begin{array}{c}0.680 \times 0.100 \\ (\cancel{mol^{-1}L}\,hr^{-1})(\cancel{mol\ L^{-1}})\end{array}} = \underline{\underline{14.7}}\ hr$$

c) How fast is a 0.839 M solution being changed to urea ?

$$Rate = k[A]^2$$

$$= 0.680\ (0.839)^2$$

$$(mol^{-1}L\,hr^{-1})(mol^2L^{-2})$$

$$= \underline{\underline{0.479}}\ mol\,L^{-1}\,hr^{-1}$$

Activation Energy [MH5; 11.4]

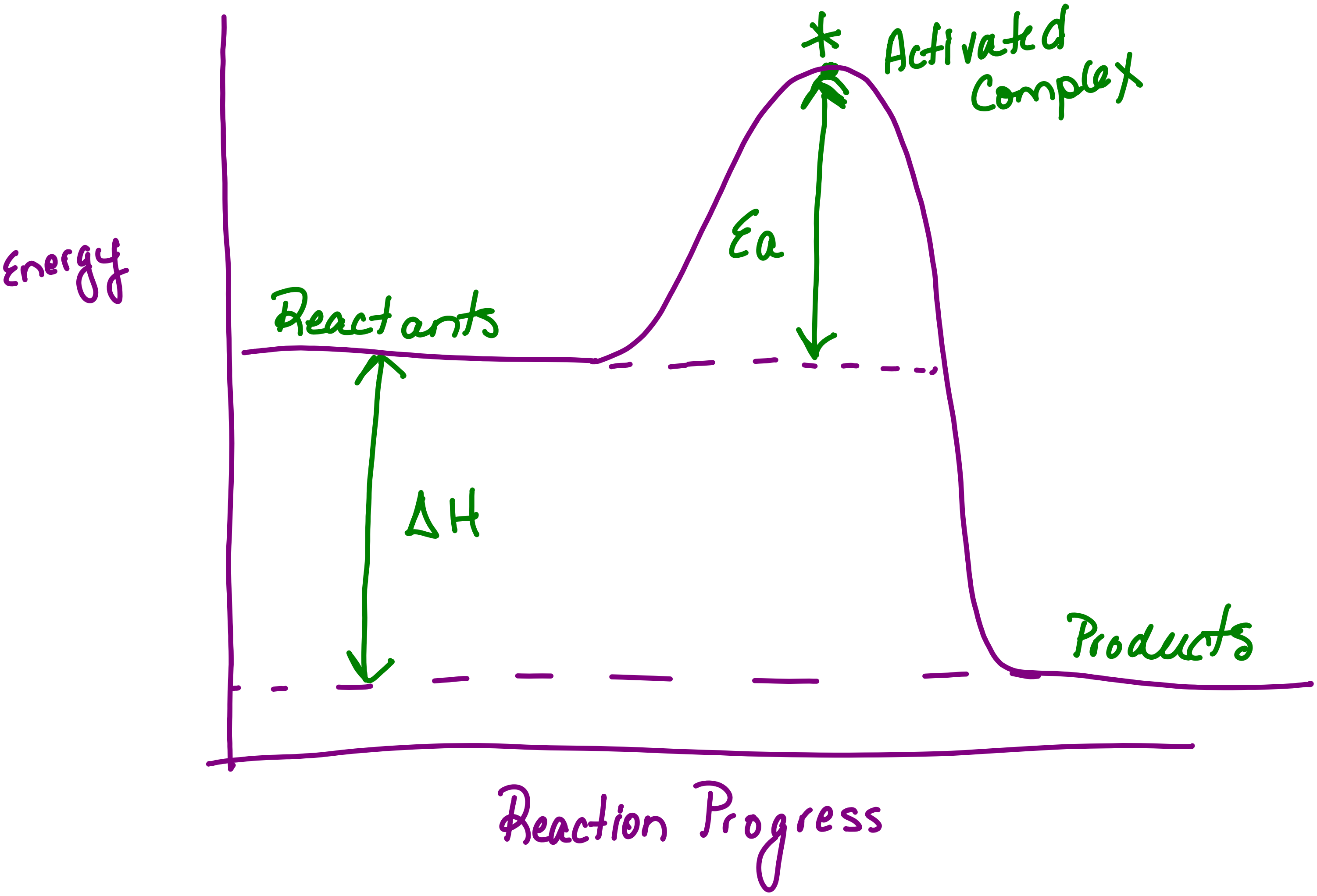
- Generally speaking, reaction rate increases when the temperature increases.
- Food spoilage is a practical example of this; refrigerated leftovers "keep" longer than if we left them at room temperature.......the cooler temperature slows the reactions which contribute to food spoilage.
- Why is this so? It can be explained using **Collision Theory**.

