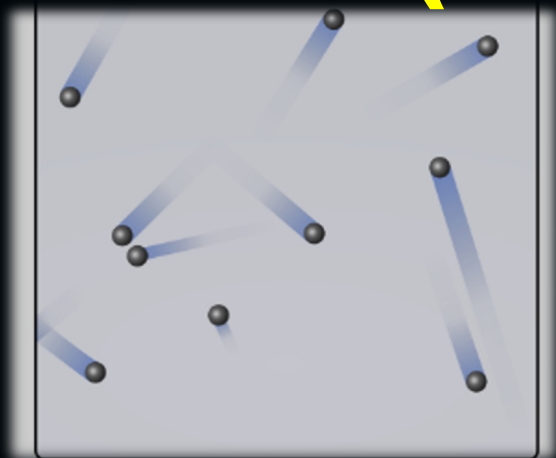
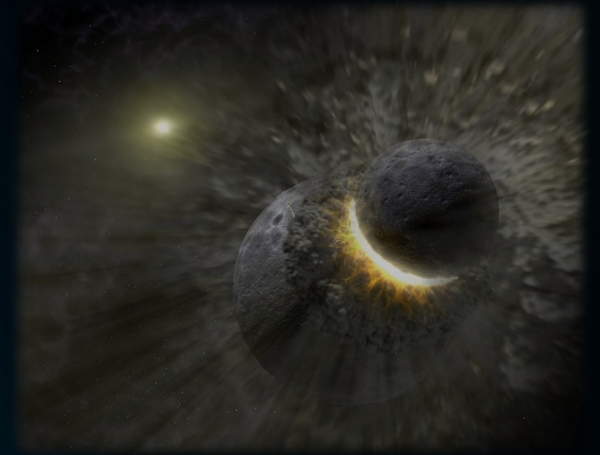


Chemical Kinetics

(Relative Rate Expressions)



What is Chemical Kinetics?

Chemical kinetics is the study of how fast reactions occur. In other words, it is the study of reactions' speeds or rates.

Chemical kinetics tells us how fast a reaction proceeds. However, it does NOT tell us if a reaction will happen, if a reaction involves an energy change, or if a reaction is at equilibrium.

For these latter things, we study ***thermodynamics***, which we'll cover in a later chapter.

For this chapter, we'll cover ***chemical kinetics***, which is (once again) the study of ***reaction rates***.

How Do You Measure Rate?

When traveling, we are very accustomed to expressing rate, or speed, as:

$$\frac{\text{miles}}{\text{hour}}$$

$$\frac{\text{distance}}{\text{time}}$$
$$\frac{\text{km}}{\text{hour}}$$

$$\frac{\text{feet}}{\text{second}}$$



CC BY 2.0,
<https://commons.wikimedia.org/w/index.php?curid=718429>

But how do we express a reaction's rate?

$$\frac{\text{amount of reactant or product appearing or disappearing}}{\text{time}}$$

An Example

Let's take a look at this reaction:



Now let's imagine that you wanted to find out how fast this reaction proceeds. To do this, you could simply measure the change in O_2 concentration, or $[\text{O}_2]$, over time:

$$\text{Rate} = \frac{\Delta[\text{O}_2]}{\Delta\text{time}}$$

An Example

Let's take a look at this reaction:



Alternatively, you could measure the change in NO_2 concentration, or $[\text{NO}_2]$, over time:

$$\text{Rate} = \frac{\Delta[\text{NO}_2]}{\Delta\text{time}}$$

An Example

Let's take a look at this reaction:



Or, you could measure the change in N_2O_5 concentration, or $[\text{N}_2\text{O}_5]$, over time:

$$\text{Rate} = \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta\text{time}}$$

An Example

Let's take a look at this reaction:



Now, based on the equation, it's hopefully obvious that as this reaction proceeds, N_2O_5 will disappear, while NO_2 and O_2 appear. Also, the balanced reaction coefficients indicate that these rate changes will proceed in a 2:4:1 ratio. Thus:

$$\text{Rate} = \frac{\Delta[\text{O}_2]}{\Delta\text{time}} = \frac{\Delta[\text{NO}_2]}{4 \Delta\text{time}} = \frac{-\Delta[\text{N}_2\text{O}_5]}{2 \Delta\text{time}}$$

Rate Expressions

In general, then, for the reaction:



. . . Its *relative rate expressions* are:

$$\text{rate} = \overbrace{-\left[\frac{1}{a}\right] \frac{\Delta[A]}{\Delta t} = -\left[\frac{1}{b}\right] \frac{\Delta[B]}{\Delta t}}^{\text{reactants}} = \overbrace{\left[\frac{1}{c}\right] \frac{\Delta[C]}{\Delta t} = \left[\frac{1}{d}\right] \frac{\Delta[D]}{\Delta t}}^{\text{products}}$$

Example Questions

Given the following reaction:

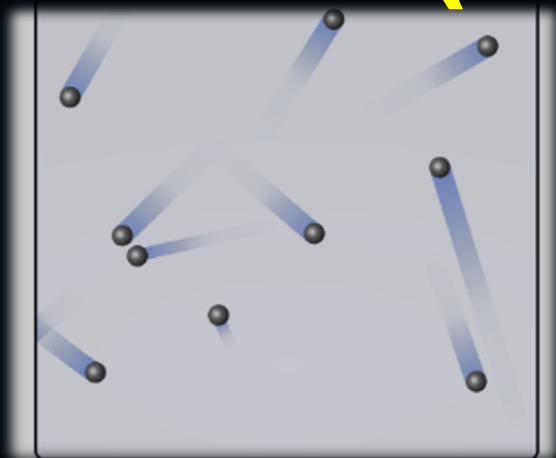
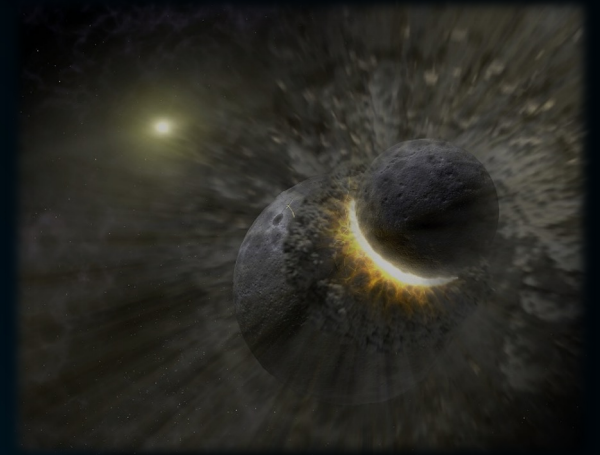


If O_2 is being produced at a rate of 2 M/s, how fast is NO_2 being produced?

If O_2 is being produced at a rate of 2 M/s, what is the rate of change of N_2O_5 ?

Chemical Kinetics

(Rate Laws and Constants)



What is a Rate Law?

The *relative rate expressions* we learned about in our previous video . . .

$$\text{rate} = -\left[\frac{1}{a}\right]\frac{\Delta[A]}{\Delta t} = -\left[\frac{1}{b}\right]\frac{\Delta[B]}{\Delta t} = \left[\frac{1}{c}\right]\frac{\Delta[C]}{\Delta t} = \left[\frac{1}{d}\right]\frac{\Delta[D]}{\Delta t}$$

. . . Tell us the rates at which reactants are being consumed, and products formed, relative to each other, for the following generic reaction, as it proceeds:



Relative reaction rates only let us to determine the rates of these components relative to each other. They do NOT let us determine how changing concentrations will affect the rate.

What is a Rate Law?

For any generic reaction:



... Its *rate law* is:

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

- Notice that products do not appear in the *rate law*.
- **k** is called the *rate constant*.
- **m** and **n** have to be determined experimentally. They are not necessarily equal to the coefficients **a** and **b**.
- **m** and **n** are the *reaction orders* for this reaction. On the EXAM, they are usually 0, 1, or 2. A reaction's *overall reaction order* equals **m** + **n**.

Rate Constant and Reaction Order

Before continuing, I have to teach you a few things about the rate constant, k :

- The units for k can sometimes look kind of weird. Don't fixate on that too much.
- Please just remember that the reaction's overall **reaction order** can be found by adding up the superscripts in k 's units and taking the answer's absolute value:

$M^1 \cdot s^{-1}$: $1 + -1 = 0$, so this is a **zero-order** reaction

s^{-1} : the absolute value of -1 is 1, so this is a **first-order** reaction

$M^{-1} \cdot s^{-1}$: $-1 + -1 = -2$, so this is a **second-order** reaction

$M^{-2} \cdot s^{-1}$: $-2 + -1 = -3$, so this is a **third-order** reaction

Example Question

When the following reaction was run and measured:



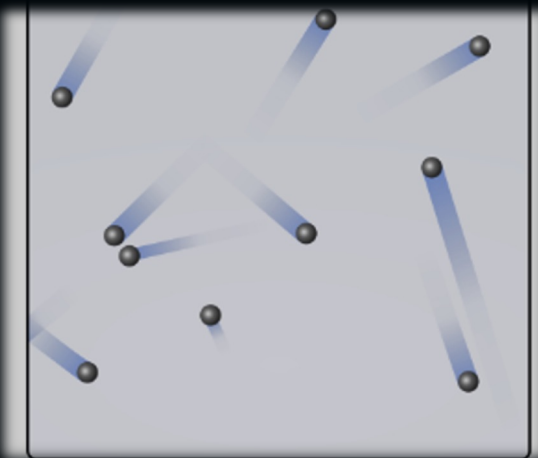
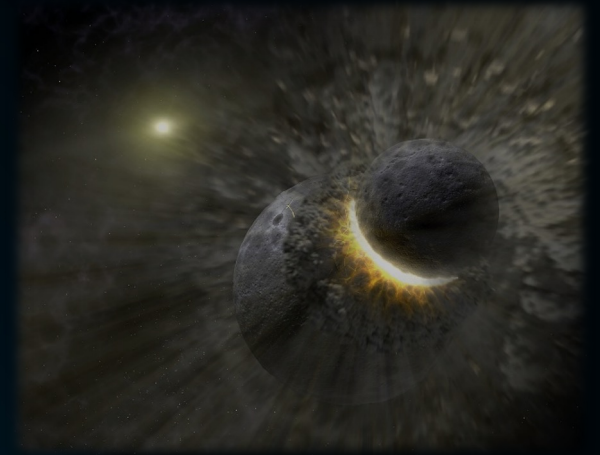
... It produced the following kinetic data:

	[A] _{initial} (M)	[B] _{initial} (M)	rate (M/s)
Trial 1	0.10	0.3	0.01
Trial 2	0.20	0.3	0.04
Trial 3	0.10	0.6	0.02

1. What is the **rate law** for this reaction?
2. What is the **overall reaction order**?
3. What is this reaction's **rate constant**?
4. What units would this reaction's **rate constant** have?

Chemical Kinetics

(Integrated Rate Laws)



By Olivier Cleynen and User:Sharayanan - Own work based on
File:Kinetic theory of gases.svg which is licensed CC-by-saThis
vector image was created with Inkscape., CC BY-SA 3.0,
<https://commons.wikimedia.org/w/index.php?curid=40017346>

To Review . . .

In prior videos in this chapter, we learned that for the generic reaction:



. . . Its *relative reaction rates* are:

$$\text{rate} = -\left(\frac{1}{a}\right)\frac{\Delta[A]}{\Delta t} = -\left(\frac{1}{b}\right)\frac{\Delta[B]}{\Delta t} = \left(\frac{1}{c}\right)\frac{\Delta[C]}{\Delta t} = \left(\frac{1}{d}\right)\frac{\Delta[D]}{\Delta t}$$

To Review . . .

We also learned that for this same generic reaction:



. . . Its *rate law* is:

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

. . . Where *k* is its rate constant and *m* and *n* (the *reaction orders*) have to be determined experimentally.

Limitations of Relative and Rate Laws

As I've mentioned in the past, ***relative reaction rates*** only let us to determine the rates of reactants' consumption or products' appearance relative to each other. ***Relative reaction rates*** do NOT let us determine how changing concentrations will affect the rate. For that, we need our reaction's ***rate law***.

By comparison, a reaction's ***rate law*** does enable us to calculate how a reaction's rate will be affected if we alter the concentrations of our reactants, **[A]** and **[B]**. However, the ***rate law*** does NOT tell us how the reactants and products' concentrations change over time, as the reaction proceeds. For that, we need something called an ***integrated rate law***.

Limitations of Relative and Rate Laws

As I've mentioned in the past, *relative reaction rates* only let us to determine the rates of reactants' consumption or products' appearance *relative to each other*. *Relative Reaction Rates* do NOT let us determine how changing concentrations will affect the rate. For that, we need our reaction's *rate law*.

Integrated rate laws can get pretty complicated. Instead of bewildering you with unnecessary details, I'm going to focus in on the stuff that you need to know for the EXAM.

By comparison, a reaction's *rate law* does enable us to calculate how a reaction's rate will be affected if we alter the concentrations of our reactants, **[A]** and **[B]**. However, the *rate law* does NOT tell us how the reactants and products' concentrations change over time, as the reaction proceeds. For that, we need something called an *integrated rate law*.

Integrated Rate Laws

The basic idea is that an ***integrated rate law*** allows us to calculate actual concentrations of reactants and products for a reaction over time, not just relative concentrations (***relative reaction rates***) or how changing concentrations will change the rate (***rate laws***).

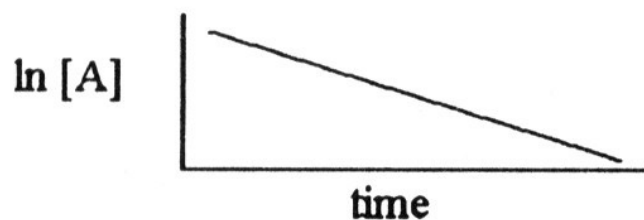
For the EXAM, you might be given a graph and asked which reaction order a reaction is. To do this, you need to memorize that in order to produce a straight-line graph, an ***integrated rate law***'s y-axis units must be:

- ***zero-order*** = [concentration]
- ***first-order*** = $\ln$ [concentration]
- ***second order*** = $1 / [\text{concentration}]$

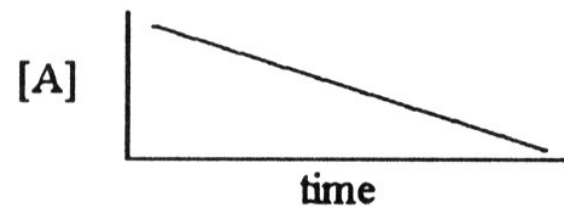
Questions

Which one of the following graphs shows the correct relationship between concentration and time for a reaction that is **second-order** in **[A]**?

