Chemical Kinetics

Kinetics studies:

The rates at which chemical reactions take place

What influences the rates of reactions

How reactions proceed with time (the reaction's *"mechanism")*

Reaction Rates

expressed as the rate of appearance of a product
or the rate of disappearance of a reactant

For

$$A + B \longrightarrow C + D$$

the rate of disappearance of A

$$-\frac{\Delta [A]}{\Delta t}$$

Appearance of Products

$$+\frac{\Delta[C]}{\Delta t}$$

since the mol relationship is 1 : 1 in the balance equation

the rate of disappearance of A must equal the rate of appearance of C

$$A + B \longrightarrow C + D$$

$$\frac{\Delta[C]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

General Equation Relationship

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

An Analogy

Given the following recipe:

2 cups flour + 3 teaspoons yeast + 1 cup water = 1 loaf bread

rate of appearance of 1 loaf
= 1/2 rate of disappearance of cups of flour
= 1/3 rate of disappearance of teaspoons of yeast
= rate of disappearance of cups of water

A Specific Example

$$H_{2(g)} + 2\ ICl_{(g)} \longrightarrow I_{2(g)} + 2\ HCl_{(g)}$$

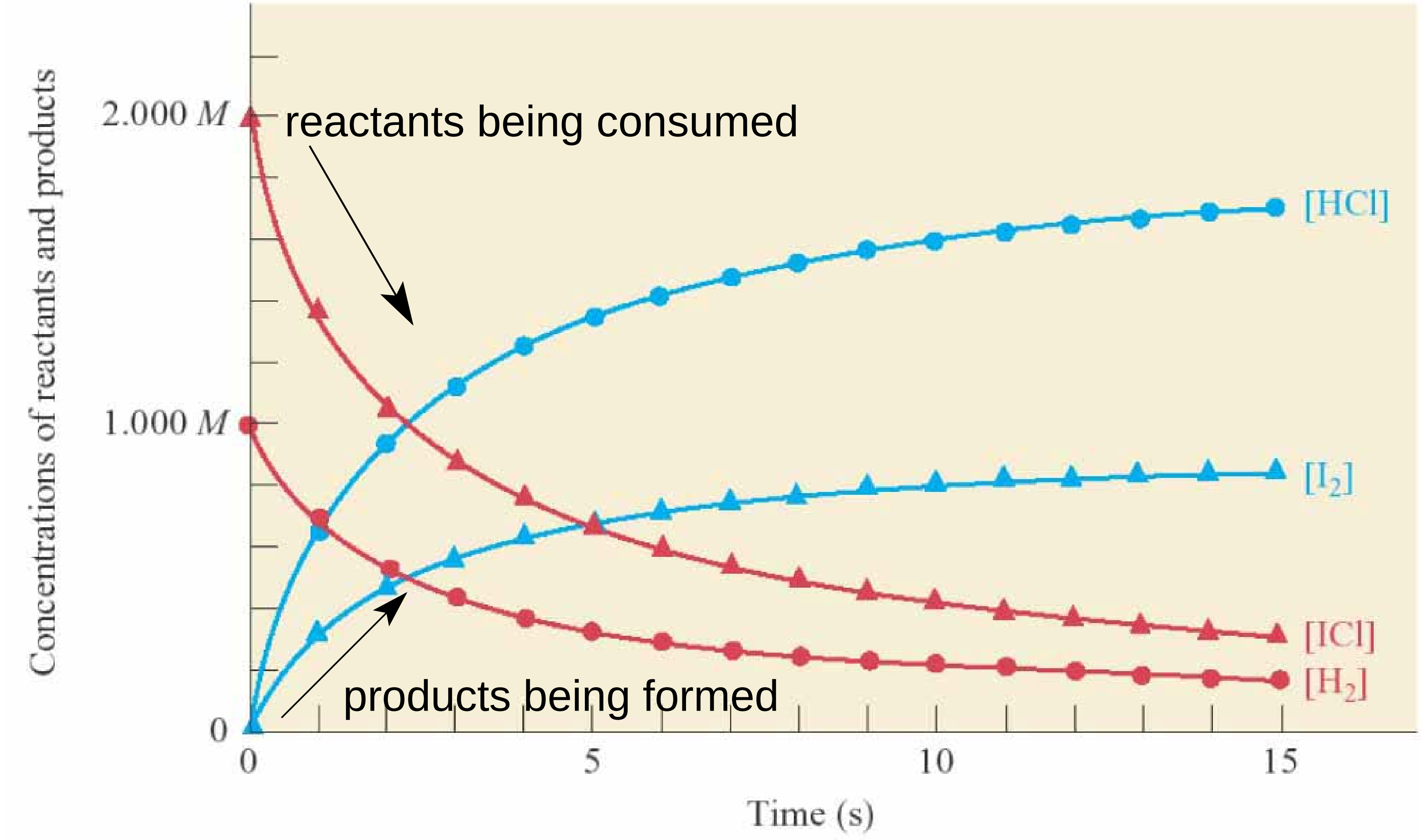
note that the rate at which I_2 is being formed is half of the rate at which HCl is being formed