- Molecules must collide for reaction to occur, and have enough energy on collision to overcome an **activation energy** barrier.
- Molecules must also be correctly "oriented" when they collide for a reaction to occur.
- For a very short time, colliding molecules remain stuck together as an activated complex.
- This then falls apart, giving either products or unchanged reactants.
- Most collisions are unproductive; they do not result in any reaction.

- For the general reaction:

$$\mathbf{A + B \rightarrow C + D}$$

we plot reaction coordinate against energy......



- E_a is the activation energy of this reaction.
- It is the minimum energy which molecules must possess on collision in order for reaction to occur.

- Remember that, even if molecules have this energy, most collisions do not result in reaction because of an unfavourable orientation of the molecules.

- So, how does increasing the temperature increase reaction rate?

Effect of Temperature : The Arrhenius Equation
[MH5; 11.5]

- As temperature increases, molecules have more energy and move faster.
- The fraction of the molecules having an energy greater than E_a is:

$$e^{-Ea/RT}$$

where R is the gas constant; units 8.314 J $K^{-1}mol^{-1}$

- This is incorporated into the specific rate constant for the reaction:

$$k = A e^{-Ea/RT}$$

where A is a constant for the reaction.

- So the complete rate law is:

$$\text{Rate} = \underbrace{A\ e^{-E_a/RT}}_{k} [\ A\ ]^a\ [\ B\ ]^b \ldots$$

and the value of E_a may be found by measuring the reaction rate at different temperatures.

$$Rate \propto k$$ (use either)

- In studying a reaction, suppose we find Rate(1) at T_1 and Rate(2) at T_2 with other conditions being kept constant:

$$Rate(1) = Ae^{-Ea/RT_1}[A]^a[B]^b$$

$$Rate(2) = Ae^{-Ea/RT_2}[A]^a[B]^b$$

Rate (2) usually greater than Rate (1)

T_2 usually higher than T_1

dividing:

$$\frac{Rate\ (2)}{Rate\ (1)} = \frac{\cancel{A}e^{-Ea/RT_2}\cancel{[A]^a}\cancel{[B]}^b}{\cancel{A}e^{-Ea/RT_1}\cancel{[A]^a}\cancel{[B]}^b}$$

- All other things being equal, changes in rate are entirely due to changes in **k** which result from changes in temperature, provided concentrations are kept constant.
- Take natural logarithms:

$$\ln\left(\frac{Rate\ 2}{Rate\ 1}\right) = -\frac{Ea}{RT_2} - \left(-\frac{Ea}{RT_1}\right)$$

And rearrange:

$$\ln\left(\frac{Rate\ 2}{Rate\ 1}\right) = \frac{Ea}{RT_1} - \frac{Ea}{RT_2}$$

$$* \boxed{\ln\left(\frac{Rate\ 2}{Rate\ 1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} *$$

- We can use this relationship to determine rate changes due to temperature changes; also to calculate E_a.

EXAMPLE 1: $R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$

When the temperature of a reaction is increased from 20 to 30°C, the rate increases from 1.50 to 2.40 mol L^{-1} s^{-1}. Calculate the activation energy, E_a, for this reaction.

$$\ln\left(\frac{\text{Rate } 2}{\text{Rate } 1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{2.40}{1.50}\right) = \frac{Ea}{8.314}\left(\frac{1}{293} - \frac{1}{303}\right)$$

$$0.470 = \frac{Ea}{8.314}\left(1.126 \times 10^{-4}\right)$$

$$Ea = 34703.2 \text{ Jmol}^{-1}$$

$$= \underline{\underline{34.7}} \text{ kJ mol}^{-1}$$

$\therefore E_a = 50,000\ J\,mol^{-1}$

EXAMPLE 2:

A reaction has E_a = 50.0 kJ mol $^{-1}$. If the specific rate constant (k) for this reaction is 0.00365 s $^{-1}$ at 25 ° C, what will the value of the specific rate constant be at 100°C ?

$$\ln\left(\frac{Rate\ 2}{Rate\ 1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

use k instead of Rate! (Rate $\propto$ k)

$$\ln\left(\frac{k_2}{0.00365}\right) = \frac{50,000}{8.314}\left(\frac{1}{298} - \frac{1}{373}\right)$$

$$\ln\left(\frac{k_2}{.00365}\right) = 4.058$$

$$\frac{k_2}{.00365} = e^{4.058} = 57.85$$

$$\therefore k_2 = \underline{0.211}\ s^{-1}$$

Another way to word this question: By what **factor** does the rate increase ?