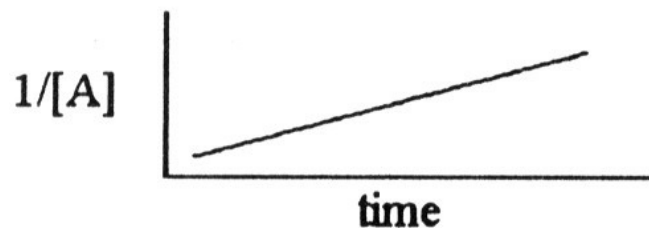
a.



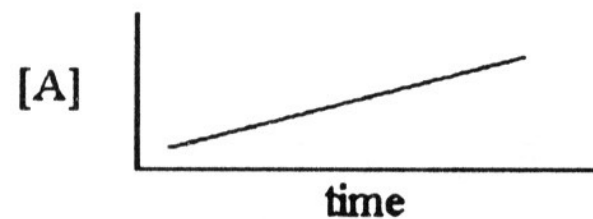
b.



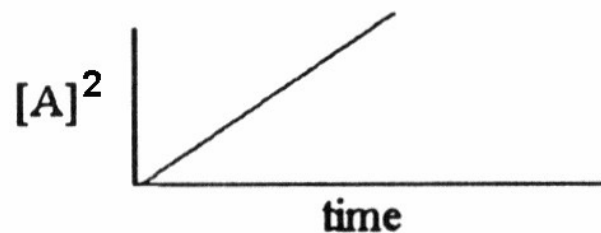
c.



d.



e.

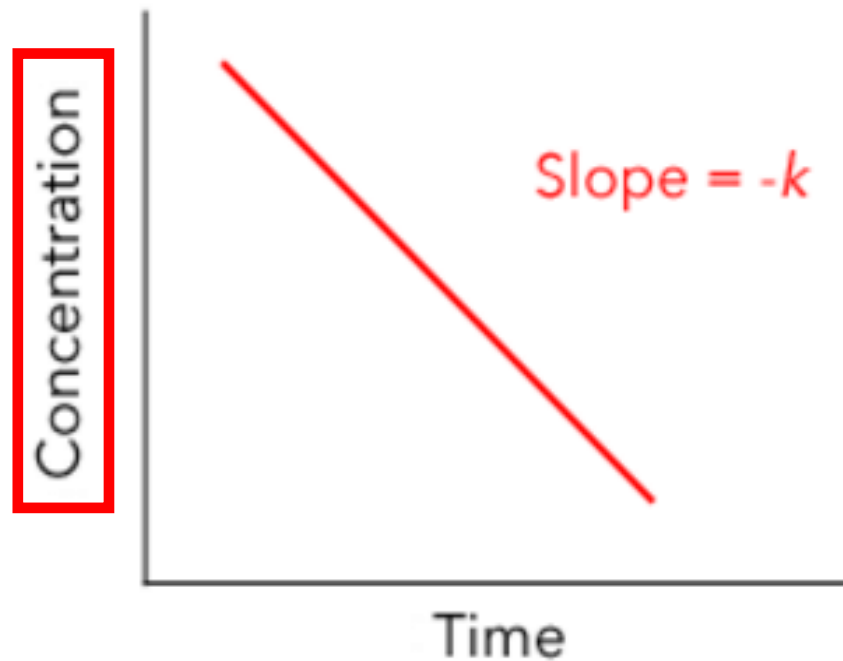


Questions

What is the **overall reaction order** for a reaction that produces the **integrated rate law** graph shown here?

If the reaction is zero order...

[concentration]
= **zero-order**

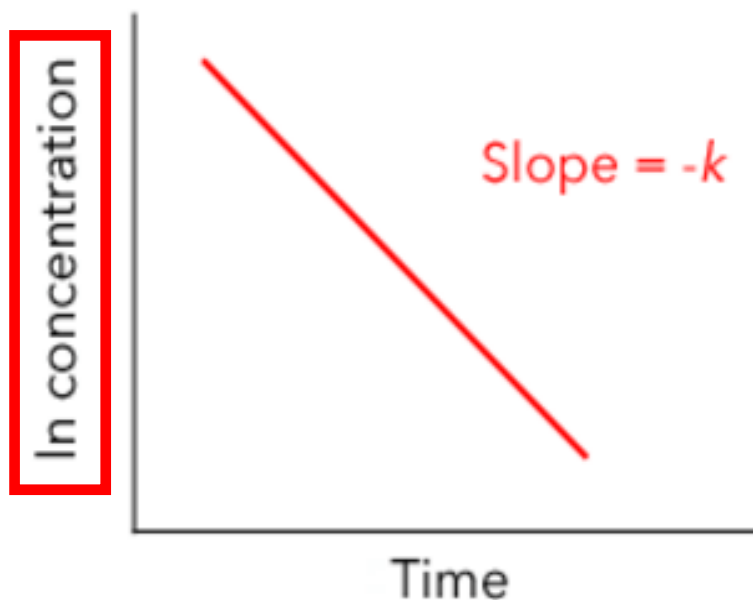


Questions

What is the **overall reaction order** for a reaction that produces the **integrated rate law** graph shown here?

If the reaction is first order...

$\ln [\text{concentration}]$
= **first-order**

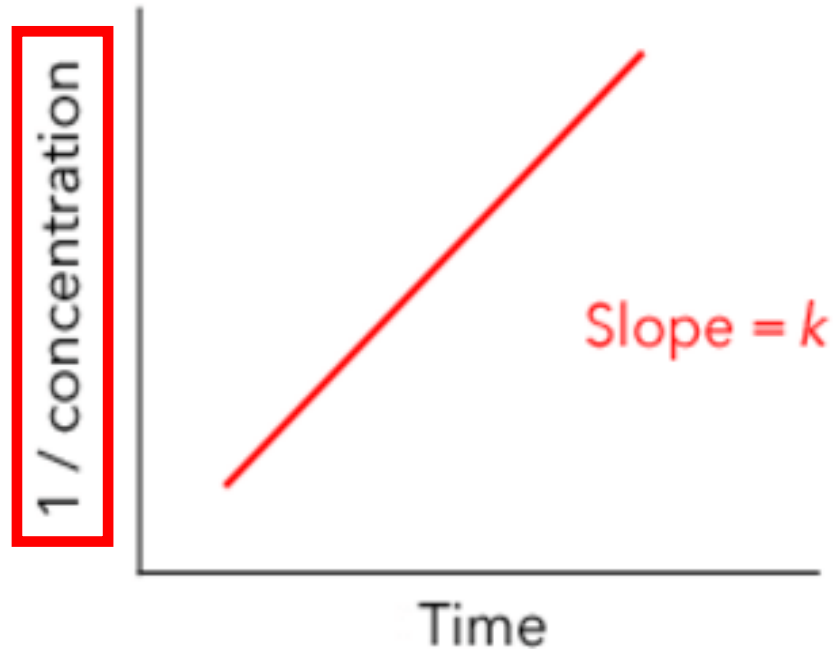


Questions

What is the **overall reaction order** for a reaction that produces the **integrated rate law** graph shown here?

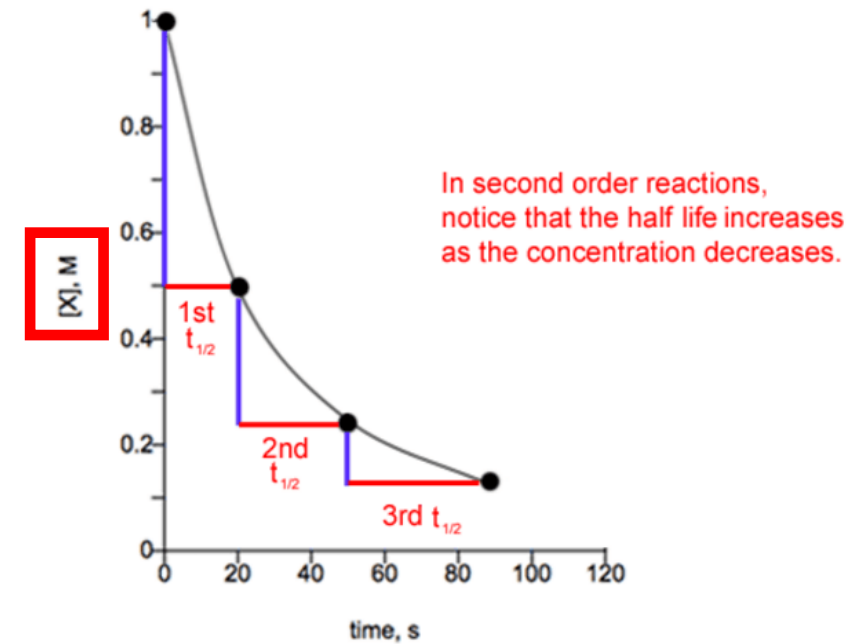
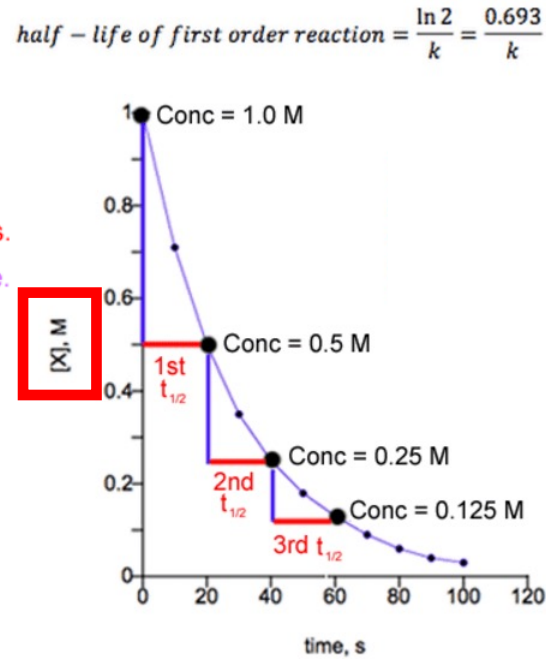
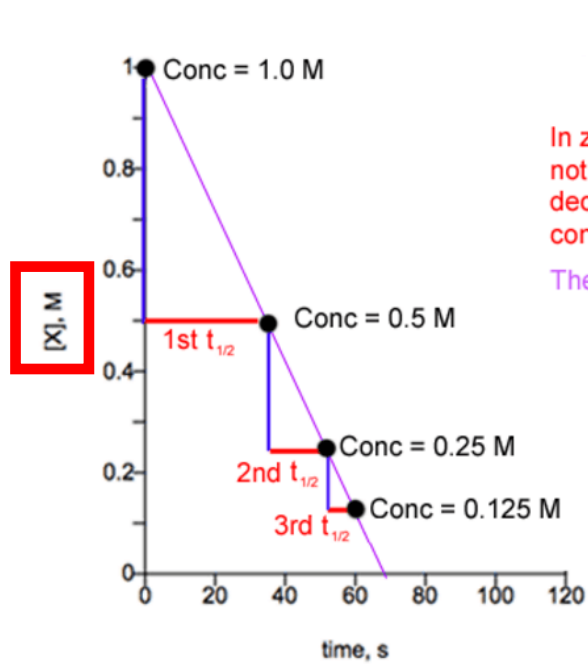
If the reaction is second order...

$1 / [\text{concentration}]$
= **second-order**



Tricky Stuff

The units that I just taught you only apply if the graphs give a straight line. For curved-line graphs:



zero-order reactions:

- The plot is a straight line
- Half-life $\approx$ concentration

first-order reactions:

- NOT a straight line
- Half-life constant is independent of concentration

second-order reactions:

- NOT a straight line
- Half-life $\approx$ concentration

Integrated Rate Laws

In addition to what I just explained, integrated rate laws also have specific **equations**, which are derived by combining their rate laws with their *relative* rate laws and then doing some calculus. You do not need to know how derive these equations, but you *do* need to memorize them, so here they are:

Order	Integrated Rate Law	Graph	Slope
0	$[A]_t = -kt + [A]_0$	$[A]_t$ vs. t	$-k$
1	$\ln[A]_t = -kt + \ln[A]_0$	$\ln[A]_t$ vs. t	$-k$
2	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]_t}$ vs. t	k

Integrated Rate Laws

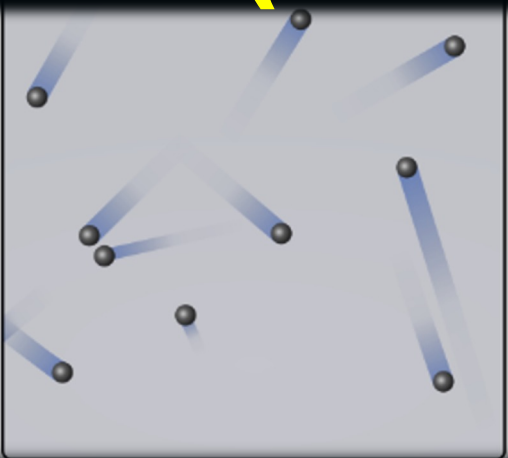
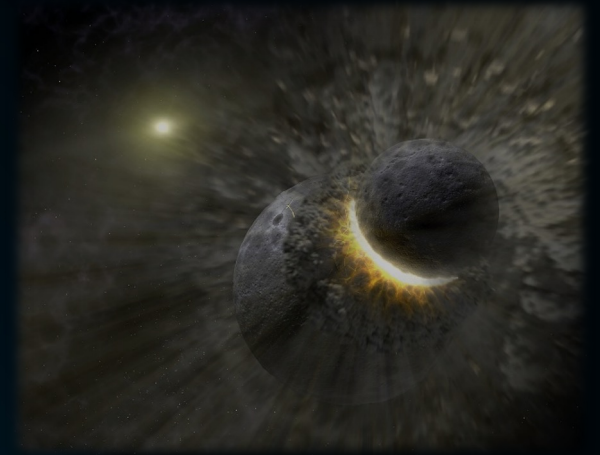
You'll notice that all of them have a simple-line format of $y = mx + b$, and that the y- and x-axis units are consistent with the y and x values in each equation.

