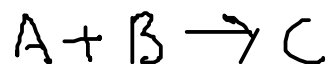


THE RATE LAW

- We express the rate of reaction using an equation called the RATE LAW.



$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k \times [A]^p \times [B]^q$$

This is the RATE CONSTANT. It depends on TEMPERATURE, but does not depend on the CONCENTRATION of any reactant or product.

"p" and "q" are called REACTION ORDERS. They indicate the effect a particular reactant or catalyst has on the rate of a reaction. Reaction orders may be positive, zero (in which case the substance has NO effect on rate) and negative (in which case the substance actually slows the reaction down).

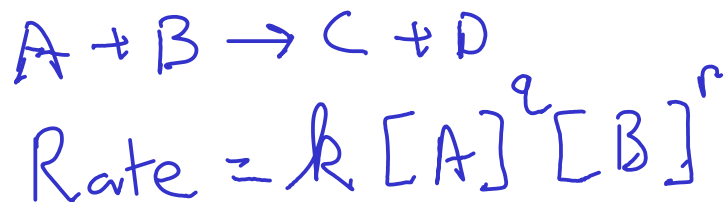
- Rate laws depend on CONCENTRATION of reactants. Since the concentrations of reactants CHANGE throughout the course of the reaction, so does the rate!
- RATE CONSTANTS and REACTION ORDERS are determined experimentally. If you do experiment 13 (the iodine clock reaction), you will see how this can be done in the lab via the INITIAL RATES METHOD.

Initial rates method:

- To determine the rate constant and reaction orders in a reaction, it's possible to monitor the rate of a reaction starting from time zero to a short time later where the concentrations of the reactants haven't changed much. In other words, we look at the INITIAL RATE.

- To determine the rate constant and orders, we need to perform several experiments - one for each order to determine and one baseline experiment to determine the rate constant.

Example:



... we want to find the rate constant 'k', and the orders 'q' and 'r'.

Trial	[A]	[B]	Rate $-\frac{\Delta [A]}{\Delta t}$
1	0.150	0.150	Baseline experiment
2	0.300	0.150	Double (A) to find 'q'
3	0.150	0.300	Double (B) to find 'r'

Trial	[A]	[B]	Rate $-\frac{\Delta[A]}{s}$
1	0.150	0.150	0.0016875
2	0.300	0.150	0.0033750
3	0.150	0.300	0.0067500

Rate doubles (green arrow from trial 1 to 2)
Rate quadruples (orange arrow from trial 1 to 3)

The rate law is:

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

... so how do we use the data above to find out the values of 'k', 'q', and 'r'?

We observe that in the second trial ((A) doubled), the rate has doubled!

$$(2 \times [A])^q = 2 \times \text{Rate} ; q = 1$$

We observe that in the third trial ((B) doubled), the rate has quadrupled.

$$(2 \times [B])^r = 4 \times \text{Rate} ; r = 2$$

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

Trial	[A]	[B]	Rate $\frac{\Delta [A]}{s}$	Calculated 'k'
1	0.150	0.150	0.0016875	0.500
2	0.300	0.150	0.0033750	0.500
3	0.150	0.300	0.0067500	0.500

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

Now, we'd like to know the value of 'k'. Solve rate law for 'k'.

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

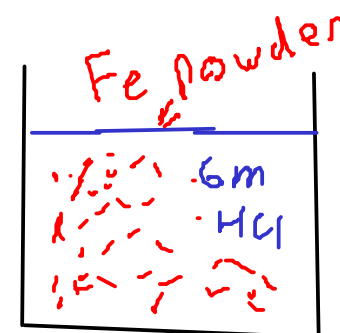
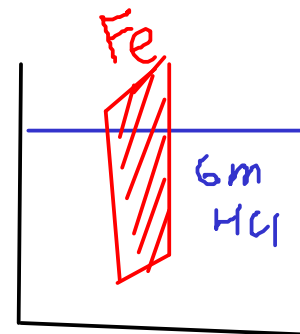
Plug in each set of data to this equation and calculate 'k'!