Q1

Write the general equation relationship for the previous equation

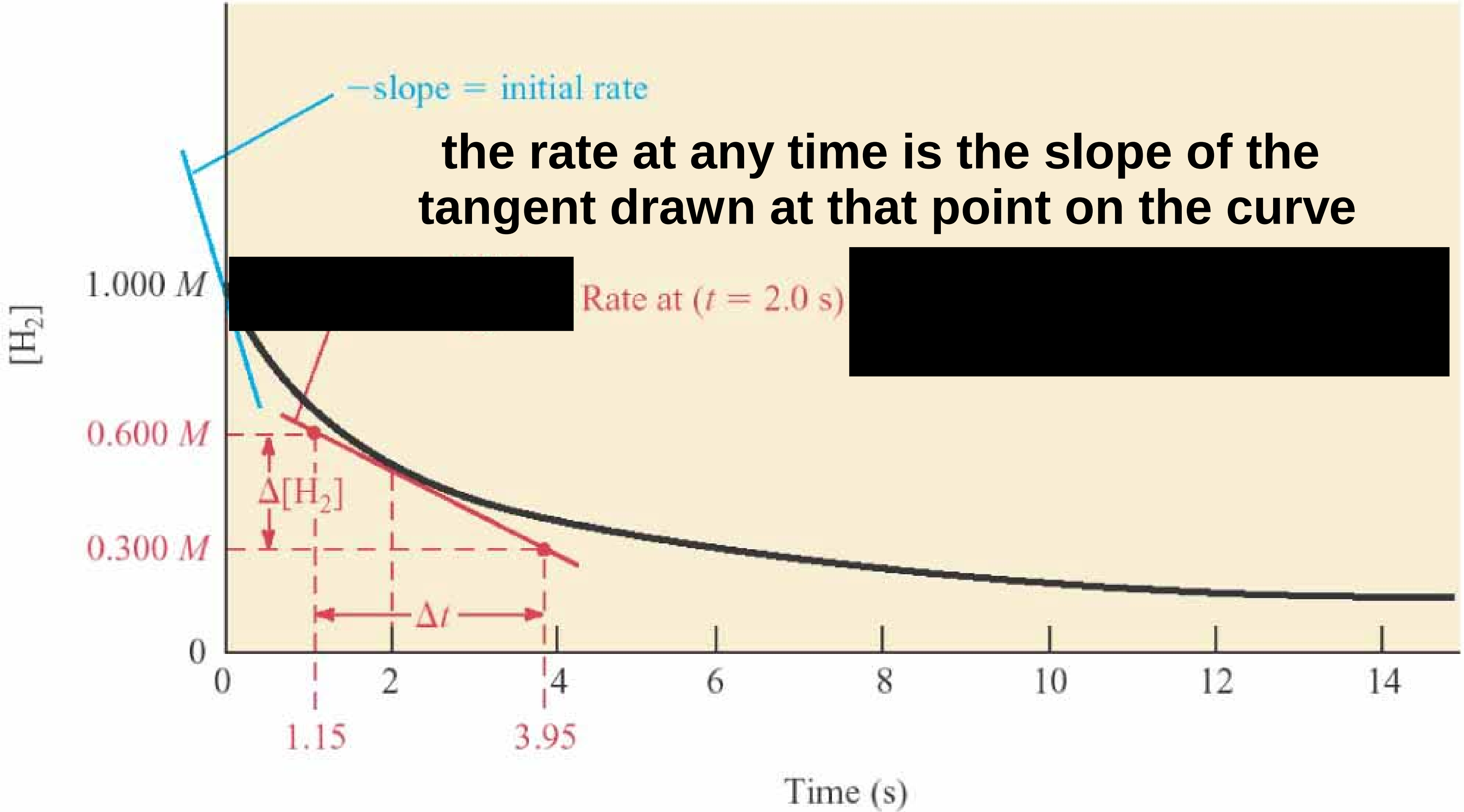
$$H_{2(g)} + 2\ ICl_{(g)} \longrightarrow I_{2(g)} + 2\ HCl_{(g)}$$

Graph of 2.00M ICL reacting with 1.00M H_2



H_2 Curve

the rate at any time is the slope of the tangent drawn at that point on the curve



Rate Law Expressions

How much influence a particular reactant's concentration affects the initial rate of a reaction

for

$$2A + 3B \longrightarrow C + 2D$$

the rate equation was determined to be:

$$\frac{\Delta [C]}{\Delta t} = k [A] [B]^2$$

Continuing

$$\frac{\Delta [C]}{\Delta t} = k [A] [B]^2$$

doubling the initial concentration of A
should double the initial rate at which the reaction occurs
(all other things held constant)

doubling the initial concentration of B
should quadruple (4X) the initial rate at which the reaction occurs
(all other things held constant)

Example

What should tripling (3X) the initial concentration of A and halving (1/2X) the initial concentration of B do to the rate?

$$\frac{\Delta [C]}{\Delta t} = k [A] [B]^2$$

Q2

given $$\left(\frac{\Delta[E]}{\Delta t}\right) = k\,[F]^2\,[G]$$

What should dividing the intial concentration of F by 3
and doubling the initial concentration of G do to the overall rate?