$$y = mx + b$$

Order	Integrated Rate Law	Graph	Slope
0	$[A]_t = -kt + [A]_0$	$[A]_t$ vs. t	$-k$
1	$\ln[A]_t = -kt + \ln[A]_0$	$\ln[A]_t$ vs. t	$-k$
2	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]_t}$ vs. t	k

Chemical Kinetics

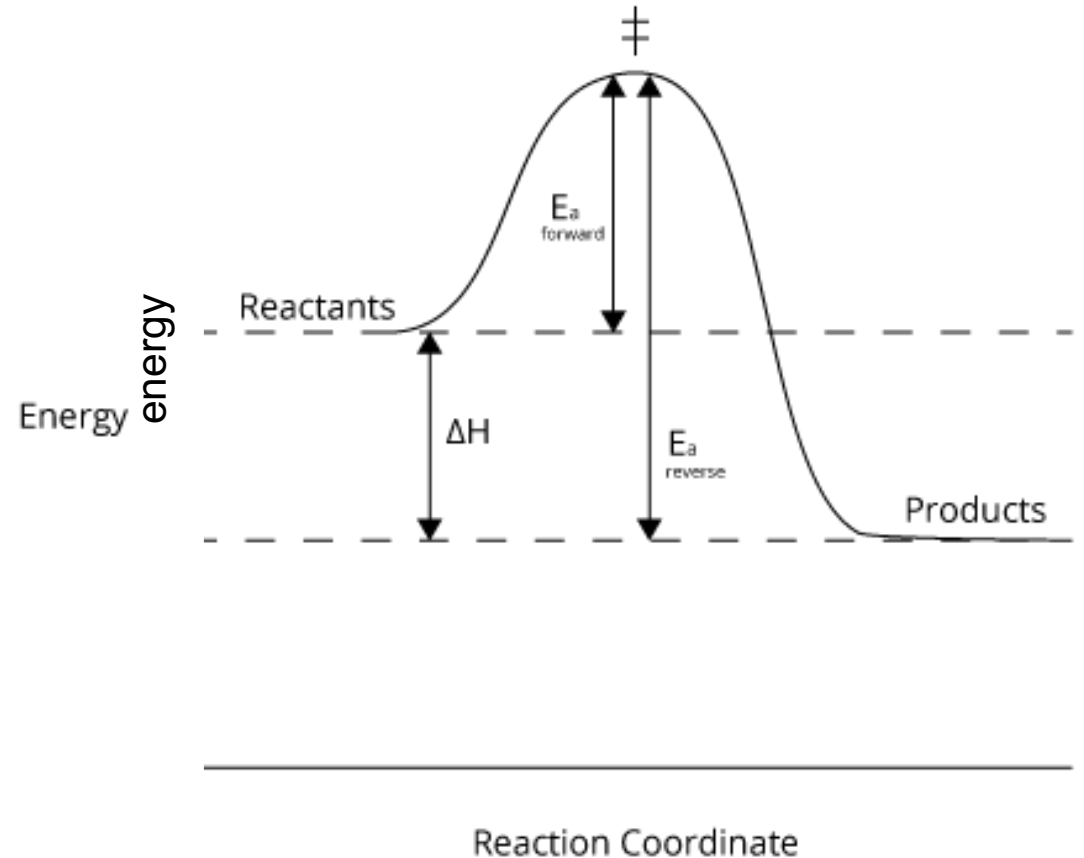
(Reaction Coordinate Diagrams)



Coordinate Diagrams

One way that we chemists convey information about chemical reactions is by drawing cute little diagrams of them. These diagrams are called ***reaction coordinate diagrams***.

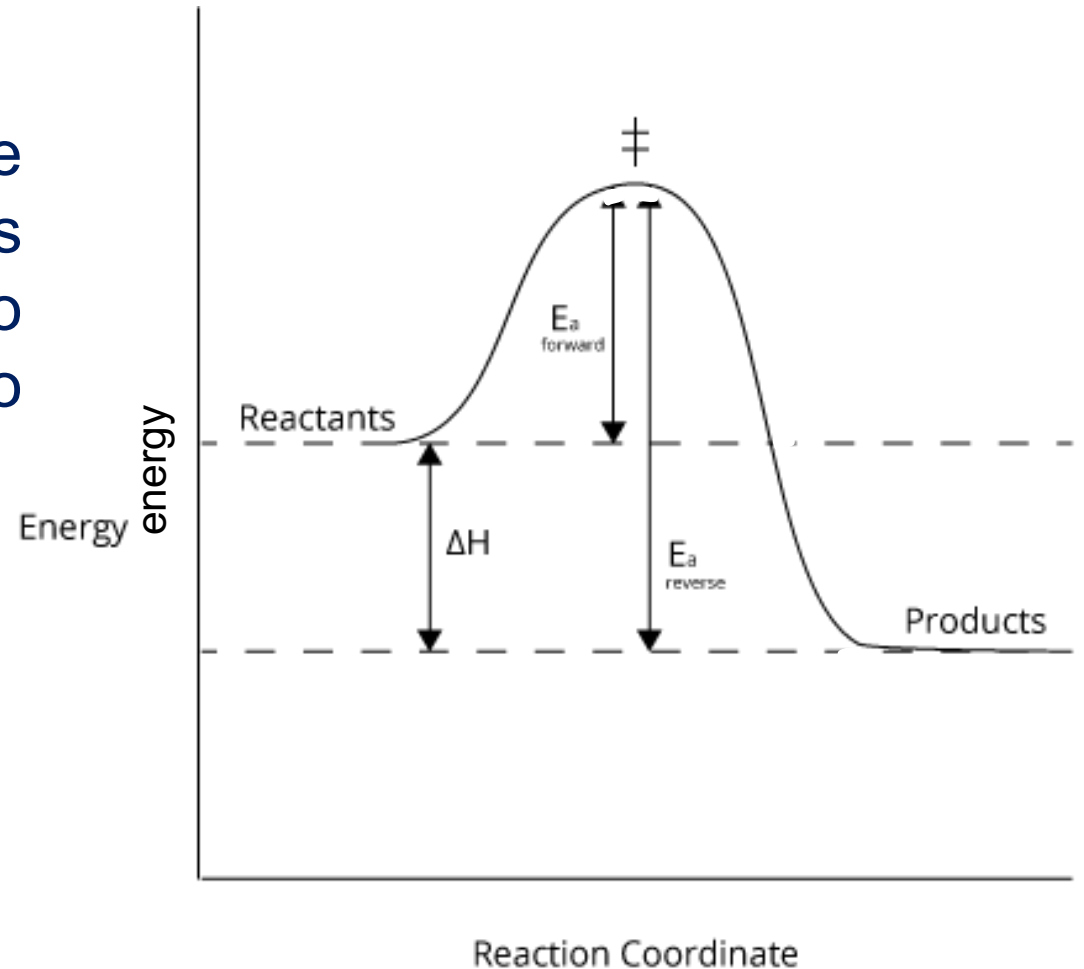
To draw these, we begin with a y-axis, whose units are **energy**, and an x-axis that represents the reaction moving forward. The reactants are then drawn on a plateau that represents their collective energy level. The products are drawn on a separate plateau. In this diagram the products are at a lower energy level (they are more stable) than the reactants.



Coordinate Diagrams

One way that we chemists convey information about chemical reactions is by drawing cute little diagrams of them. These diagrams are called ***reaction coordinate diagrams***.

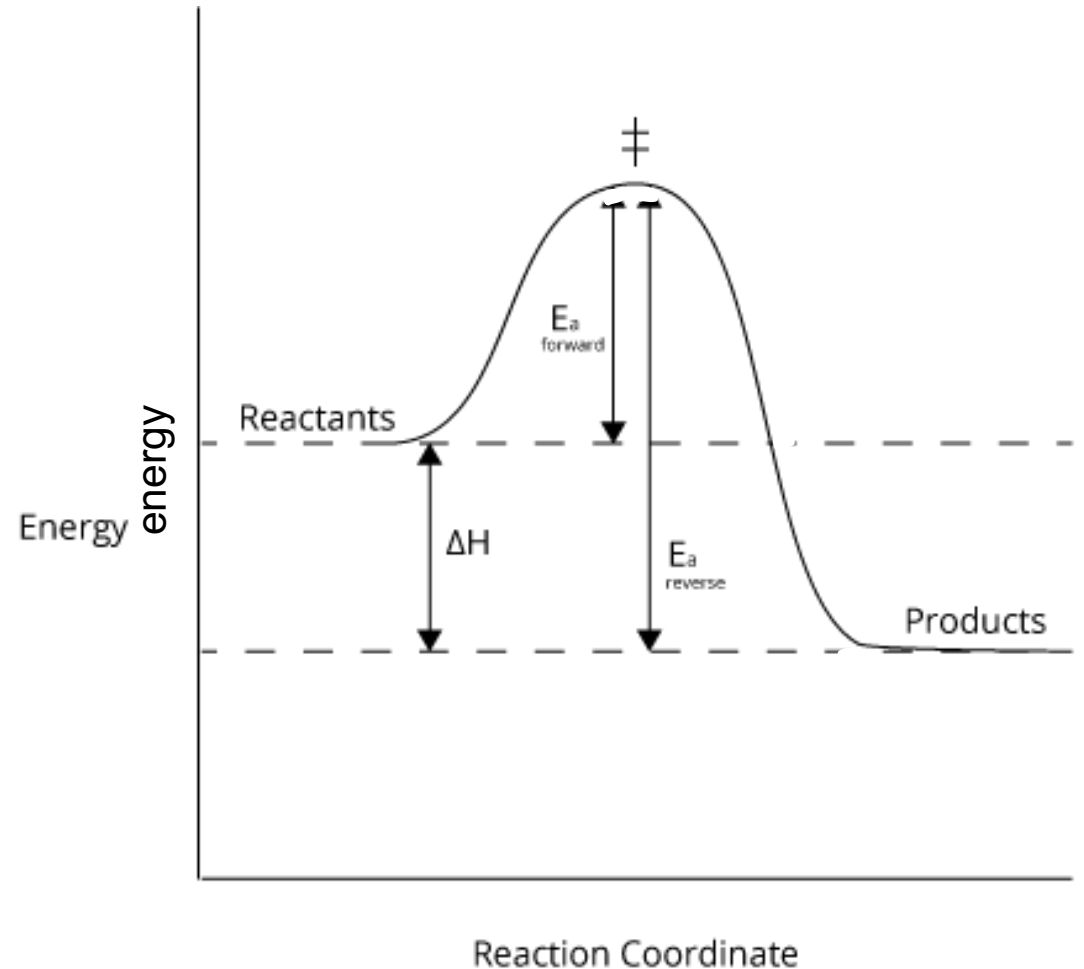
We now draw a hill-shaped line between the reactants and products. This hill represents the amount of energy the reaction has to traverse in order to convert the reactants into products.



Coordinate Diagrams

There are few things you NEED to know:

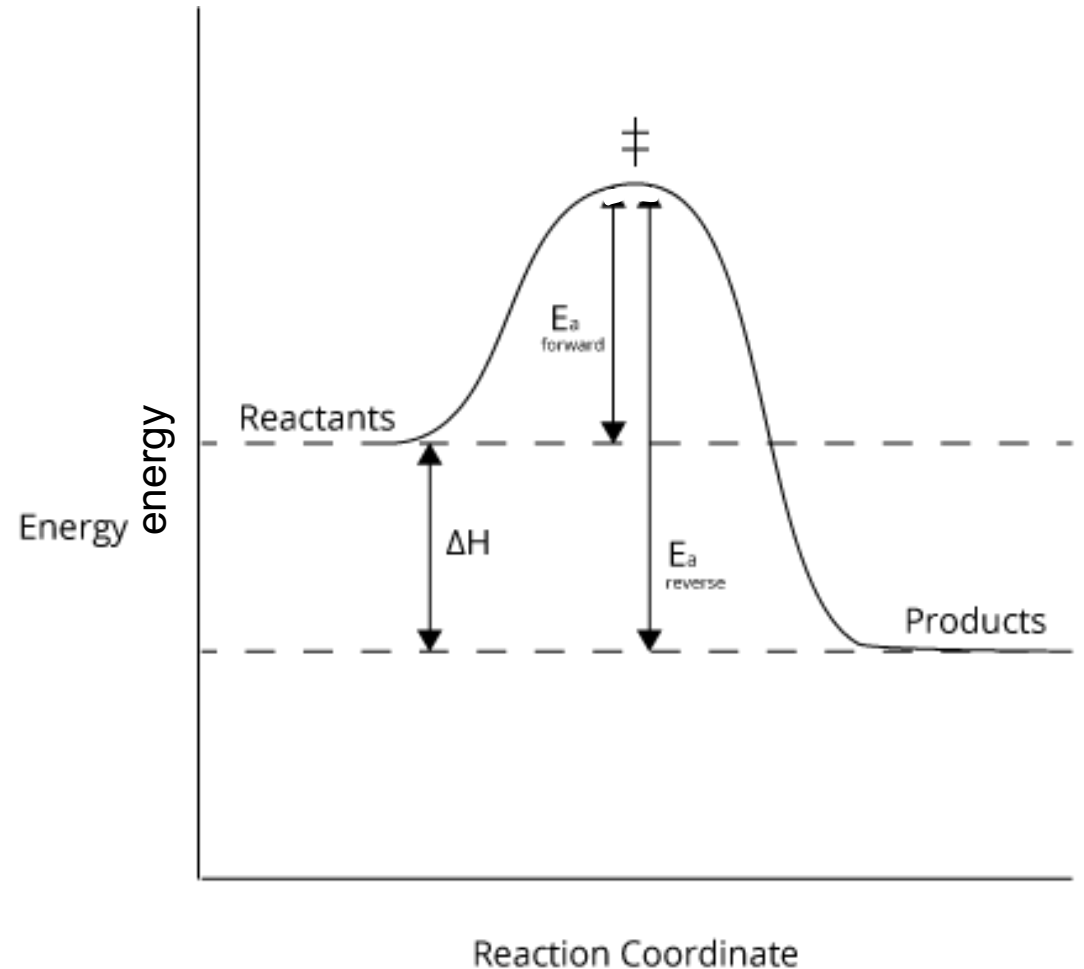
- ΔH is the difference between the energy levels of the reactants and the products.