Ratio of $\frac{Rate\ 2}{Rate\ 1}$ or of $\frac{k_2}{k_1}$

$$\frac{k_2}{k_1} = 57.85$$

∴ The rate increases by a factor of ~58!

What if: Rate is 5X faster than Rate 1

$$\frac{Rate\ 2}{Rate\ 1} = 5 \Longrightarrow \ln\left(\frac{Rate\ 2}{Rate\ 1}\right) = \ln 5$$

Some things to note:

- Be very careful to have E_a in energy units **J**, not **kJ**; because **8.314** is **J mol^{-1} K^{-1}**
- Remember to convert °C to K
- Remember that E_a must be positive: if you get a negative answer, you have two terms in the equation reversed.

- As we saw previously, we could determine the Activation Energy by plotting a graph........

$$k = A\, e^{-E_a/RT} \Rightarrow \ln k = \ln A - \frac{E_a}{RT}$$

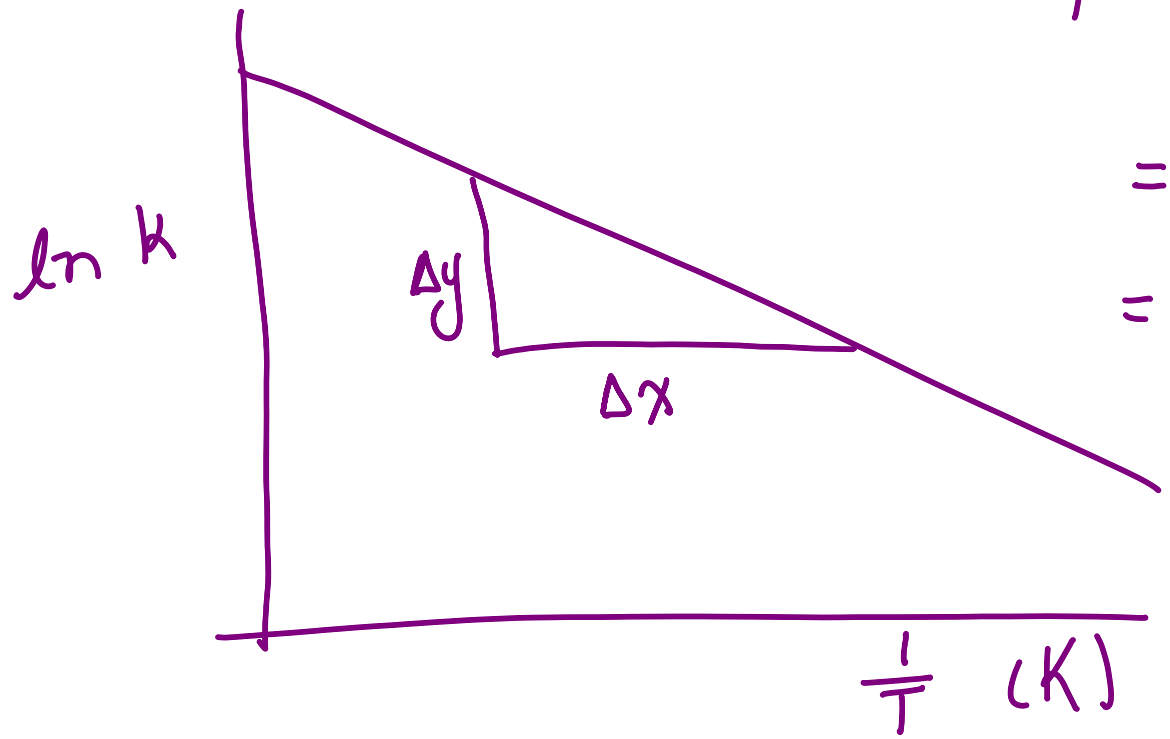
Rearrange: $\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$