"0" order

means the rate is **NOT** influenced at all by changing the intial concentration of that reactant

for

$$2A + B \longrightarrow C + 2D$$

the rate equation was determined to be:

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

Notice that [B] is not in the rate equation

remember that $x^0 = 1$

so $[B]^0 = 1$

Method of Initial Rates

Used to determine the rate equation for a reaction

$$2A + B \longrightarrow C + 2D$$

Experiment	Initial [A]	Initial [B]	Initial $\frac{\Delta [C]}{\Delta t}$
1	0.010M	0.010M	2.0×10^{-3} Mmin^{-1}
2	0.020M	0.010M	4.0×10^{-3} Mmin^{-1}
3	0.020M	0.020M	8.0×10^{-3} Mmin^{-1}

Continuing

Experiment	Initial [A]	Initial [B]	Initial $\frac{\Delta [C]}{\Delta t}$
1	0.010M	0.010M	$2.0 \times 10^{-3} M min^{-1}$
2	0.020M	0.010M	$4.0 \times 10^{-3} M min^{-1}$
3	0.020M	0.020M	$8.0 \times 10^{-3} M min^{-1}$

The Rate Equation

1st order in A

1st order in B

$$\frac{\Delta [C]}{\Delta t} = k [A] [B]$$

the rate constant for this reaction

Q3

Determine the rate equation from the following data

Experiment	Initial [A]	Initial [B]	Initial $\frac{\Delta [F]}{\Delta t}$
1	0.15M	0.15M	3.90×10^{-3} Ms^{-1}
2	0.15M	0.30M	7.80×10^{-3} Ms^{-1}
3	0.30M	0.60M	6.24×10^{-2} Ms^{-1}

How to calculate "order"

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

for A:

$$x = \frac{\ln(\Delta\ \text{rate})}{\ln(\Delta\ \text{concentration})}$$

An Example

Experiment	Initial [A]	Initial $\frac{\Delta [C]}{\Delta t}$
1	0.0100M	4.50×10^{-3} Mmin^{-1}
2	0.0150M	1.01×10^{-2} Mmin^{-1}

$$x = \frac{\ln(\Delta \text{ rate})}{\ln(\Delta \text{ concentration})}$$

$$\text{change in rate} = \frac{1.01 \times 10^{-2}}{4.50 \times 10^{-3}} = 2.24$$

$$\text{change in [A]} = \frac{0.0150}{0.0100} = 1.50$$

Q4
Determine the order wrt A

Experiment	**Initial [A]**	**Initial $\frac{\Delta [C]}{\Delta t}$**
1	0.240M	$3.44x10^{-3}$ Mmin^{-1}
2	0.408M	$9.94x10^{-3}$ Mmin^{-1}

Concentration vs. Time

A way to determine the concentration of a reactant left after any time period

Integrated Rate Equations

for a 1st order reaction

$$a\,A \longrightarrow \text{products}$$

the integrated rate equation is:

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = a\,k\,t$$

Q5

For the reaction:

$$2\ N_2O_5 \longrightarrow 2\ N_2O_4 + O_2$$

The reaction is first order and $k = 8.40 \times 10^{-3} s^{-1}$

If 0.500M N_2O_5 is allowed to react

a. what would be the concentration of N_2O_5 in 1.00 minute?

b. how many seconds to reduce the amount of N_2O_5 by 90.0%?

Part b.