Coordinate Diagrams

There are few things you NEED to know:

- ΔH is the difference between the energy levels of the reactants and the products.
- ΔE ($\ddagger$) is the height between the reactants and the top of the hill.



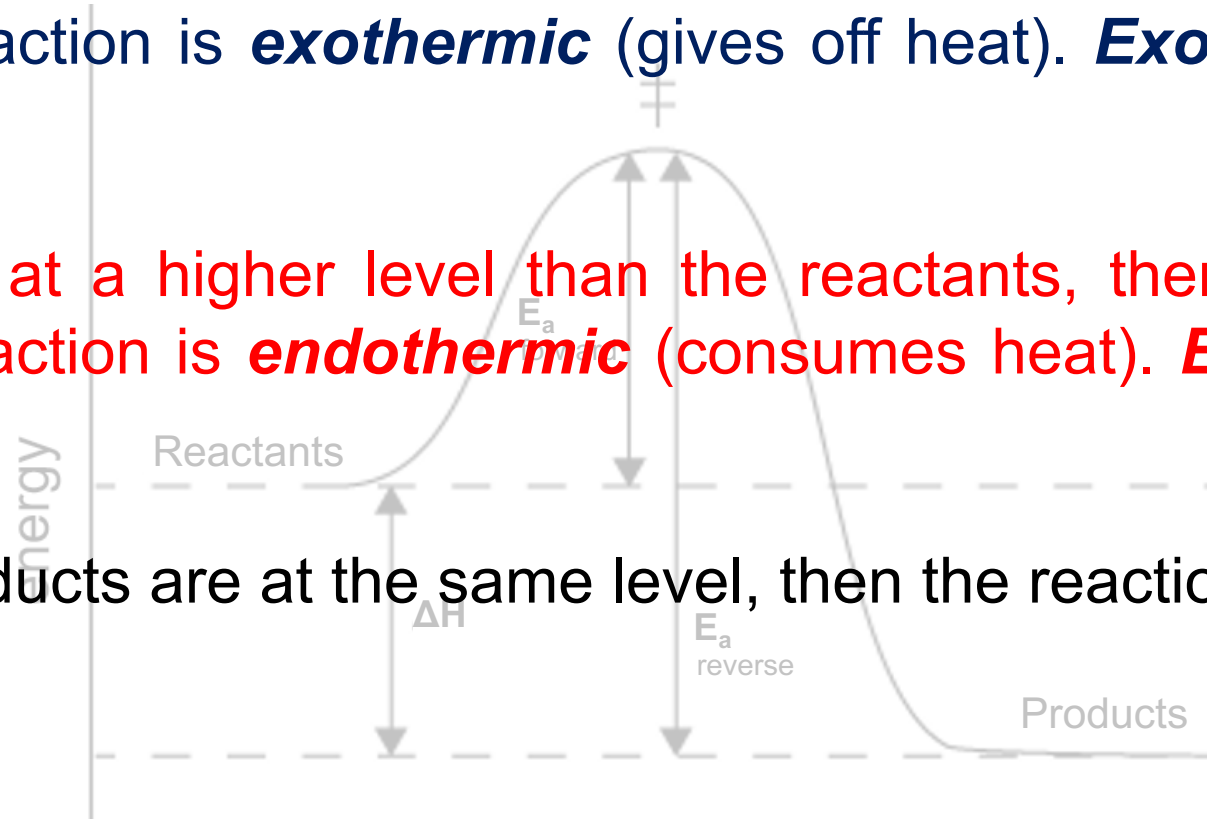
What is ΔH ?

ΔH is the difference between the energy levels of reactants and products. In other words: $\Delta H = \text{Energy}_{\text{products}} - \text{Energy}_{\text{reactants}}$.

If the products are at a lower level than the reactants, then ΔH is negative, which means that your reaction is **exothermic** (gives off heat). **Exothermic** processes feel warm.

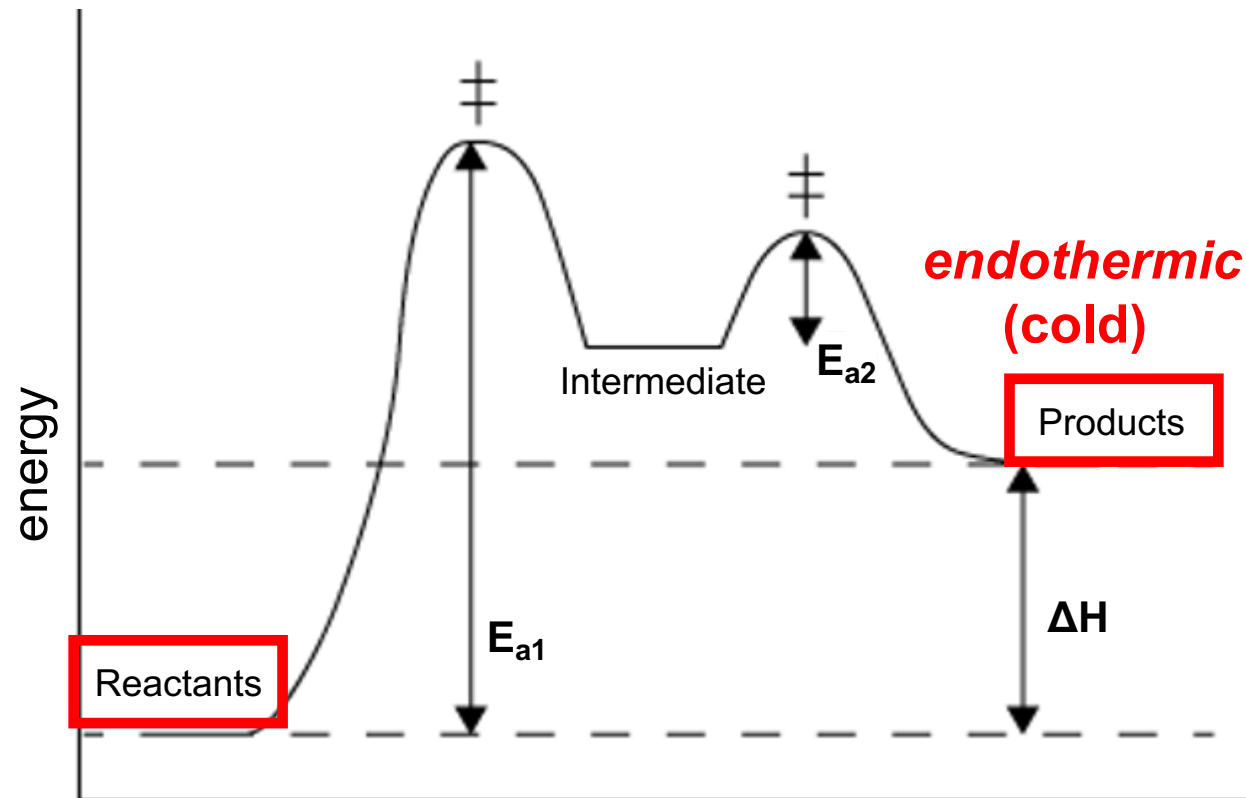
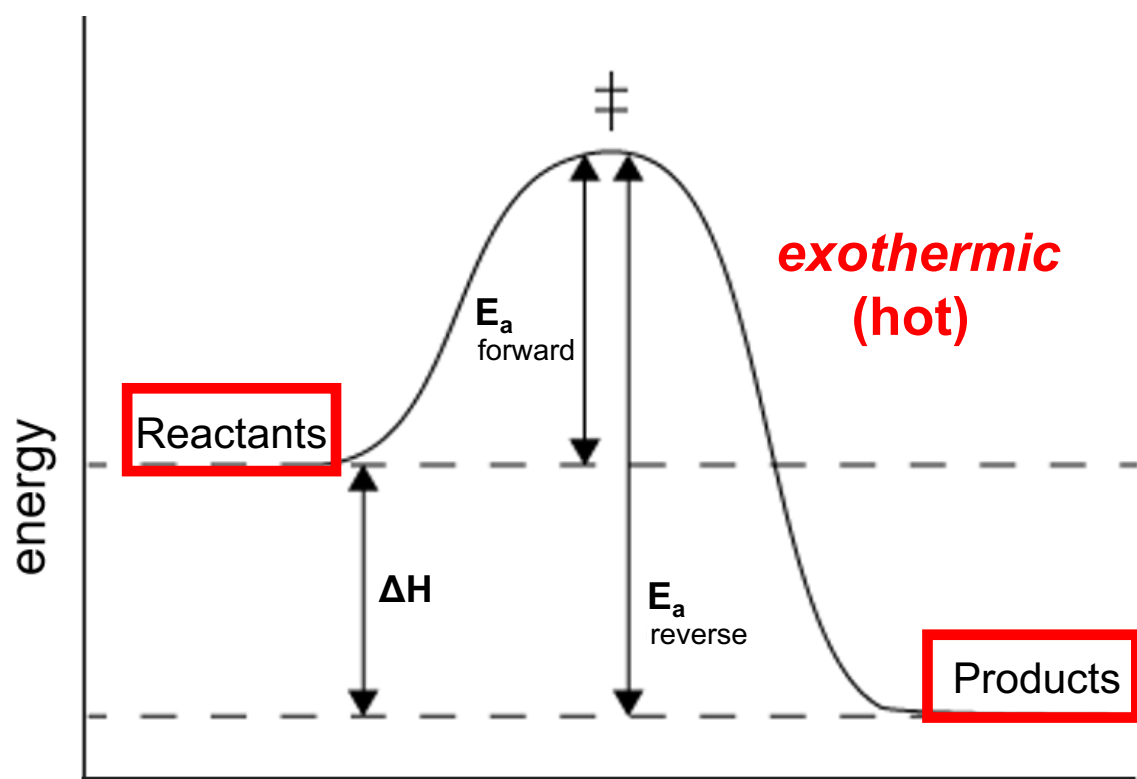
If the products are at a higher level than the reactants, then ΔH is positive, which means that your reaction is **endothermic** (consumes heat). **Endothermic** processes feel cold.

If reactants and products are at the same level, then the reaction is **isothermic**.



Questions

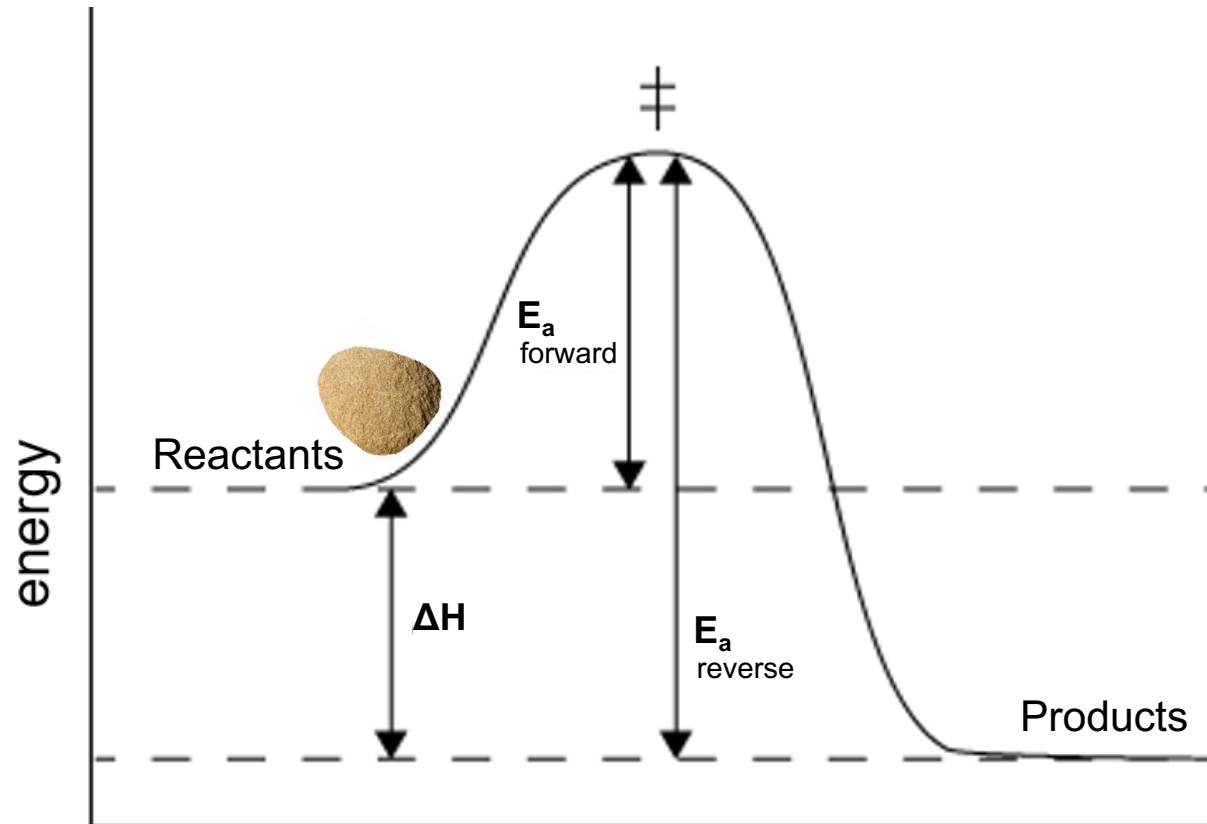
Please label the following processes as **exothermic**, **endothermic**, or **isothermic**, based on their **reaction coordinate diagrams**. Would each one feel hot or cold to the touch?



What is ΔE ?

ΔE is the difference between the energy level of the reactants and the top of the hill.