The average of these calculated 'k' values equals the rate constant.
(For real data, expect some experimental error in these numbers!)

$$\text{Rate} = 0.500 [A][B]^2$$

FACTORS THAT AFFECT REACTION RATE

- ① CONCENTRATION OF REACTANTS
- ② SURFACE AREA OF CONTACT BETWEEN REACTANTS
- ③ CONCENTRATION OF / PRESENCE OF A CATALYST
- ④ TEMPERATURE



CONCENTRATION OF REACTANTS

- Usually, the reaction rate increases as you increase the concentration of a reactant. This is true if the order for that reactant is greater than zero!

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

$$[A]^0$$

$$[A]^1$$

$$[A]^{-1} \quad \frac{1}{[A]}$$

If the order is 0 the value of this term will be 1 no matter what (A) is!

If the order is -1, this term will get SMALLER (reducing rate) as (A) gets larger!

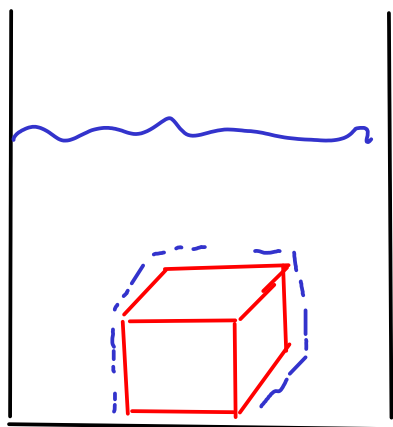
"inhibitor"

- In most cases, reaction orders ARE positive numbers!

SURFACE AREA OF CONTACT BETWEEN REACTANTS

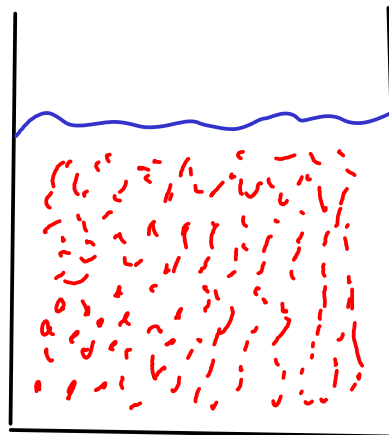
- If a reaction takes place at an INTERFACE, then the reaction rate will depend on the SURFACE AREA of that interface!

Consider a reaction between a liquid and a solid. The reaction can only take place where the liquid and the solid TOUCH each other,



The reaction takes place only on the surface of the cube.

Next, try the same reaction, but break the cube into small fragments first!



Here, the reaction takes place on the surface area of each fragment. In total, this is a much LARGER surface than the cube.

- The larger the SURFACE AREA of the INTERFACE between the reactants, the faster the reaction will occur!

- This is not an important factor for reactions that take place IN SOLUTION, since there is no interface.

CONCENTRATION OF / PRESENCE OF A CATALYST

- a CATALYST is a substance that INCREASES the rate of a reaction without being consumed in the reaction.

- Appear in the rate law equation, but are written as "reaction conditions" in traditional chemical equations. Typically, the higher the concentration of catalyst, the faster the reaction.



$$\text{Rate} = k [A]^p [B]^q [C]^r$$

└ The catalyst shows up in the rate law like the reactants!

- Work via many different mechanisms. Some provide surfaces for reactants to bind to and react. Some react with reactant molecules to leave them in a state more suitable for the main reaction (and are then regenerated during the main reaction). Some catalysts bind to and bend reactants into favorable orientations for reactions, etc.

- Biological catalysts are usually called ENZYMES.

TEMPERATURE

- We observe that chemical reactions proceed FASTER at HIGHER temperatures.

... but sometimes reactions are run at low temperatures for other reasons - like safety, decomposition of desired products at high temperatures, formation of competing undesirable products at high temperatures, etc.

Note: Changing temperature affects the RATE CONSTANT, k !

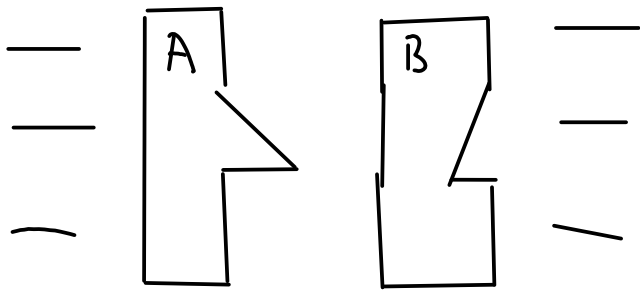
REACTION RATE THEORY

- We'd like to have an explanation for how the four factors we discussed affect the reaction rate!
- COLLISION THEORY and TRANSITION STATE THEORY attempt to explain reaction rate.