$$\ln\left(\frac{[N_2O_5]_0}{[N_2O_5]_t}\right) = a\,k\,t$$

Graphical Considerations

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = a\,k\,t$$

$$\ln [A]_0 - \ln[A]_t = a\,k\,t$$

$$-\ln[A]_t = ak(t) - \ln[A]_0$$

$$\ln[A]_t = -ak(t) + \ln[A]_0$$

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

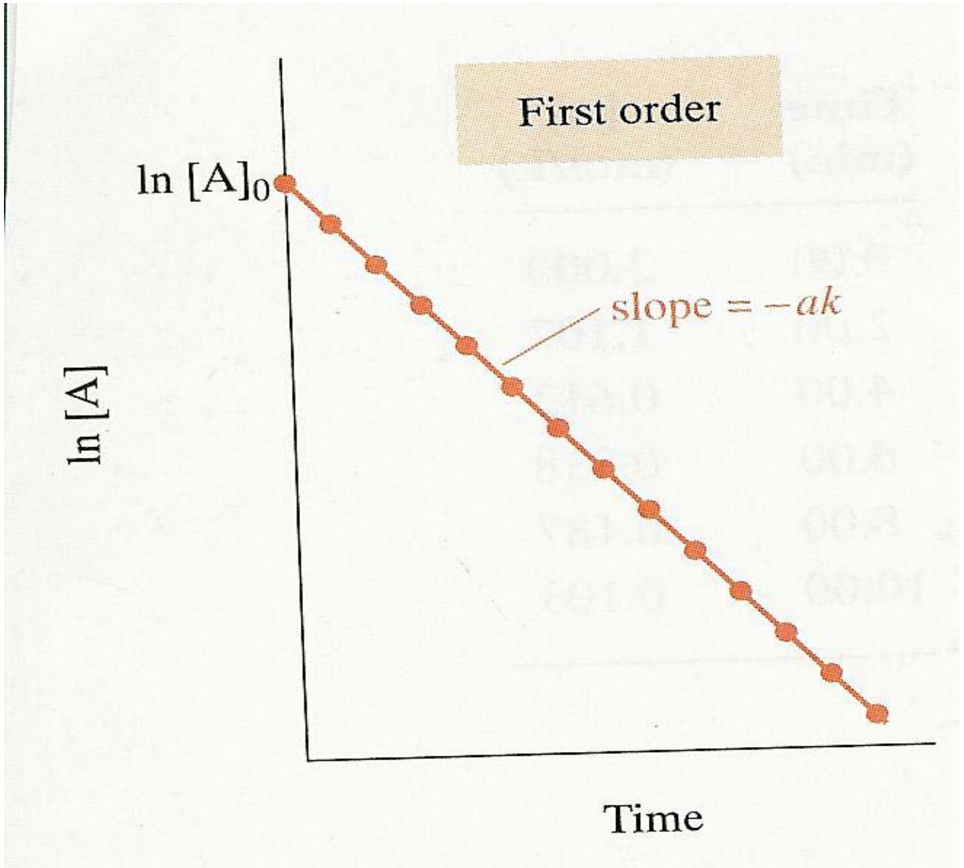
Continuing

$$\ln[A]_t = -ak(t) + \ln[A]_0$$

plot $\ln[A]_t$ vs t ...

the slope will be -ak

and the y intercept is $\ln[A]_0$



Half Life: $t_{1/2}$

the time it takes for half of the reactant to be consumed

1st order reactions:

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = a\,k\,t$$

when half of the reactant has been consumed:

$[A]_t = 1/2\,[A]_0$

substituting in

$$\ln\left(\frac{[A]_0}{1/2[A]_0}\right) = a\,k\,t_{1/2}$$

Q6

according to the first order reaction:

$$N_2O_4 \longrightarrow 2\ NO_2$$

how many minutes would it take for 0.100 mols of N_2O_4 to be reduced to 0.0500 mols? $k = 1.8x10^{-3}\ s^{-1}$

2^{nd} Order Reactions

by similar methods we can derive the following for 2nd order reactions

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = a\ k\ t$$

and:

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

0 Order Reactions

In a "0 order" reaction the rate of reaction is independent of the inital concentration of reactant

many enzymes function under 0 order kinetics

Avocados turn brown when peeled due to an enzyme's action. The rate of browning is independent of how much avocado you leave exposed to air.