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

$$\text{Slope} = \frac{\Delta y}{\Delta x}$$

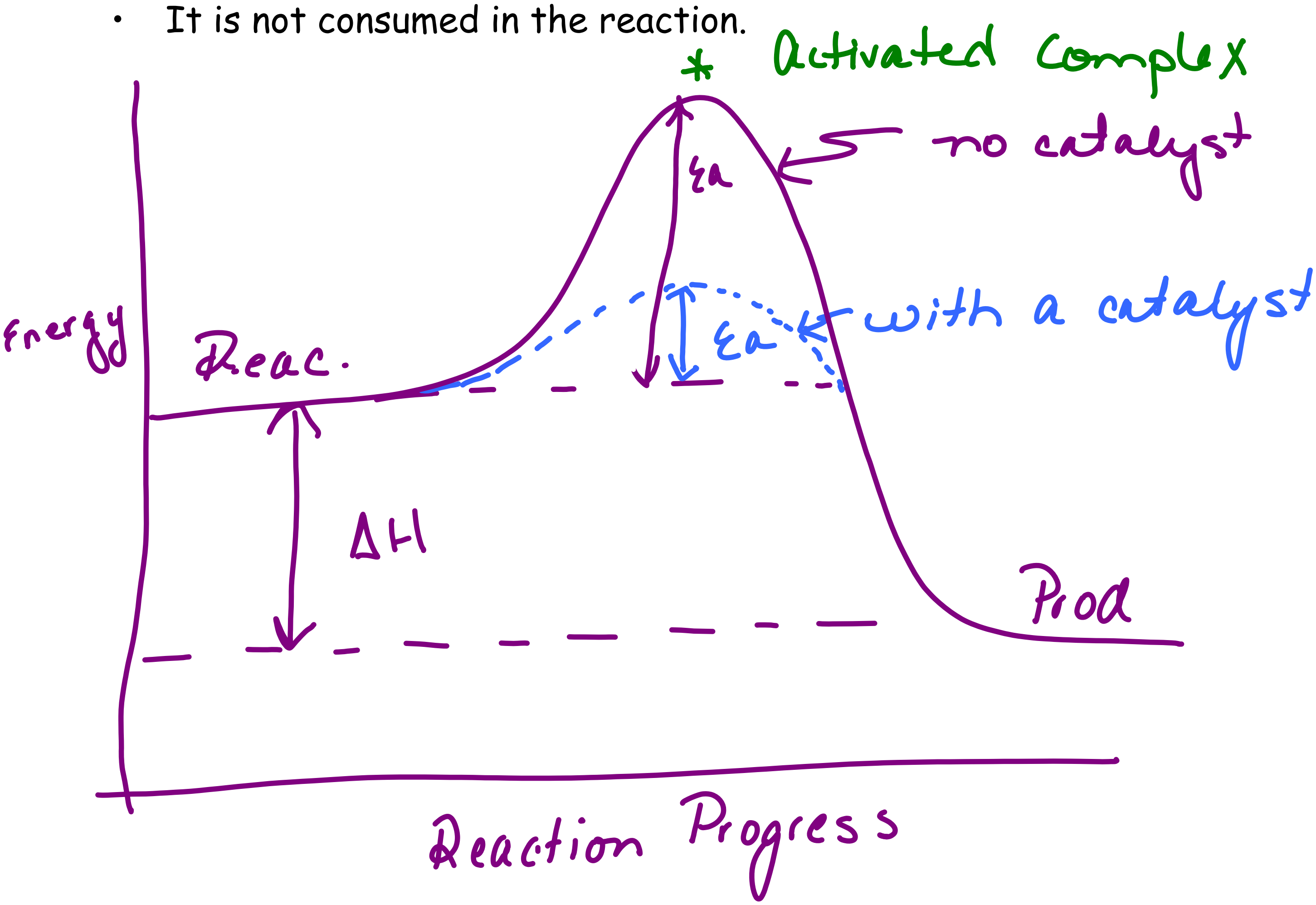
$$= m$$

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



Effect of a Catalyst [MH5; 11.6]

- A catalyst speeds up a reaction by providing an alternate pathway with a lower activation energy.
- It is not consumed in the reaction.