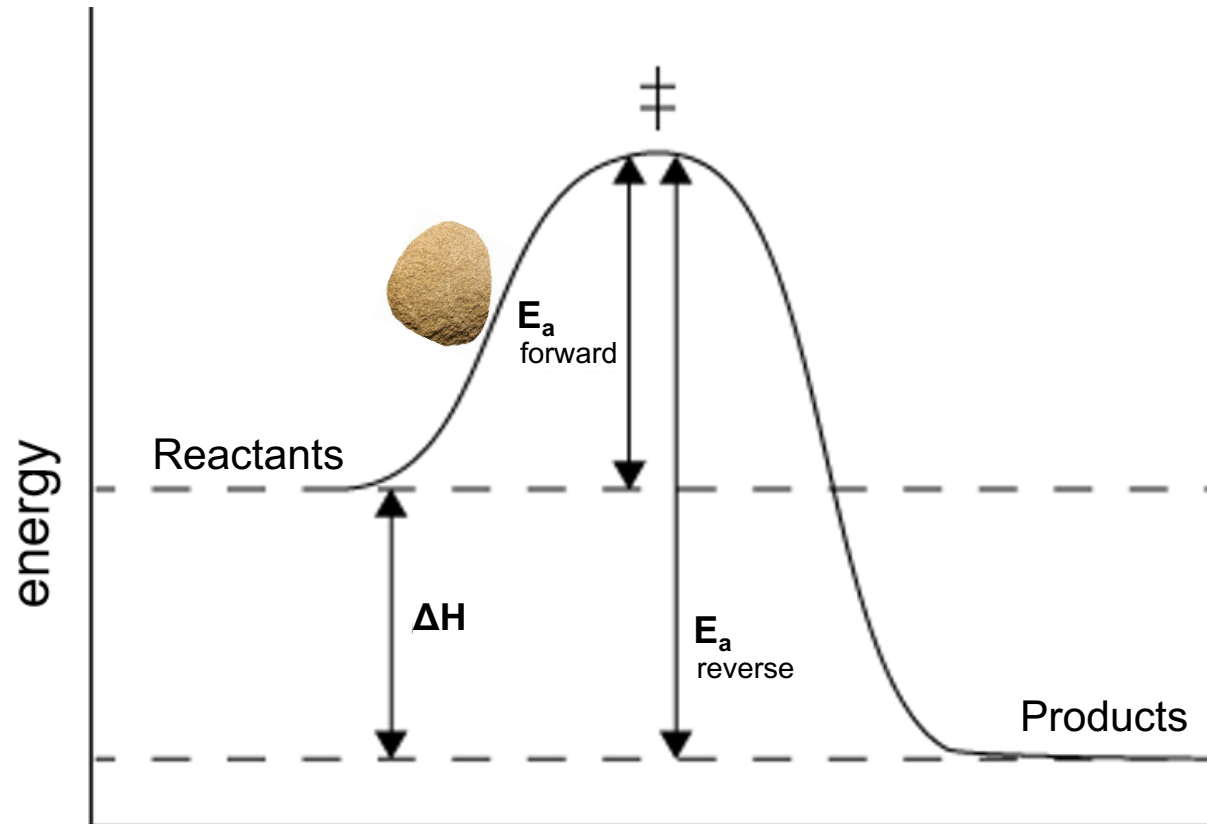
ΔE is also called **activation energy**, E_a , $E_{\text{activation}}$, or $\ddagger$.



What is ΔE ?

ΔE is the difference between the energy level of the reactants and the top of the hill.

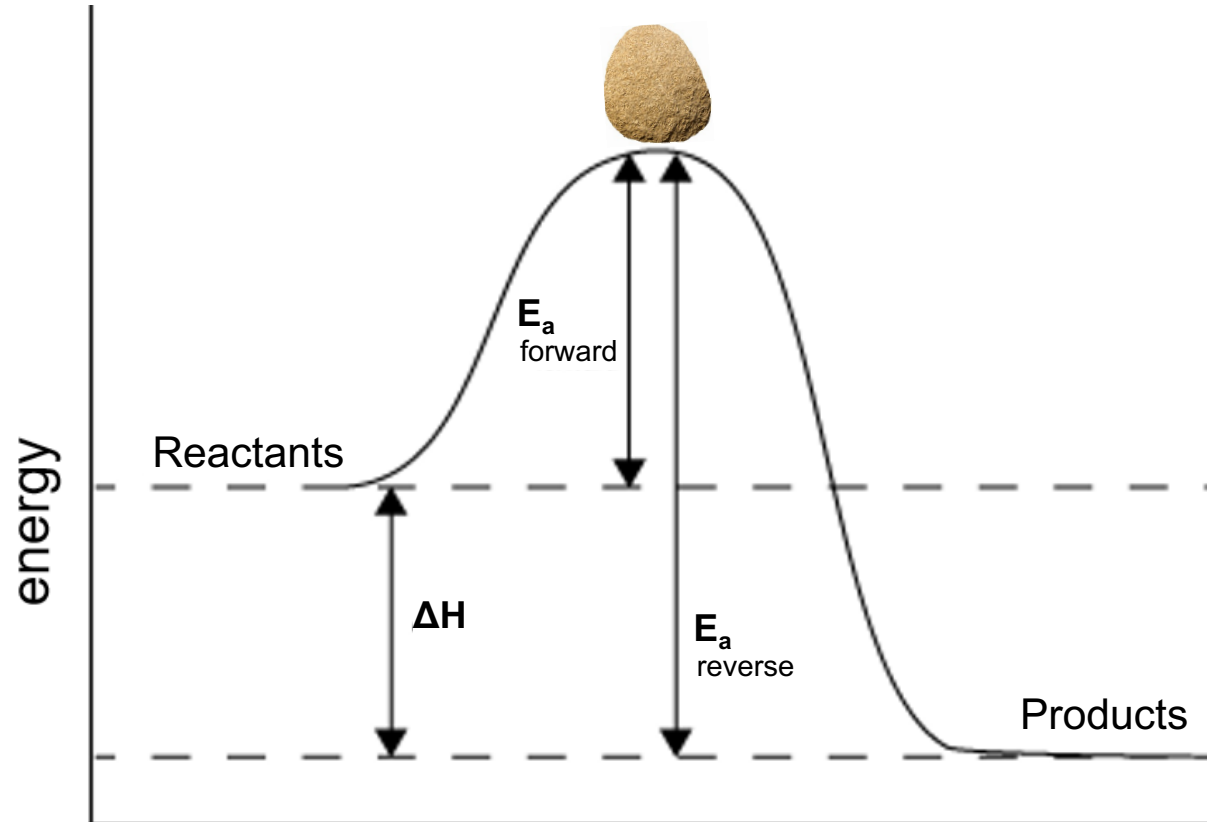
ΔE is also called **activation energy**, E_a , $E_{\text{activation}}$, or $\ddagger$.



What is ΔE ?

ΔE is the difference between the energy level of the reactants and the top of the hill.

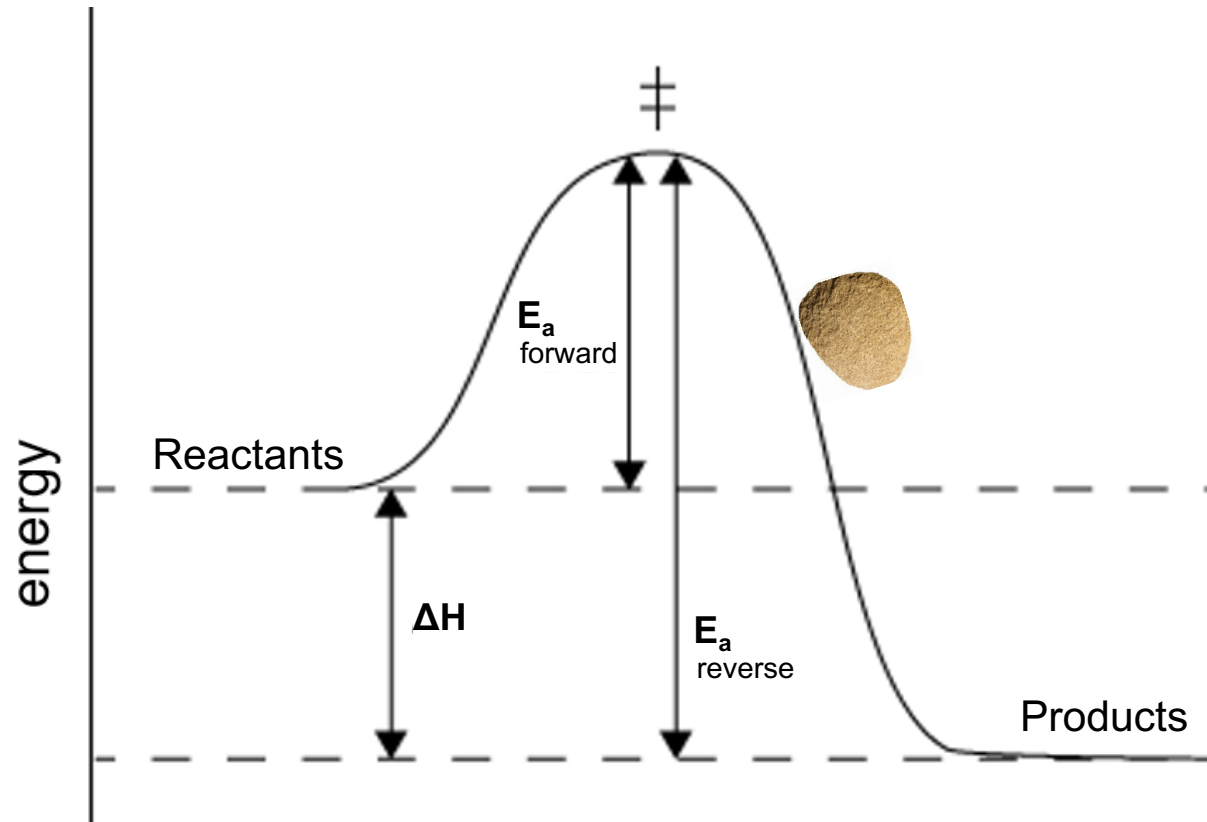
ΔE is also called **activation energy**, E_a , $E_{\text{activation}}$, or $\ddagger$.



What is ΔE ?

ΔE is the difference between the energy level of the reactants and the top of the hill.

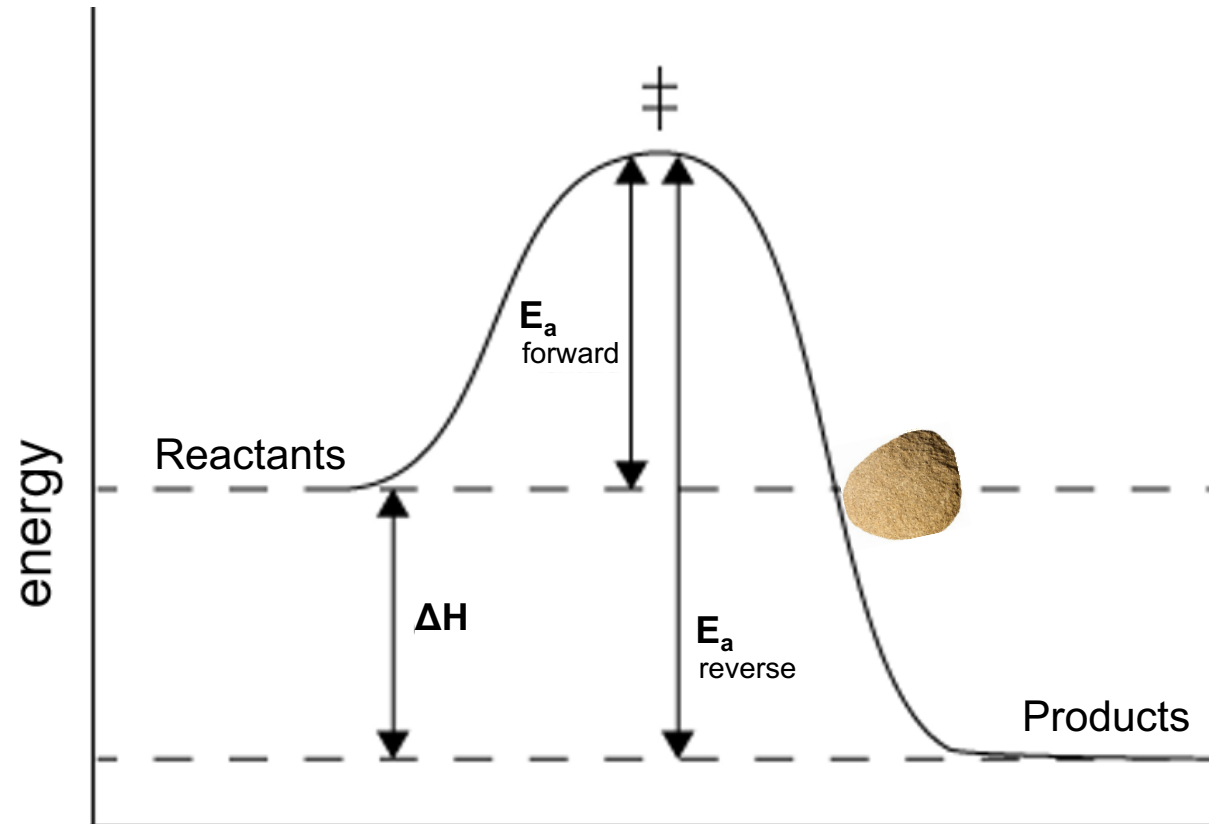
ΔE is also called **activation energy**, E_a , $E_{\text{activation}}$, or $\ddagger$.



What is ΔE ?

ΔE is the difference between the energy level of the reactants and the top of the hill.