The Equations for 0 Order Reactions

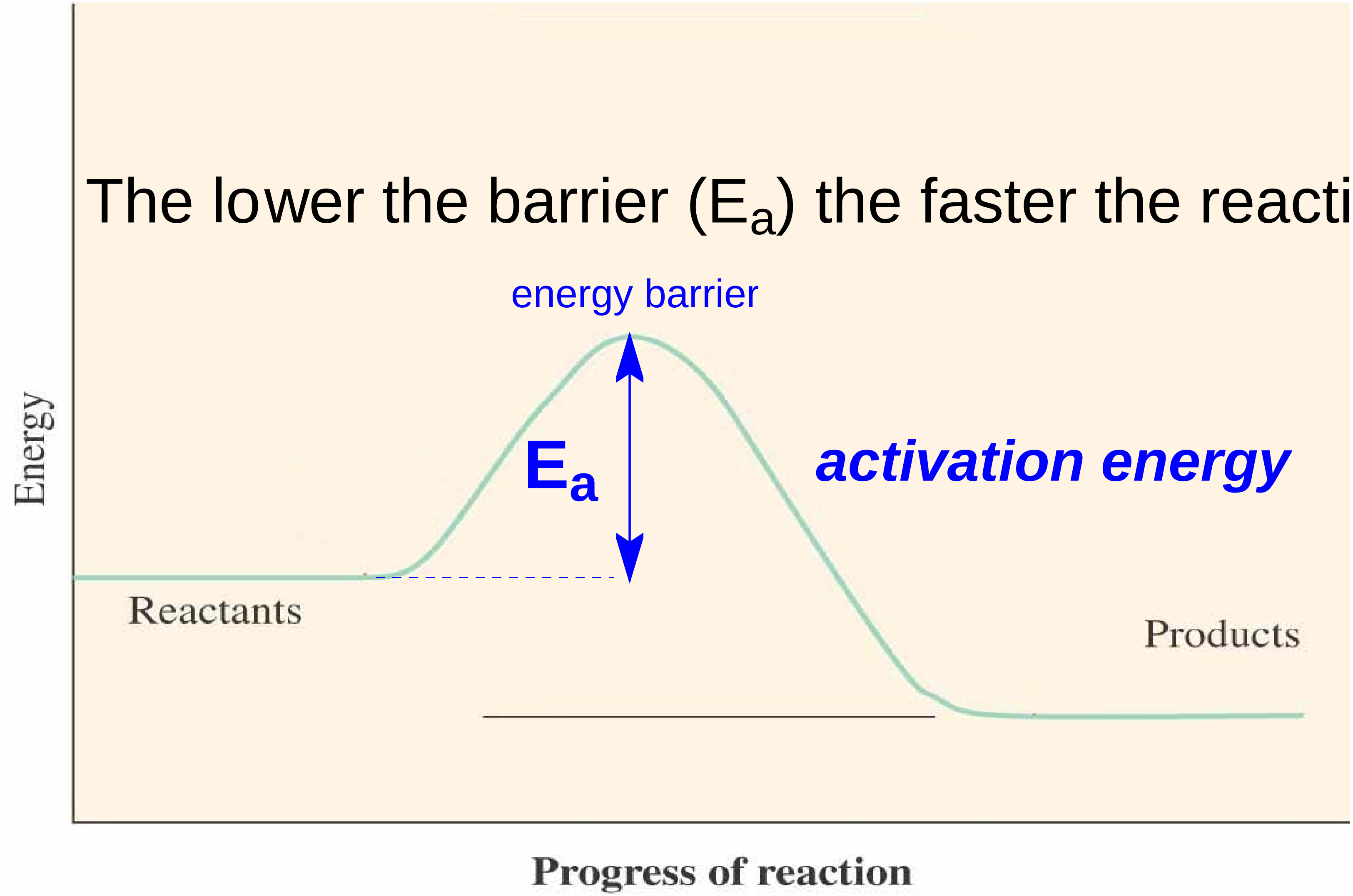
$$[A]_t = [A]_0 - akt$$

and

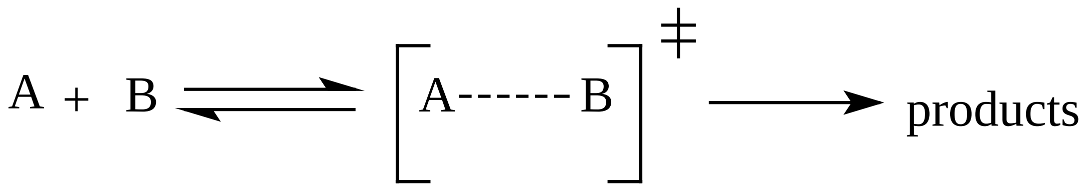
$$t_{1/2} = \frac{[A]_0}{2ak}$$

Reaction Rates and Temperature
The Arrhenius Equation

The lower the barrier (E_a) the faster the reaction