- Suppose E_a changes from $\overset{\text{uncat.}}{E_a(1)}$ to $\overset{\text{catalyzed}}{E_a(2)}$ when a catalyst is used.
- The temperature is kept constant.

$$\frac{\text{Rate }(2)}{\text{Rate }(1)} = \frac{\cancel{A}\, e^{-Ea_2/RT}\ \cancel{[A]}^a\ \cancel{[B]}^b}{\cancel{A}\, e^{-Ea_1/RT}\ \cancel{[A]}^a\ \cancel{[B]}^b}$$

$$\ln\left(\frac{\text{Rate } 2}{\text{Rate } 1}\right) = -\frac{Ea_2}{RT} - \left(-\frac{Ea_1}{RT}\right)$$

$$= \frac{Ea_1}{RT} - \frac{Ea_2}{RT}$$

$$\boxed{\ln\left(\frac{\text{Rate } 2}{\text{Rate } 1}\right) = \frac{Ea_1 - Ea_2}{RT}}$$

NOTE: Ea_1 is uncatalyzed rxn
Ea_2 is catalyzed rxn

$$Ea_1 > Ea_2$$

$$Ea_1 - Ea_2 = \Delta Ea$$

EXAMPLE 1:

A catalyst lowers E_a for a reaction from 85.0 to 70.5 kJ mol^{-1} at 27°C. If the rate of the uncatalyzed reaction is 2.00 x 10^{-3} mol $L^{-1}s^{-1}$, what is the rate of the catalyzed reaction ?

$$\ln\left(\frac{\text{Rate 2}}{\text{Rate 1}}\right) = \frac{Ea_1 - Ea_2}{RT}$$

$$\ln\left(\frac{\text{Rate 2}}{2.00 \times 10^{-3}}\right) = \frac{85000 - 70500}{8.314 \times 300}$$

$$= 5.813$$

$$\frac{\text{Rate 2}}{2.00 \times 10^{-3}} = e^{5.813}$$

$$= 334.6$$

$$\therefore \text{Rate} = \underline{0.669} \text{ mol } L^{-1}s^{-1}$$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = 334.6$$

EXAMPLE 2: $\nearrow Ea_1$

A reaction has E_a = 60.0 kJ mol^{-1} at 27°C. A catalyst speeds up reaction by a factor 10^6. What is E_a with the catalyst present ?

$\hookrightarrow Ea_2$?

Rate (1) = 1 , then Rate (2) = 10^6

$$\ln\left(\frac{\text{Rate }(2)}{\text{Rate }(1)}\right) = \frac{Ea_1 - Ea_2}{RT}$$

$$\ln\left(\frac{10^6}{1}\right) = \frac{60{,}000 - Ea_2}{8.314 \times 300}$$

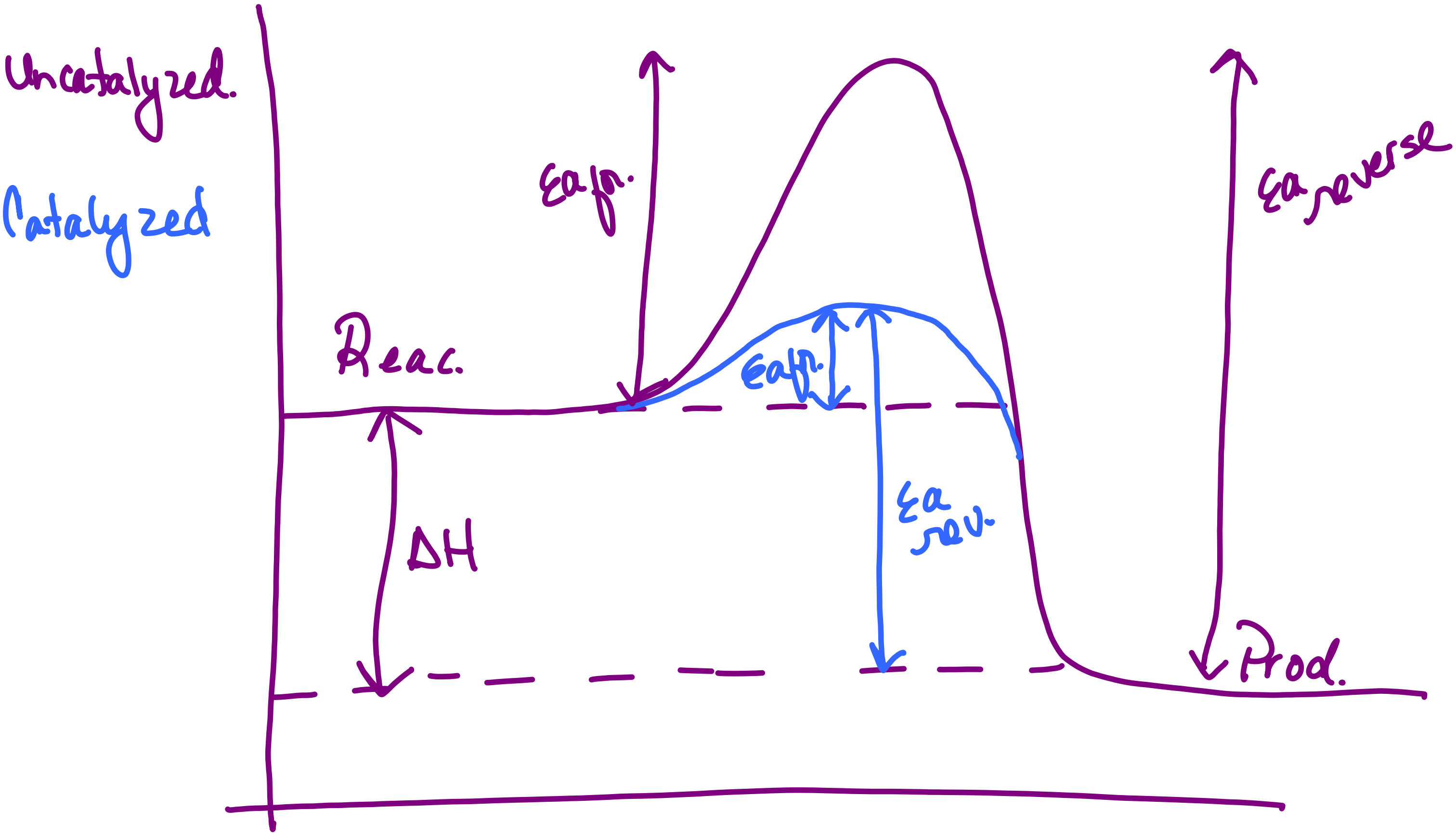
$$13.8 = \frac{60{,}000 - Ea_2}{8.314 \times 300}$$