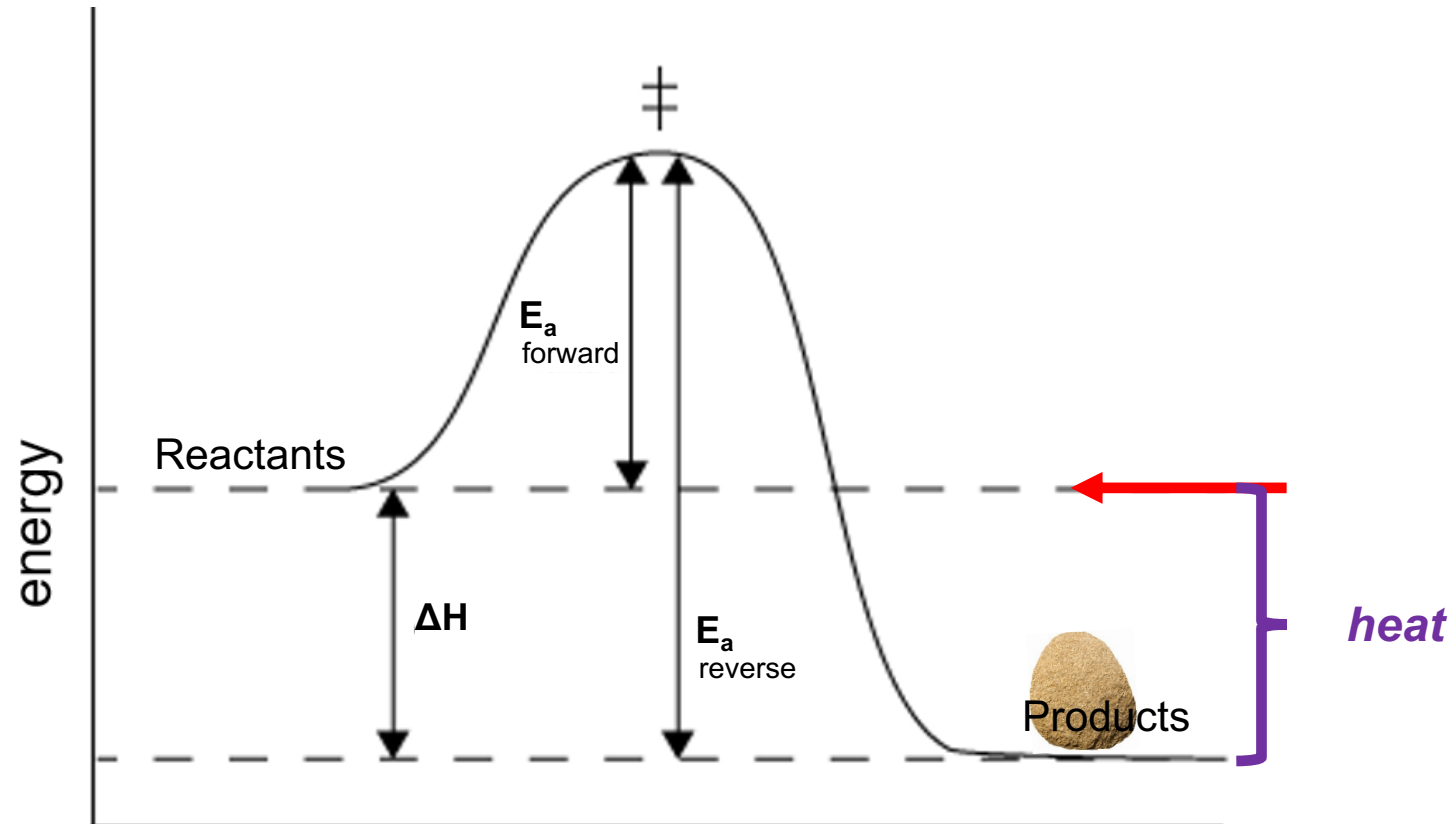
ΔE is also called **activation energy**, E_a , $E_{\text{activation}}$, or $\ddagger$.



What is ΔE ?

ΔE is the difference between the energy level of the reactants and the top of the hill.

ΔE is also called **activation energy**, E_a , $E_{\text{activation}}$, or $\ddagger$.



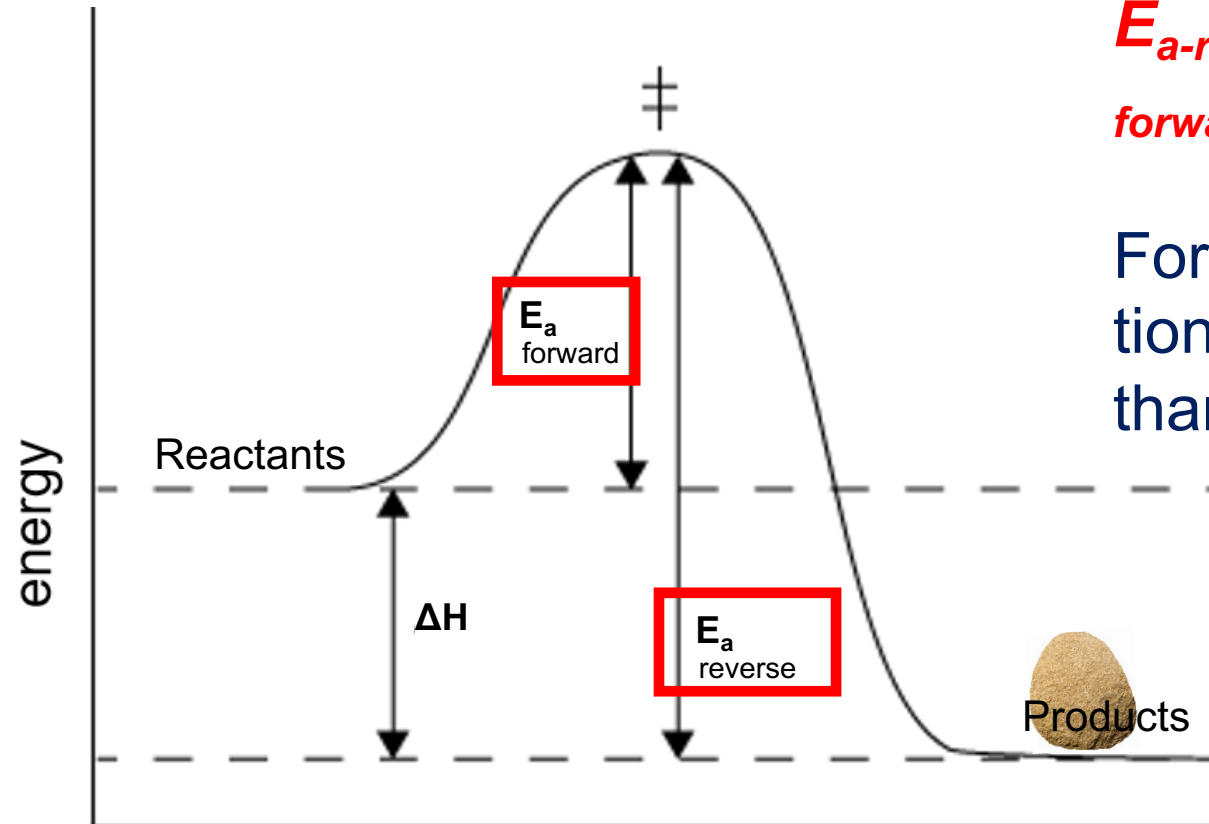
Can the Reaction Go Backwards?

ΔE is the difference between the energy level of the reactants and the top of the hill.

ΔE is also called **activation energy**, E_a , $E_{activation}$, or $\ddagger$.

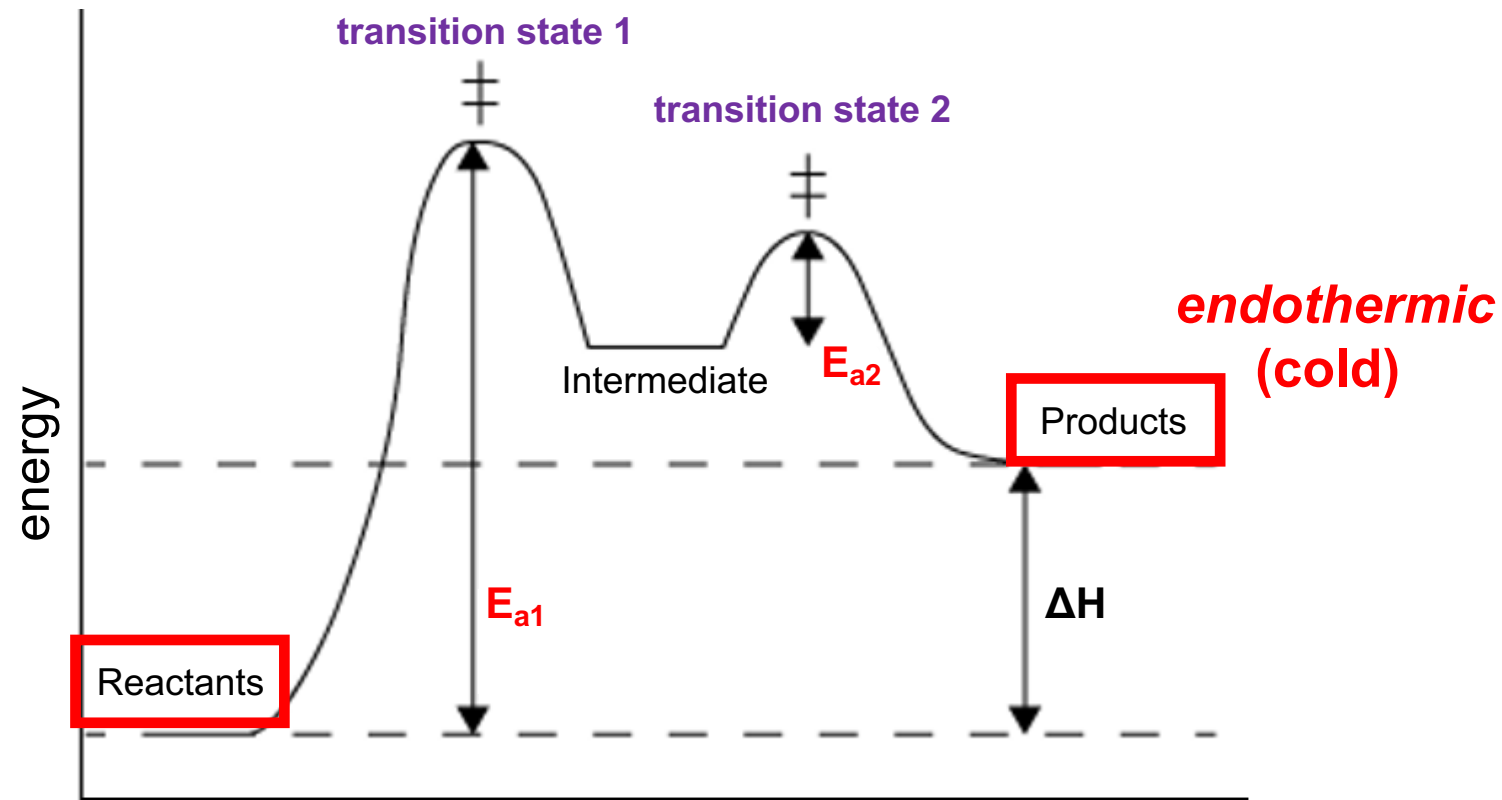
For **exothermic** reactions, $E_{a-reverse}$ is larger than $E_{a-forward}$.

For **endothermic** reactions, $E_{a-reverse}$ is smaller than $E_{a-forward}$.



Multistep Reactions

Some reactions have multiple steps, with multiple *activation energies*.

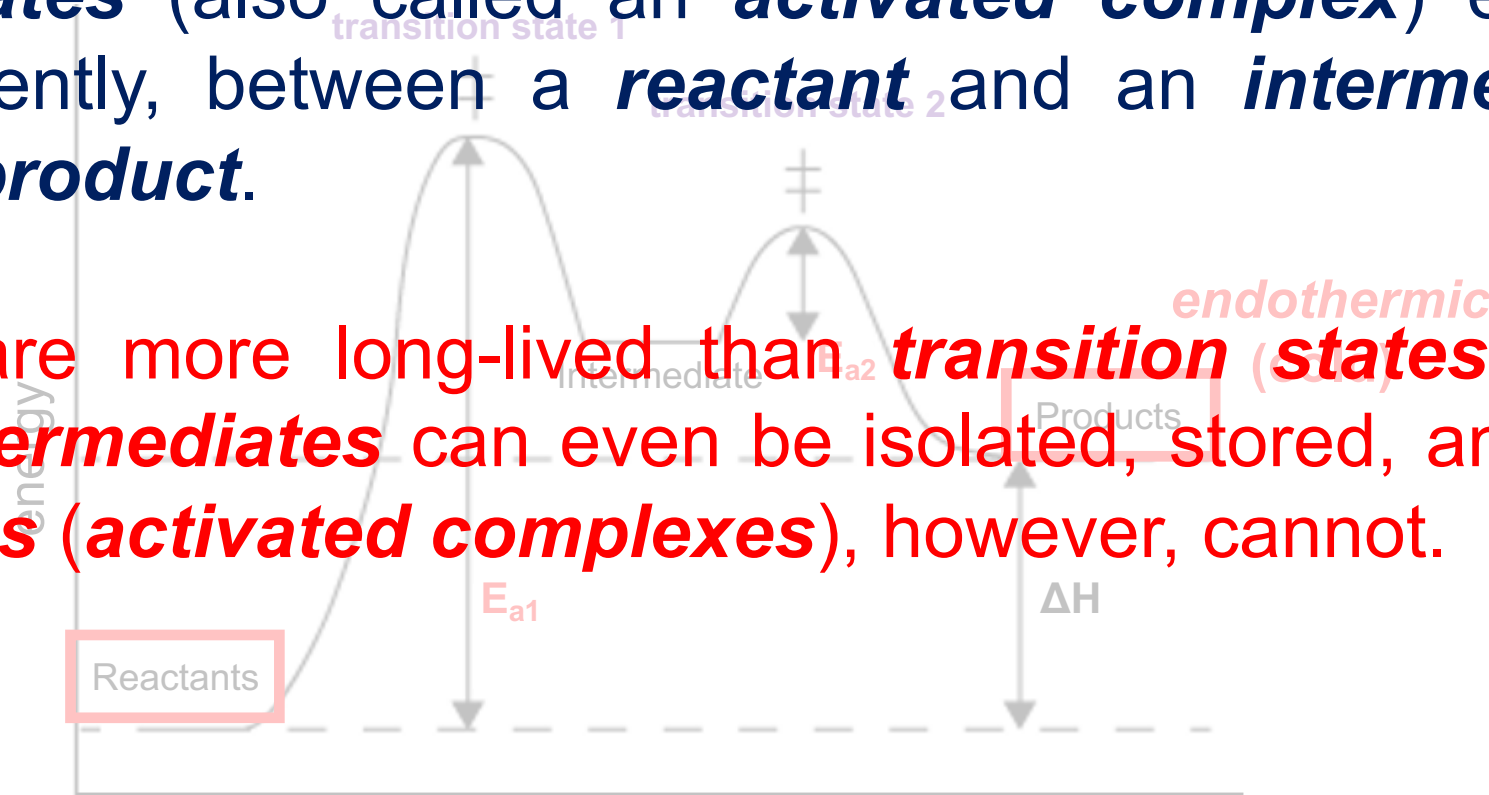


Transition State vs. Intermediate

What is the difference between a *transition state* and an *intermediate*?