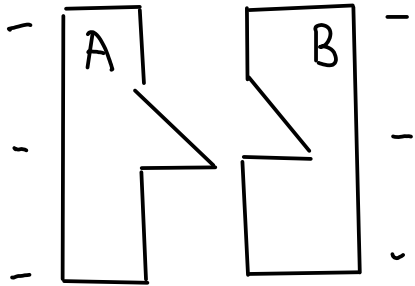
COLLISION THEORY

- states that for a reaction to occur between atoms or molecules, three things must occur:

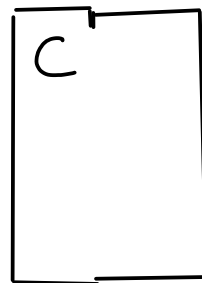
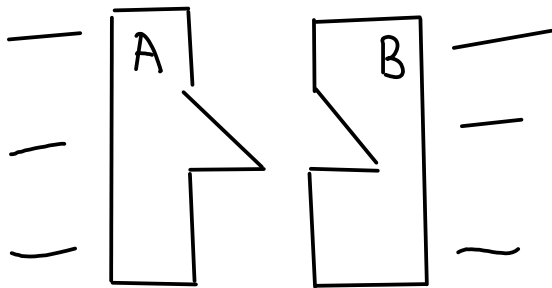
- ① Reactants must COLLIDE with each other.
- ② Colliding reactants must hit each other with the correct ORIENTATION to react.
- ③ Colliding reactants must also hit each other with ENOUGH ENERGY to react (called the ACTIVATION ENERGY)



A collision like this - even an energetic one, would lead to NO REACTION, since the molecules are not aligned properly to react. This is particularly important for larger molecules (like biomolecules) where reactive parts of the molecule are small compared to the size of the whole molecule!



A collision where molecules don't hit each other very hard will not lead to a reaction. There isn't enough ENERGY available for the molecules to react with one another.



A collision where molecules hit each other with the correct orientation AND enough energy may lead to a reaction!

EXPLAINING SOME OF THE FACTORS

- Increasing the concentration of reactants increases THE NUMBER OF COLLISIONS that occur in a reaction mixture - increasing rate.
- Increasing SURFACE AREA provides more opportunities for reactant molecules to COLLIDE - increasing rate.
- Increasing temperature INCREASES THE ENERGY (and number) of collisions, since temperature is proportional to the average kinetic energy of molecules. More collisions will have the ACTIVATION ENERGY needed to react, so rate increases.
- Some catalysts work by bending reactant molecules into ORIENTATIONS favorable for reaction - making it easier for large molecules to react with one another.

... but what about this ACTIVATION ENERGY? Let's look at TRANSITION STATE THEORY

⁹⁵ TRANSITION STATE THEORY

- States that when reactant molecules collide, they first form a TRANSITION STATE which then decomposes and/or loses energy to form product molecules.
- A TRANSITION STATE is a high-energy state: It may be an unstable combination of several reactant molecules or an excited (high energy) state of a single product molecule. The transition state breaks down and loses energy to form the products of the reaction.
- The ACTIVATION ENERGY is the energy required to form the transition state, and it acts as a barrier to reaction.
- We model the rate constant "k" using collision and transition state theory with the ARRHENIUS EQUATION:

$$k = A \times e^{\frac{-E_a}{R \times T}}$$

rate
constant

E_a = ACTIVATION ENERGY

R = ideal gas constant

T = absolute temperature

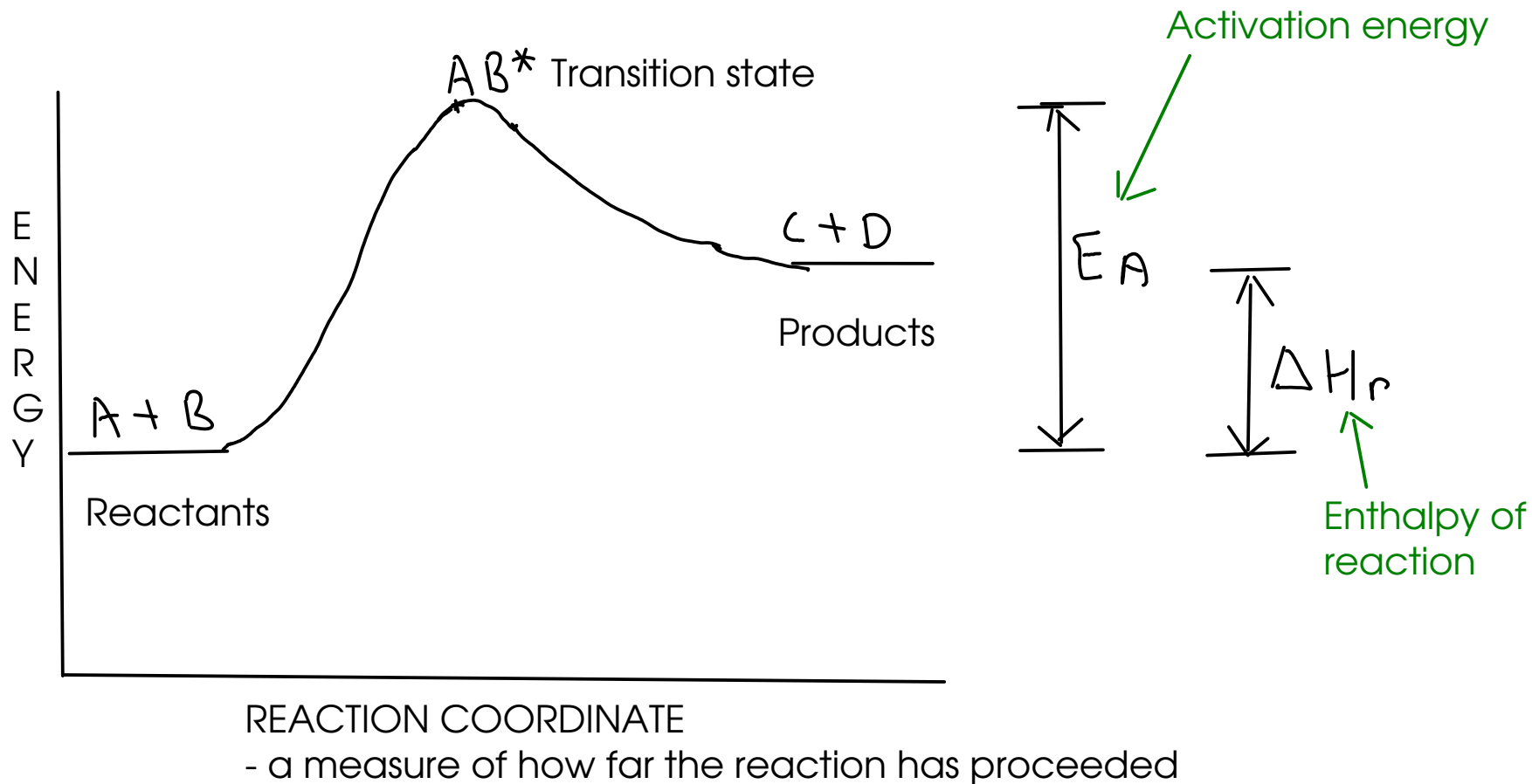
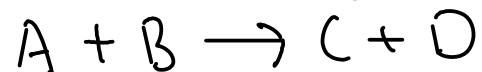
A = frequency factor ... the fraction of collisions with the right orientation to react

... this equation allows us to calculate the rate constant for different temperatures if we have values for "A" and "E_a". We can get these values by examining a reaction at two (or more) different temperatures.