$$34420 = 60{,}000 - Ea_2$$

$$\therefore Ea_2 = \underline{\underline{25580}} \text{ J mol}^{-1}$$

Things to Note....

- A catalyst cannot **decrease** the rate of a reaction; the original (uncatalyzed) pathway is always available.
- A catalyst has no effect on ΔH for a reaction.
- A catalyst cannot alter the final equilibrium position; both forward and reverse reactions speed up.
- A catalyst enables the system to reach equilibrium more rapidly.
- The factor by which the reactions speed up depends only on the change in E_a and this is the same for both reactions.



- At equilibrium, the reaction is proceeding at the same rate in each direction, where k_f and k_r are the rate constants for the forward and reverse reactions respectively.
- What happens when a catalyst is added ? Both rates are increased, as $E_a(f)$ and $E_a(r)$ are both reduced...

Reaction Mechanisms [MH5; 11.7]

- What is actually happening at the molecular level when reaction occurs ? Which atoms are colliding to produce the reaction?
- A **reaction mechanism** describes the sequence of reactions that the molecules follow.......
- The simplest example is one where there is only one step involved......

$$\mathbf{CO\ (g) + NO_2\ (g) \rightarrow NO\ (g) + CO_2\ (g)} \quad \text{(Temp > 600 K)}$$

- What happens if the temperature is lower than 600 K? The reaction takes place in two steps:

Step 1) $NO_2\ (g) + \cancel{NO_2}\ (g) \rightarrow \cancel{NO_3}\ (g) + NO\ (g)$ (slow)

Step 2) $CO\ (g) + \cancel{NO_3}\ (g) \rightarrow CO_2 + \cancel{NO_2}\ (g)$ (fast)

Overall: $CO + NO_2 \rightarrow CO_2 + NO$

- Even though the route is different, the eventual destination is the same.....the overall reaction does not change.

- The Rate Laws for these two processes are different though.....

- At High Temperatures: Rate = $k\,[CO]\,[NO_2]$
- At Low Temperatures: Rate = $k\,[NO_2]^2$

- The Rate Law (and therefore reaction order) depends on the mechanism by which the reaction occurs.
- The Rate Law can be determined from the reaction mechanism.

- A mechanism may consist of several steps; each one is called an **elementary step**.
- The term **molecularity** may be used to describe the number of reactant molecules participating in each step.
- A **unimolecular** process is one that involves only one molecule and no collision occurs; for example;

$$NO_2C\ell\,(g) \rightarrow NO_2(g) + C\ell\,(g)$$

- In a **bimolecular** reaction, two molecules must collide for reaction to occur; these molecules may be identical or different.....

$$NO_2C\ell\,(g) + C\ell\,(g) \rightarrow NO_2\,(g) + C\ell_2\,(g)$$

- In an elementary step, the rate of that step is equal to the rate constant (k) multiplied by the concentration of each reactant molecule.
- The rate of collision (and therefore, rate of reaction) is directly proportional to the concentration of each reactant.......