The Transition State

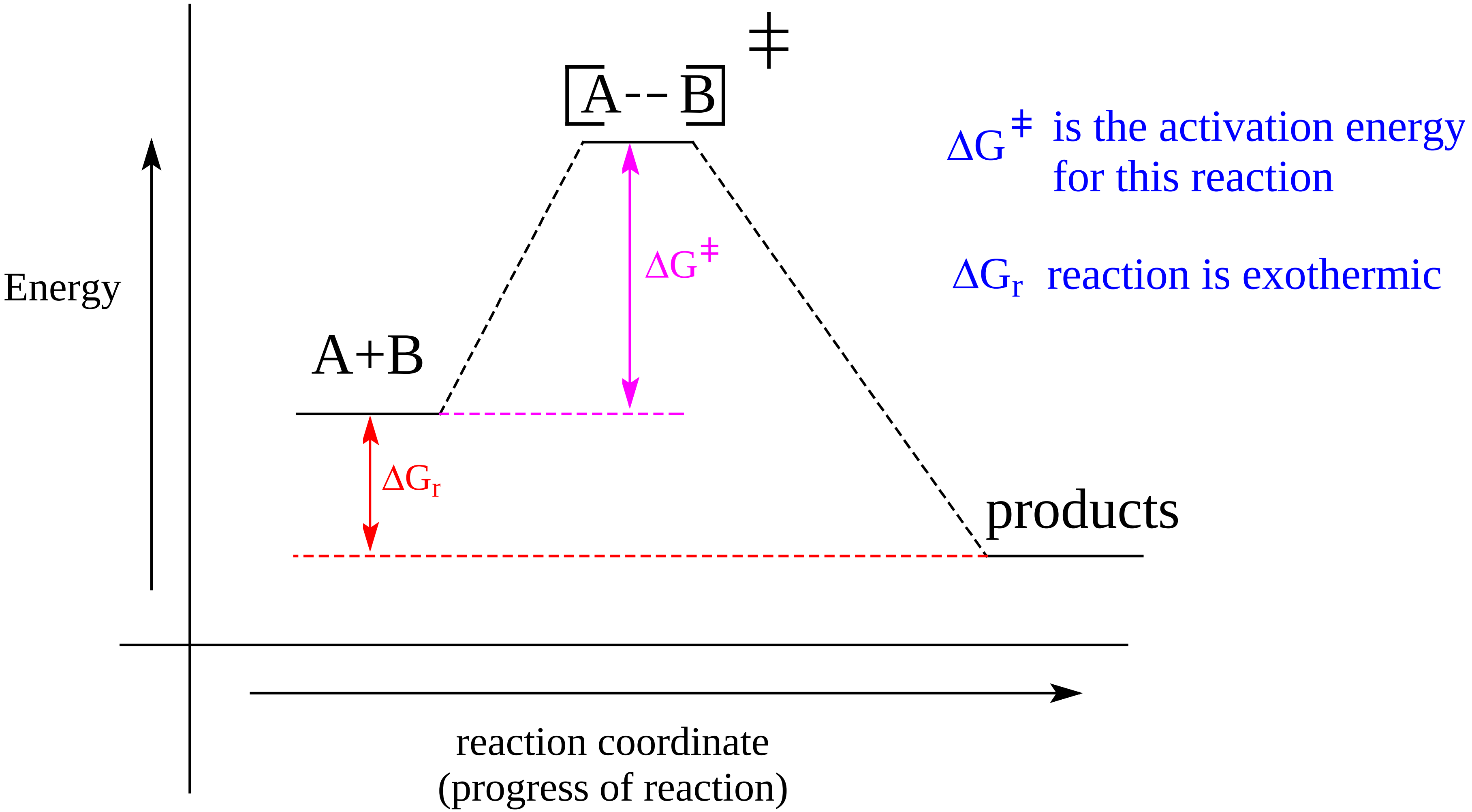


transition state

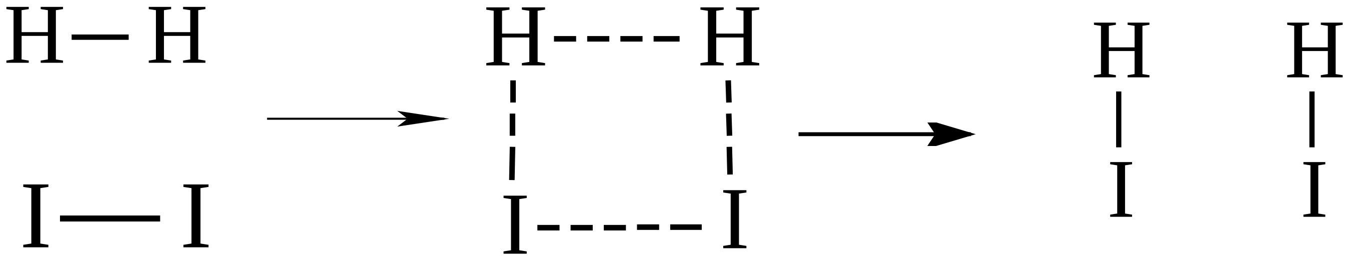
Note: rate is dependent on both A and B

$$\frac{\Delta\,[\text{products}]}{\Delta t} = k\,[A]\,[B]$$

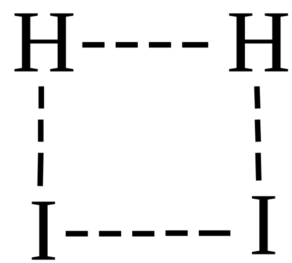