A *transition state* (also called an *activated complex*) exists VERY briefly, or transiently, between a *reactant* and an *intermediate*, or a *reactant* and a *product*.

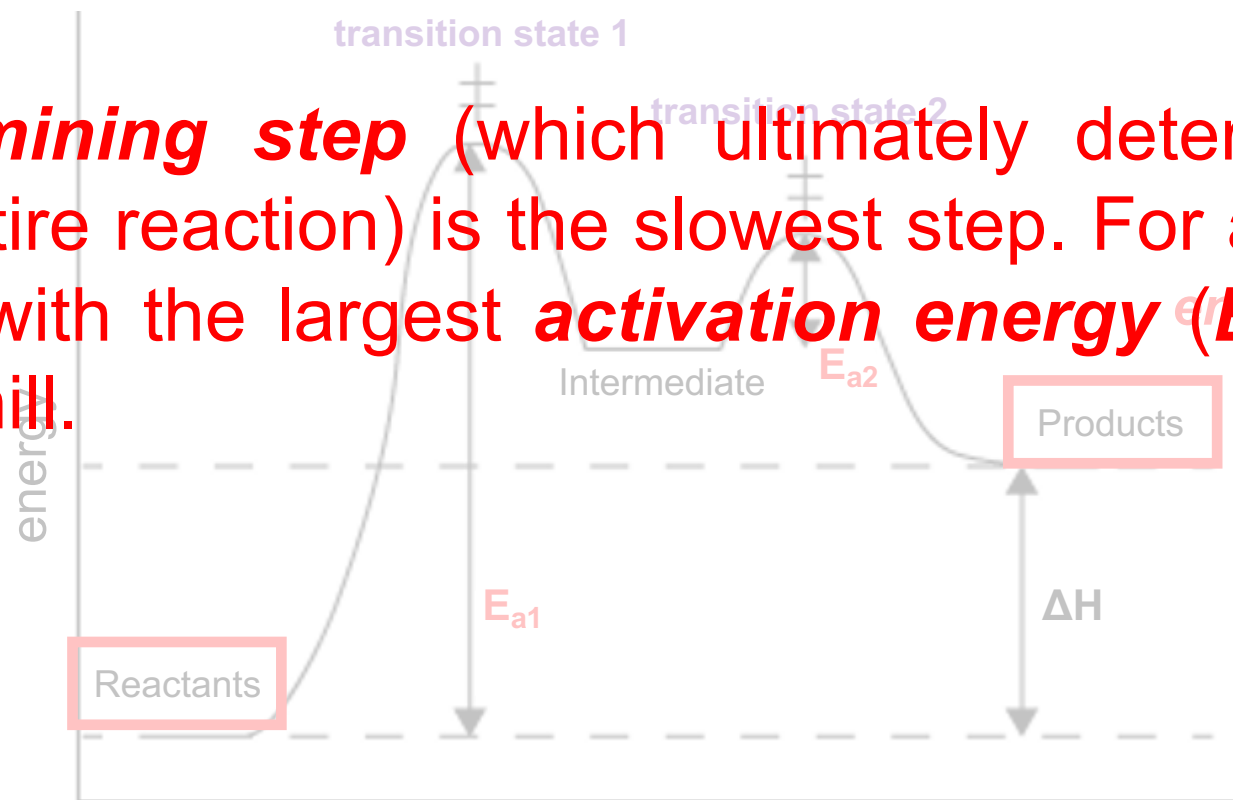
Intermediates are more long-lived than *transition states*. In fact, in some cases, *intermediates* can even be isolated, stored, and analyzed. *Transition states* (*activated complexes*), however, cannot.



Rate Determination

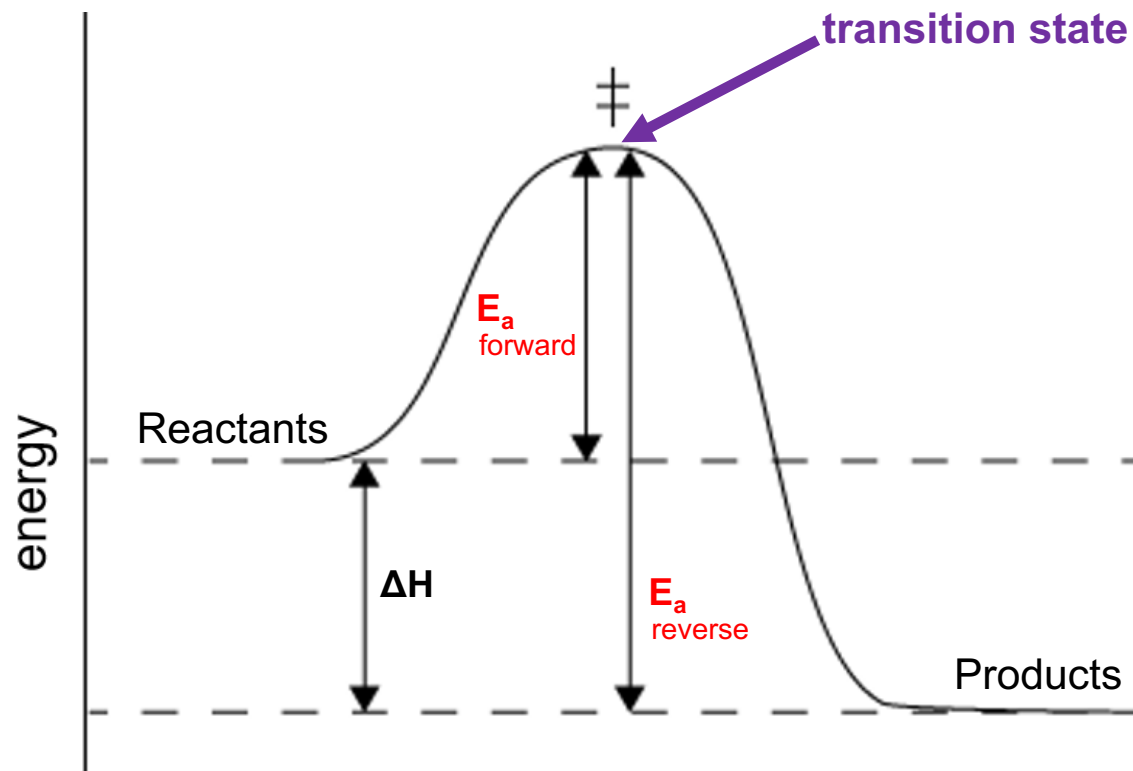
In a multistep reaction, which step is the *rate-determining step*?

The *rate-determining step* (which ultimately determines the rate, or speed, of the entire reaction) is the slowest step. For a multistep reaction, this is the step with the largest *activation energy* (E_a): that is, the step with the largest hill.



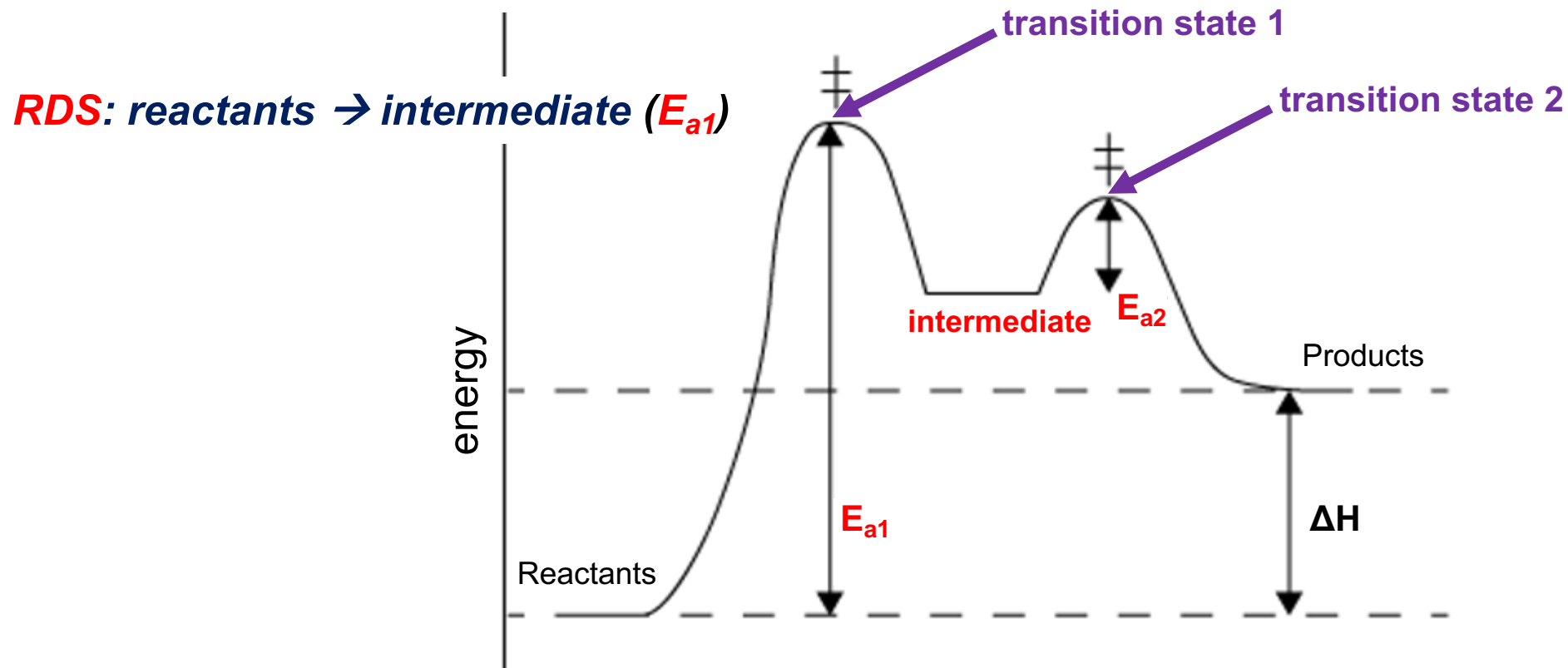
Questions

For the following exothermic **reaction coordinate diagram**, please label the activation energies (E_a) for both the forward reaction and the reverse reaction. Also, please label the **transition state**.

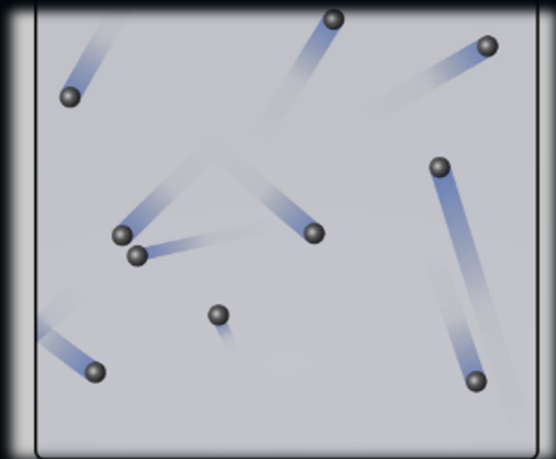
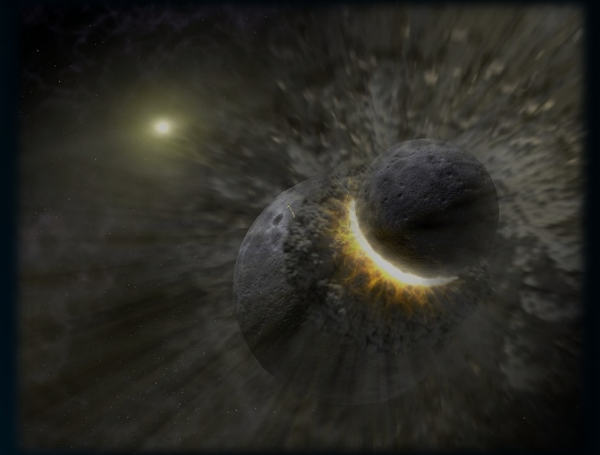


Questions

For the following endothermic **reaction coordinate diagram**, please label both of the activation energies (E_a) for the forward reaction. Also, please label any **transition states** and **intermediates**. Which step is the **rate-determining step**?