Rate Laws for General Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \rightarrow$ prod	unimolecular	Rate = $k\,[A]$
$A + A \rightarrow$ prod	Bimolecular	Rate = $k\,[A]^2$
$A + B \rightarrow$ prod.	Bimolecular	Rate = $k\,[A]\,[B]$
$A + B + C \rightarrow$ prod	Termolecular	Rate = $k\,[A]\,[B]\,[C]$

- Consider the reactions involving $NO_2C\ell$ (g) from the previous page……
- These reactions make up the reaction mechanism for the decomposition of $NO_2C\ell$ (g).

Step 1) $\mathbf{NO_2C\ell\ (g) \rightarrow NO_2(g) + \cancel{C\ell}\ (g)}$

Step 2) $\mathbf{NO_2C\ell\ (g) + \cancel{C\ell}\ (g) \rightarrow NO_2\ (g) + C\ell_2\ (g)}$

- What is the Rate Law for Step 1) ?

$$Rate_1 = k_1 [NO_2 Cl]$$

- What is the Rate Law for Step 2) ?

$$Rate_2 = k_2 [NO_2 Cl][Cl]$$

- What is the overall reaction ?

$$2 NO_2 Cl \longrightarrow 2 NO_2 + Cl_2$$

- The Rate Law for the overall reaction ?

$$Rate = k [NO_2 Cl]^x$$

- overall rxn NOT an elementary step!

- The **$C\ell$ (g)** that appeared in both steps is called a **reaction intermediate**; a species that is formed and then consumed.
- Intermediate species never appear in the overall reaction, and therefore, do not appear in the Rate Law for the overall reaction.

- So how do we go about determining the rate law from the reaction mechanism ?

- First, we need a bit more information about the elementary steps.
- Do any of the steps involve an equilibrium between reactants and products, and at what stage in the mechanism do they occur?

- In a mechanism there will always be one step that is slower than all the others; this is known as the **Slow**, or **Rate Determining Step**.
- This step is ultimately responsible for the rate of the overall reaction.

- The following mechanism give us the information we need.....

Step 1) $NO\,(g) + NO\,(g) \rightleftharpoons \cancel{N_2O_2}\,(g)$ (Fast)

Step 2) $\cancel{N_2O_2}(g) + O_2\,(g) \rightarrow 2\,NO_2\,(g)$ (Slow)

- We could write the Rate Law for each of these elementary steps...
- **BUT**, the Rate Law for any reaction **must** be written in terms of the Overall Reaction, which is:

$$2NO + O_2 \rightarrow 2\,NO_2$$

- Rate Law for the overall reaction:

$$Rate = k\,[NO]^x\,[O_2]^y$$

- Are there any reaction intermediates ? It's important to be able to recognize these!

N_2O_2 : - formed in Step 1
- consumed in Step 2

- To determine the rate law from a mechanism, we **always** begin by writing the rate law for the slow, or rate determining step.

$$\text{Rate}_2 = k_2 [N_2O_2][O_2]$$

- Compare this to the form of the rate law for the overall reaction; it probably won't match! What is the problem species ?

- intermediate species N_2O_2 present
- reactant NO not present

- Look at the step(s) occurring before the slow step.......one of them must contain the N_2O_2 intermediate.
- Is this step an equilibrium? For an equilibrium:

Rate forward = Rate reverse

$$k_1 [NO]^2 = k_{-1} [N_2O_2]$$

- Rearrange to isolate the intermediate species......

$$[N_2O_2] = \frac{k_1}{k_{-1}} [NO]^2$$

- Now substitute for the intermediate in the rate law for the slow step: Slow step: $\text{Rate}_2 = k_2[N_2O_2][O_2]$

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

$$\therefore \text{Rate} = k_2 \boxed{\frac{k_1}{k_{-1}}[NO]^2} [O_2]$$

↳ subbed for $[N_2O_2]$

$$= \underline{k'[NO]^2[O_2]}$$

- The rate law determined from this mechanism is consistent with the experimentally observed Rate Law.
- It is not usually possible to "prove" that a suggested mechanism is correct; only that it is consistent.
- However, an equilibrium where two molecules associate to give a short-lived, reactive intermediate such as N_2O_2 above is quite common.

- What happens if a reactant has to dissociate for reaction to occur ?