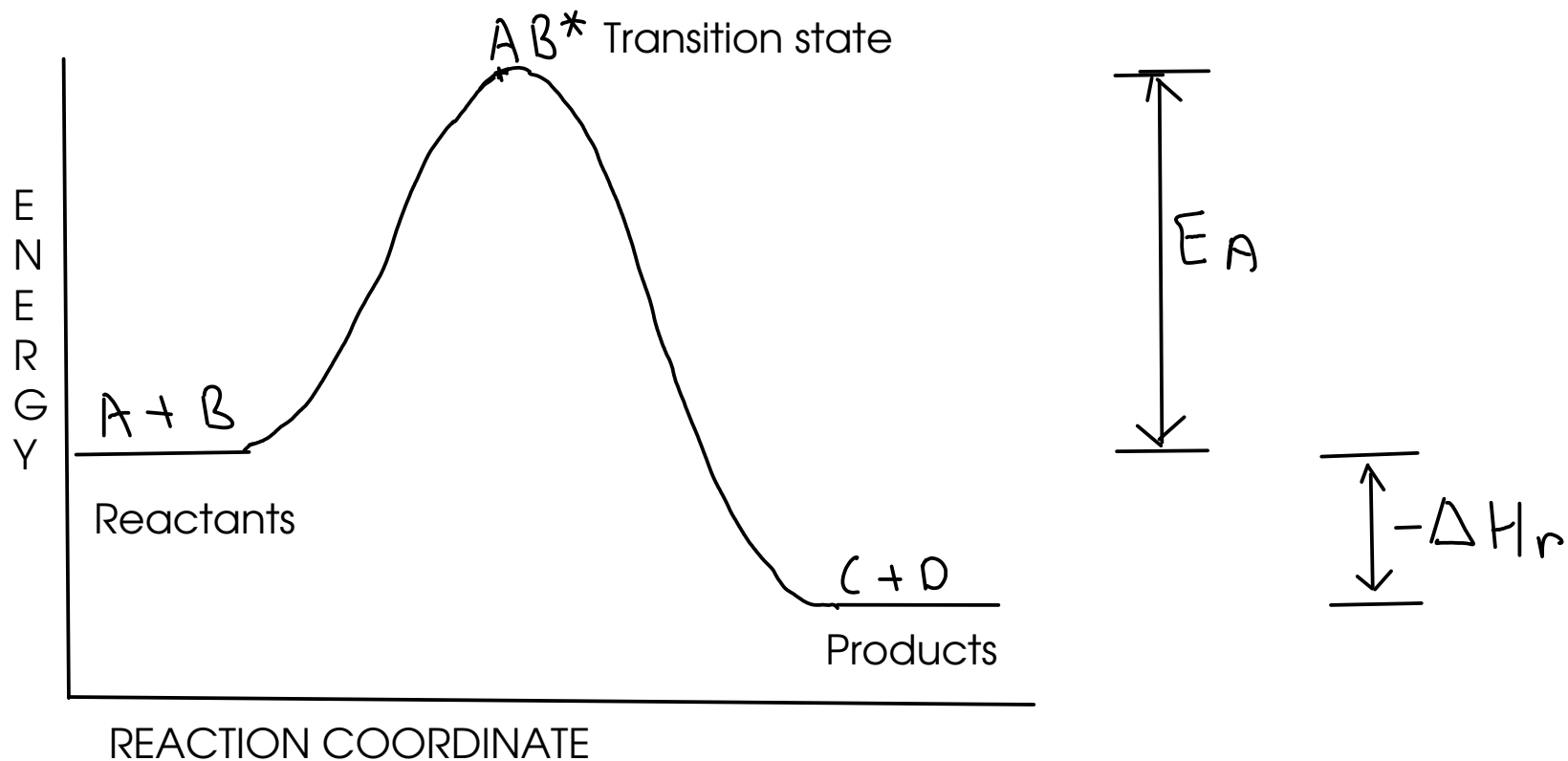
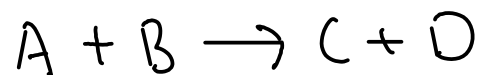
ENERGY DIAGRAMS

- graphically, we can look at transition state theory via an ENERGY DIAGRAM

For an ENDOTHERMIC REACTION, the products have a higher energy than the reactants