Energy Diagram



an effective collision

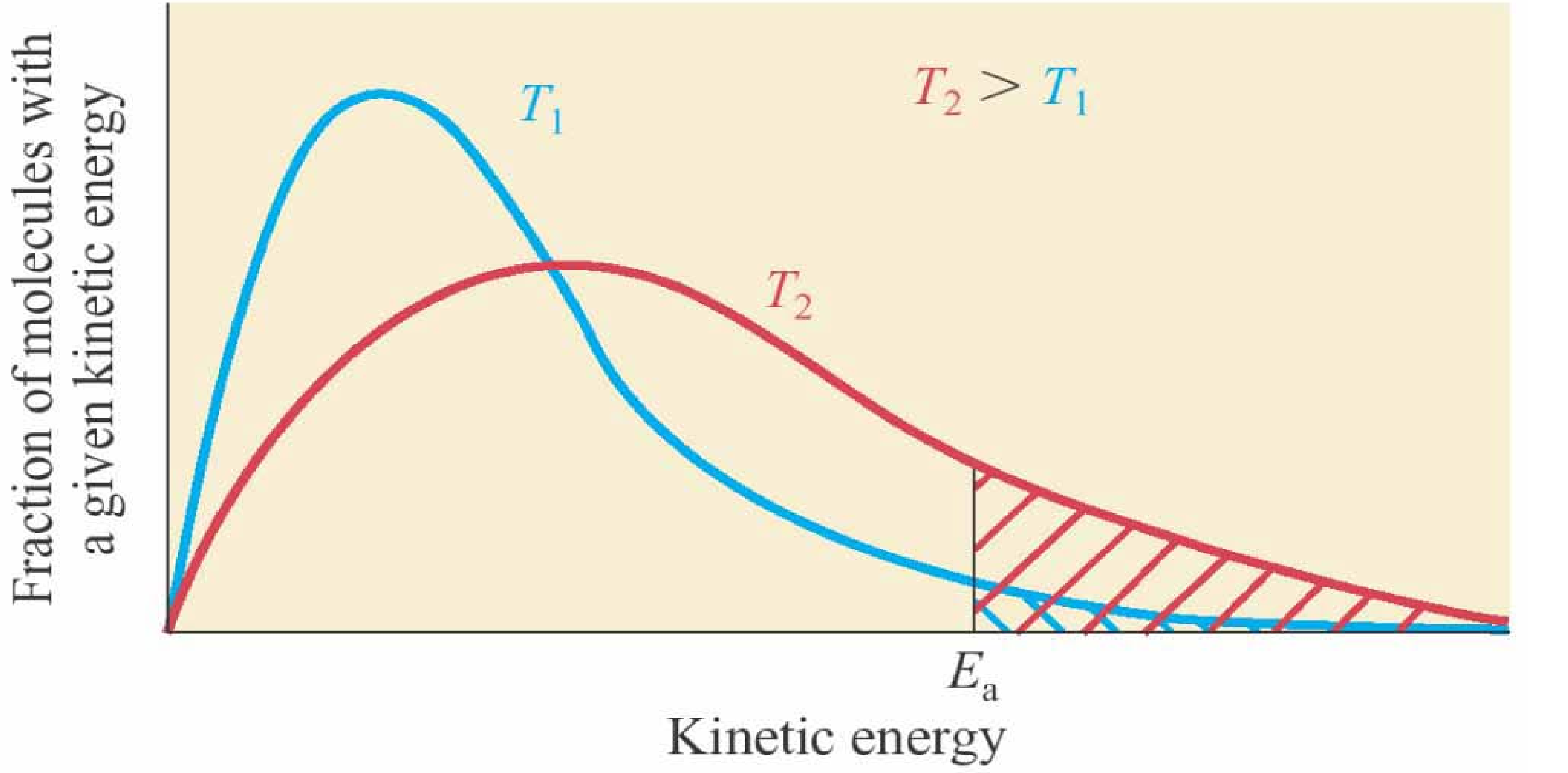


More About the Transition State



Temperature effects

Increasing the temperature increases the average energy of the reactants and the barrier is more easily overcome