EXAMPLE: $Rate = k[Cl_2]^x[CO]^y$

Synthesis of phosgene (the overall reaction):

$$Cl_2(g) + CO(g) \rightarrow COCl_2(g)$$

Suppose the reaction occurs in 3 steps:

1) $Cl_2(g) \rightarrow Cl(g) + Cl(g)$

2) $CO(g) + Cl(g) \rightarrow COCl(g)$

3) $COCl(g) + Cl_2(g) \rightarrow COCl_2(g) + Cl(g)$

What rate law would be expected IF:

(i) 1 is slow, and 2 and 3 are fast.

$Rate\ 1 = k_1[Cl_2]$

$\therefore x = 1$

$y = 0$ (So $[CO]$ does not appear in Rate Law)

- Over reasonable limits, the concentration of CO does not affect the rate.
- Any step occurring **after** the Slow step has no effect on the Rate of the reaction, and therefore, no effect on the Rate Law.

(ii) 1 is a fast equilibrium, 2 is slow (RDS) and 3 is fast.

- For step 1: $Cl_2 \rightleftharpoons 2Cl$

Rate forward = Rate reverse

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

- Step 2 is the RDS: $CO + Cl \rightarrow COCl$

$$\text{Rate } 2 = k_2[CO][Cl]$$

Compare to Rate Law for overall reaction

Use Eq Step 1 to substitute for [Cl]:

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

Substitute for [Cl] in slow step:

$$\text{Rate} = k_2[CO]\underbrace{\overbrace{\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{1/2}}}$$

$$= k'[CO][Cl_2]^{1/2}$$

$x = 1/2$

$y = 1$

- A rate law in which a reactant has an exponent of 0.5 results from a dissociative equilibrium.

Overall: $\text{Rate} = k[\text{Cl}_2]^x[\text{CO}]^y$

(iii) 1 and 2 are both fast equilibria while 3 is the slow rate-determining step?

For step 3: $\text{Rate} = k_3[\text{COCl}][\text{Cl}_2]$

COCl is an intermediate formed in step 2 ...

EQ step 2: $k_2[\text{CO}][\text{Cl}] = k_{-2}[\text{COCl}]$

$$\therefore [\text{COCl}] = \frac{k_2}{k_{-2}}[\text{CO}][\text{Cl}]$$

Substitute for [COCl] in slow step:

$$\text{Rate} = k_3\frac{k_2}{k_{-2}}[\text{CO}]\underline{[\text{Cl}]}[\text{Cl}_2]$$

Substitute for $\underline{[\text{Cl}]}$, using EQ 1 as before:

$$\text{Rate} = k_3\frac{k_2}{k_{-2}}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[\text{CO}][\text{Cl}_2]^{1/2}[\text{Cl}_2]$$

$$= k'[\text{CO}][\text{Cl}_2]^{1.5}$$

$x = 1.5$

$y = 1$

- What happens if the reaction is catalyzed ?
- Recall that a catalyst is present at the beginning of the reaction and can be retrieved at the end of the reaction...therefore a catalyst does not appear in the overall reaction.
- But it **may** appear in the rate law!

EXAMPLE 3:

The proposed mechanism for a reaction is:

1) $A\,(g) + \enclose{circle}{B}\,(g) \rightleftharpoons \cancel{XY}\,(g)$ [fast]

2) $\cancel{XY}\,(g) + C\,(g) \rightarrow \cancel{D}\,(g)$ [slow]

3) $\cancel{D}\,(g) \rightarrow E\,(g) + \enclose{circle}{B}\,(g)$ [fast]

- What is the overall reaction ?

  $A + C \longrightarrow E$

- What are the intermediate species ?

  XY, D

- Is there a catalyst ? yes; B

Overall : $\text{Rate} = k\,[A]^x[C]^y$

- What is the rate law ?

Slow Step : $\text{Rate} = k_2\,[XY][C]$

XY is an intermediate formed in Step 1

Eq step 1: Rate forward = Rate reverse

$$k_1\,[A][B] = k_{-1}\,[XY]$$

$$\therefore [XY] = \frac{k_1}{k_{-1}}\,[A][B]$$

Substitute for [XY] in slow step:

$$\text{Rate} = k_2\,\overbrace{\underbrace{\frac{k_1}{k_{-1}}\,[A][B]}}\,[C]$$

$$= k'\,[A]\underline{[B]}[C]$$

$x = 1$
$y = 1$

Catalyst B appears in Rate Law, which is okay!