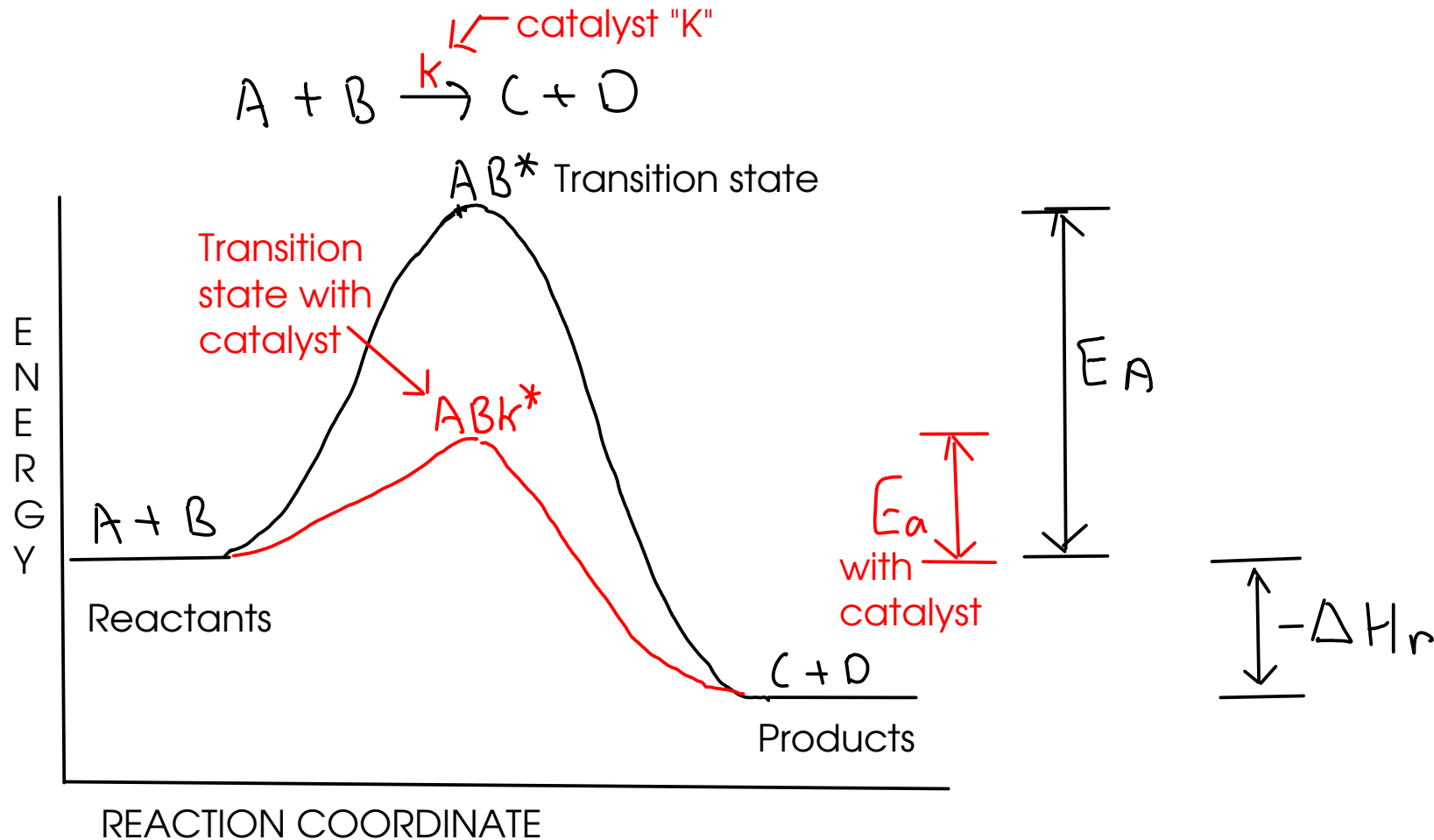
For an EXOTHERMIC REACTION, the products have a lower energy than the reactants



- Whether a reaction is endothermic OR exothermic, there is still an activation energy barrier that must be crossed in order to react.
- This explains why a pile of wood that's exposed to air doesn't just burst into flames. Even though the combustion of wood is EXOTHERMIC, there's still an activation energy barrier preventing the reaction from occurring without an initial input of energy - a "spark"!

CATALYSTS?

- So how does a catalyst fit into this picture? A catalyst LOWERS the activation energy for a reaction.



- The exact mechanism by which a catalyst lowers the energy of the transition state may be simple ... or complex. As we mentioned before, some catalysts hold molecules so that it's easier for reactants to come together, some react with reactant molecules to produce an intermediate that reacts more easily with other reactants to make the final product, etc.