The Arrhenius Equation

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

the gas constant

8.314 $Jmol^{-1}K^{-1}$

Graphical Considerations

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

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

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

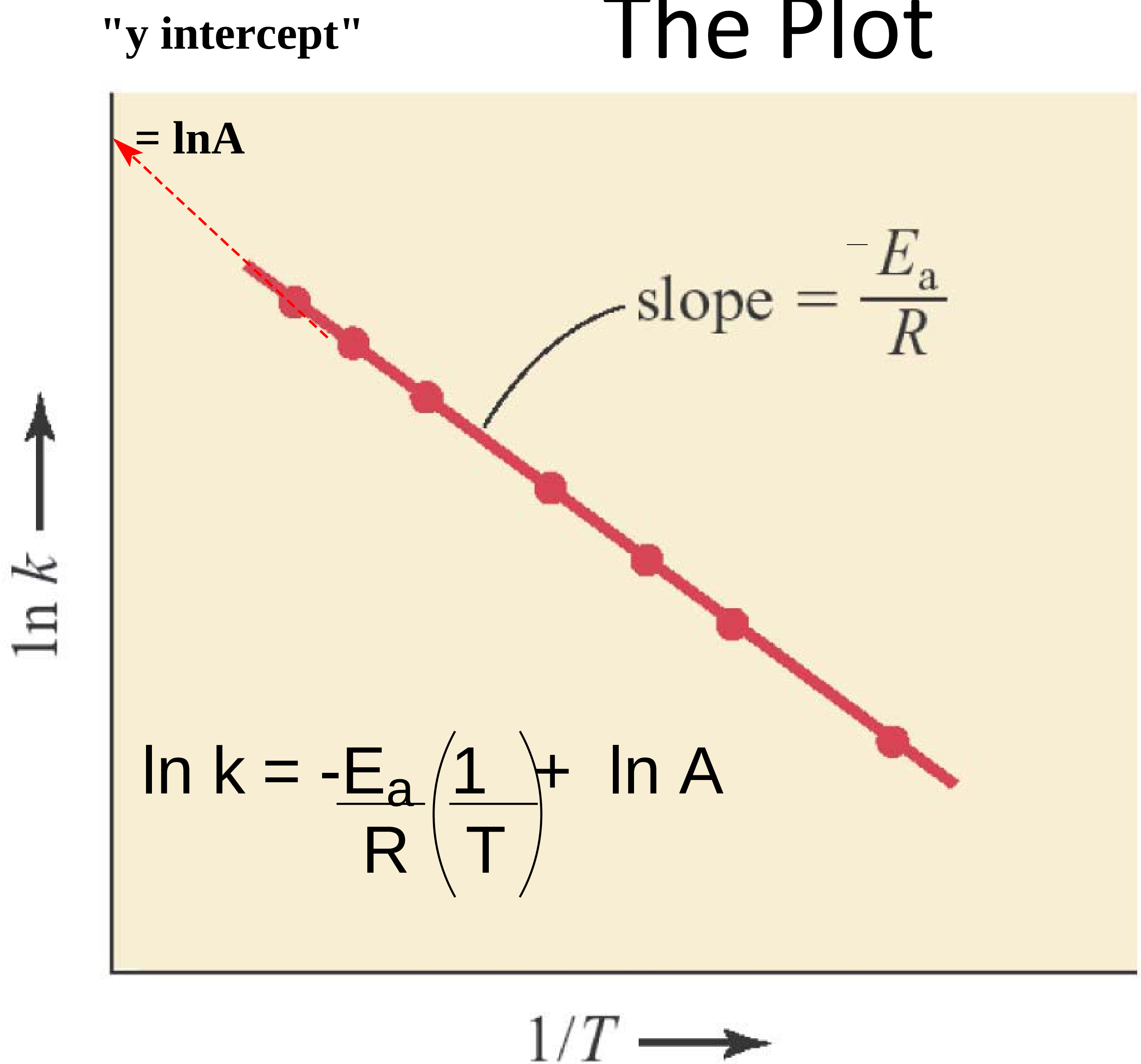
(ln e = 1)

rearrange:

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

$$\mathbf{y} = m\,(x) + b$$

The Plot



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

Temperature Variations

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

A good way to determine activation energies is to measure rate constants at two temperatures

An Example

Calculate E_a for a reaction whose rate constant is $1.60 \times 10^{-5}\ s^{-1}$ at 600. K and $6.36 \times 10^{-3}\ s^{-1}$ at 700. K

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

$$\ln \frac{(6.36 \times 10^{-3}\ s^{-1})}{(1.60 \times 10^{-5}\ s^{-1})} = \frac{E_a}{8.314\ Jmol^{-1}K^{-1}}\left(\frac{1}{600\ K} - \frac{1}{700\ K}\right)$$

$$\ln 398 = \frac{Ea}{8.314\ Jmol^{-1}K^{-1}}(2.38 \times 10^{-4})$$

$$5.986 = \frac{Ea}{8.314\ Jmol^{-1}K^{-1}}(2.38 \times 10^{-4})$$

Q7

For a reaction, E_a = 103 kJ/mol. If the rate constant is 0.0850 min^{-1} at 273^oC, what would it be at 383^oC?

Reaction Mechanisms: How Reactions Take Place

Consider the overall reaction:

$$NO_2 + CO \longrightarrow NO + CO_2$$

At first glance it seems that one molecule of NO_2 should collide with one molecule of CO.

If that is true, then the rate equation should be:

$$\frac{\Delta[CO_2]}{\Delta t} = k\,[NO_2]\,[CO]$$

Rate equations can only contain reactants that are in the "rate determining steps" of a reaction.

Rate determining steps are the **slow steps** of a reaction.

Continuing

The rate equation was determined experimentally:

$$\frac{\Delta[CO_2]}{\Delta t} = k\,[NO_2]^2$$

The Proposed Mechanism

$$NO_2 + NO_2 \longrightarrow N_2O_4 \quad (\textit{slow})$$

$$N_2O_4 + CO \longrightarrow NO + CO_2 + NO_2 \quad (\textit{fast})$$

$$NO_2 + CO \longrightarrow NO + CO_2$$

one of the NO_2 cancels
(only one NO_2 in the reaction!)

$$\frac{\Delta[CO_2]}{\Delta t} = k\,[NO_2]^2$$

An Alternate Proposed Mechanism

Is this a reasonable mechanism for the reaction?

$$NO_2 \longrightarrow NO + O \quad \text{(slow)}$$

$$CO + O \longrightarrow CO_2 \quad \text{(fast)}$$

$$NO_2 + CO \longrightarrow NO + CO_2$$