Chemical Kinetics (Catalysts)

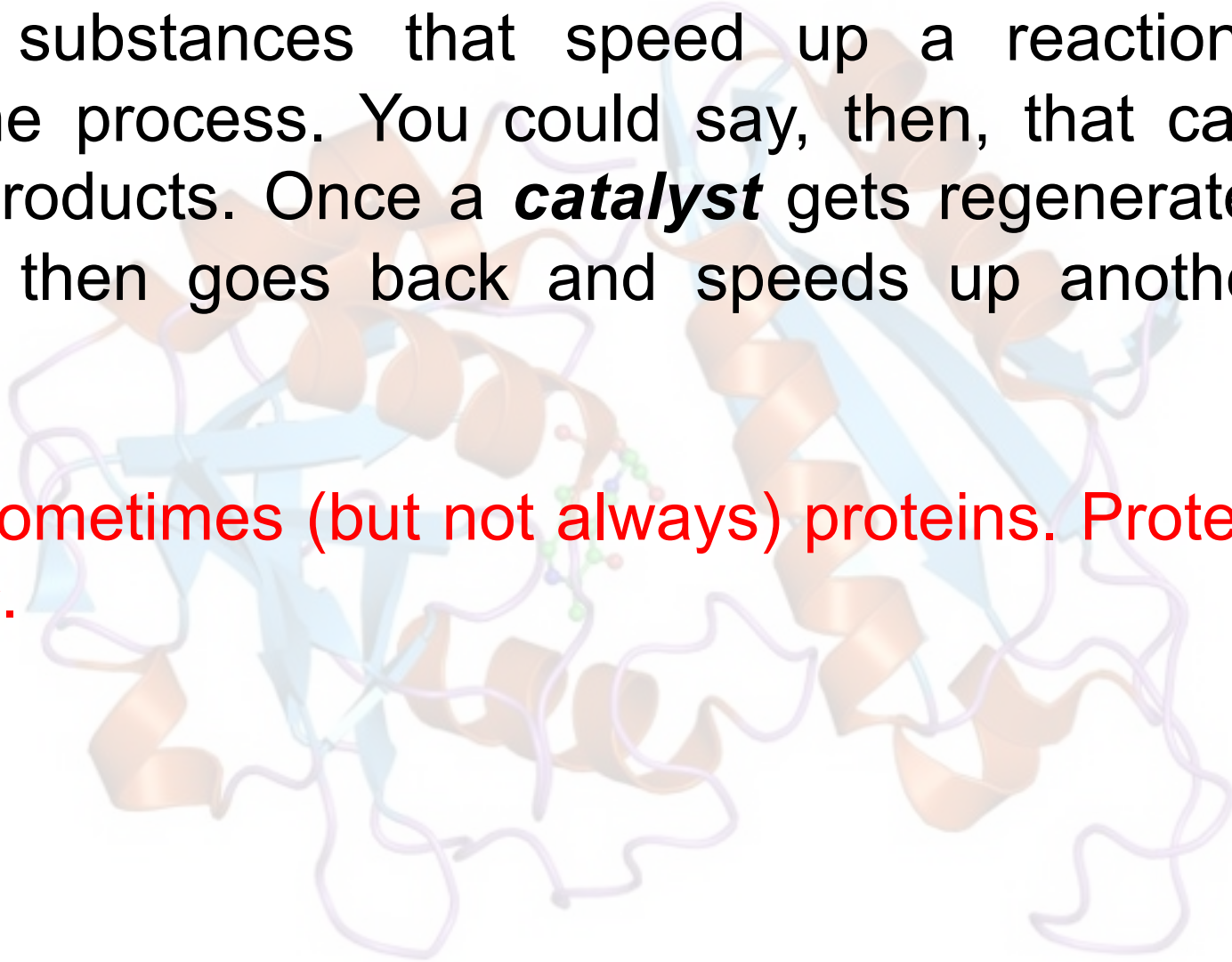


By Olivier Cleynen and User:Sharayanan - Own work based on File:Kinetic theory of gases.svg which is licensed CC-by-saThis vector image was created with Inkscape., CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=40017346>

Intro Stuff

Catalysts are substances that speed up a reaction without being consumed in the process. You could say, then, that catalysts are both reactants and products. Once a **catalyst** gets regenerated at the end of the reaction, it then goes back and speeds up another round of the reaction again.

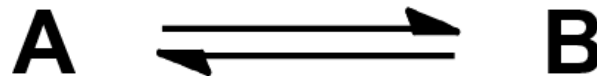
Catalysts are sometimes (but not always) proteins. Protein **catalysts** are called **enzymes**.



Things You Should Know

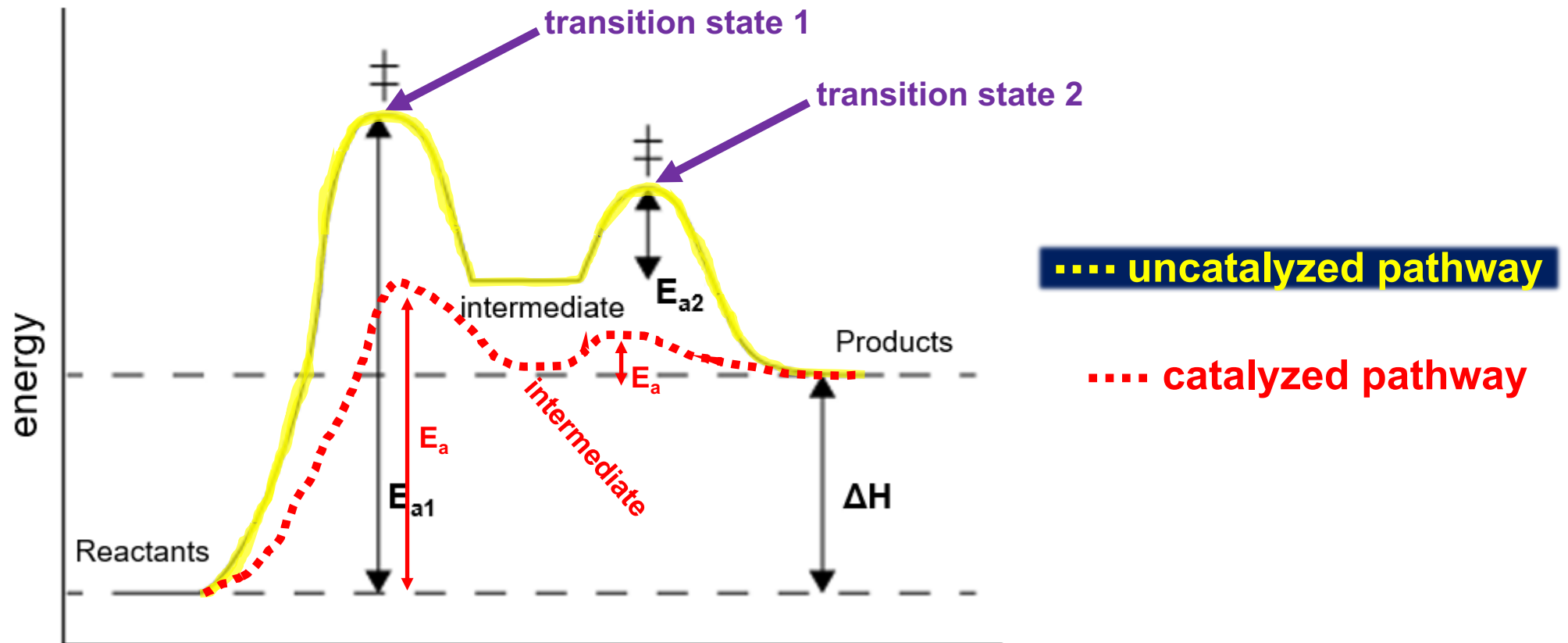
For EXAM, you need to know the following about ***catalysts***:

1. ***Catalysts*** are NOT consumed in the reactions they catalyze.
2. ***Catalysts*** speed up a reaction by lowering its ***activation energy***, NOT by changing the energy levels of the reactants or products.
3. ***Catalysts*** lower a reaction's activation energy by providing an alternative pathway (a different mechanism) between reactants and products.
4. ***Catalysts*** do NOT shift ***equilibrium reactions***. They only help the reaction reach ***equilibrium*** more quickly.



How Do Catalysts Work?

Again, the **catalyst** speeds up the reaction by lowering its **activation energy**, NOT by changing the energy levels of the reactants or products. The catalyst lowers the **activation energy** by providing an alternative lower-energy pathway (a different **mechanism**) between reactants and products.



Questions

True or False: Adding a catalyst will shift the following equilibrium reaction to the right, increasing product yield:



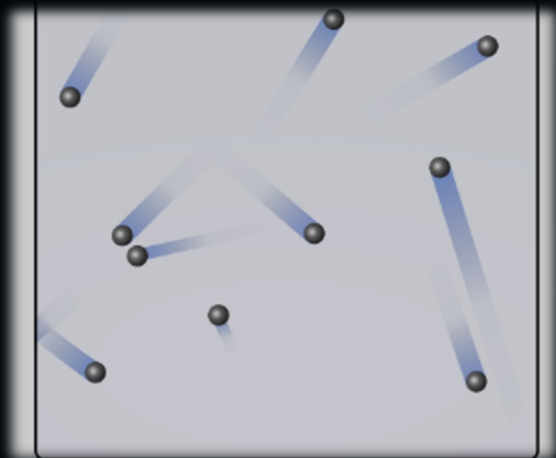
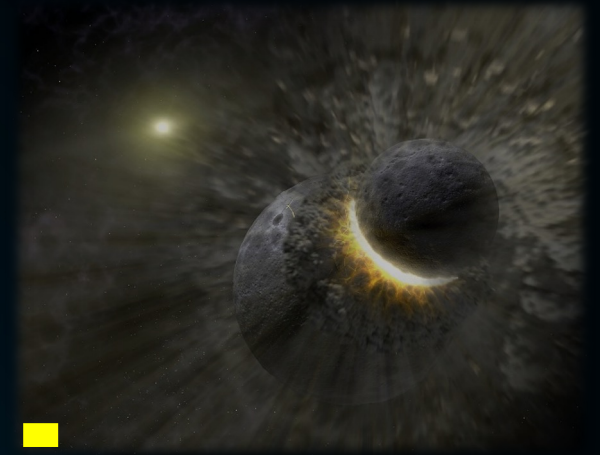
Questions

A catalyst increase a reaction's rate by _____.

- A. Providing an alternative pathway with a lower **activation energy**
- B. Increasing the overall **activation energy** (E_a) of the reaction
- C. Changing the value of the **Van't Hoff factor** (i)
- D. Lowering the **activation energy** of the reverse reaction
- E. Changing the energy levels of the reactants and products.
- F. All of these are ways that a catalyst might act to increase the rate of reaction.

Chemical Kinetics

(Collision Theory and the Arrhenius Equation)



Collision Theory

Molecules have to collide (hit each other) to react. The greater the number of collisions per second, the greater the chance that molecules will hit each other in a way that leads them to react.

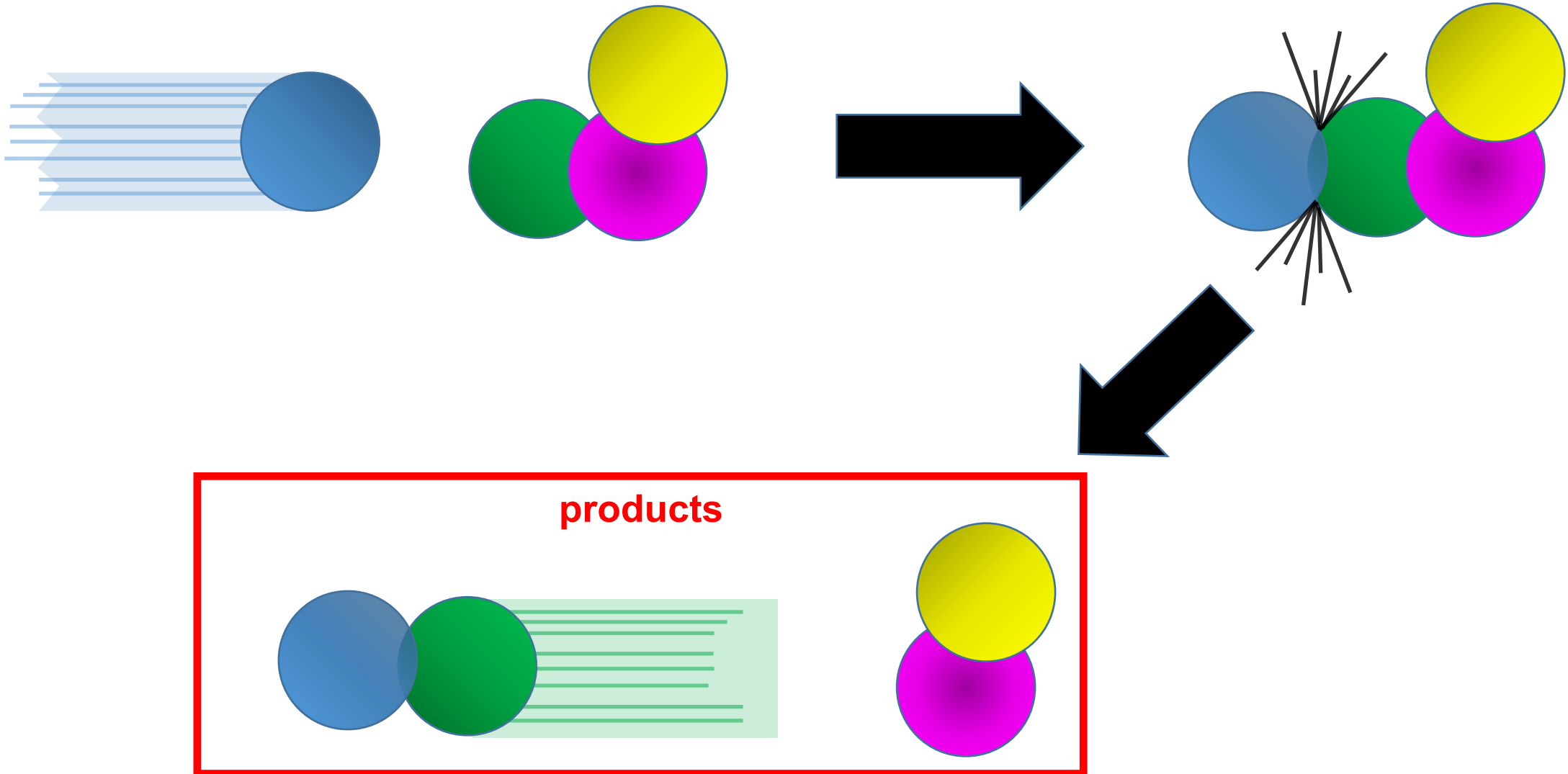
Increasing a reaction's temperature increases individual molecules' speeds. This increases the total number of collisions they experience and, hence, the overall likelihood that molecules will hit each other in a way that leads them to react. This whole idea is called ***collision theory***.

Collision Theory

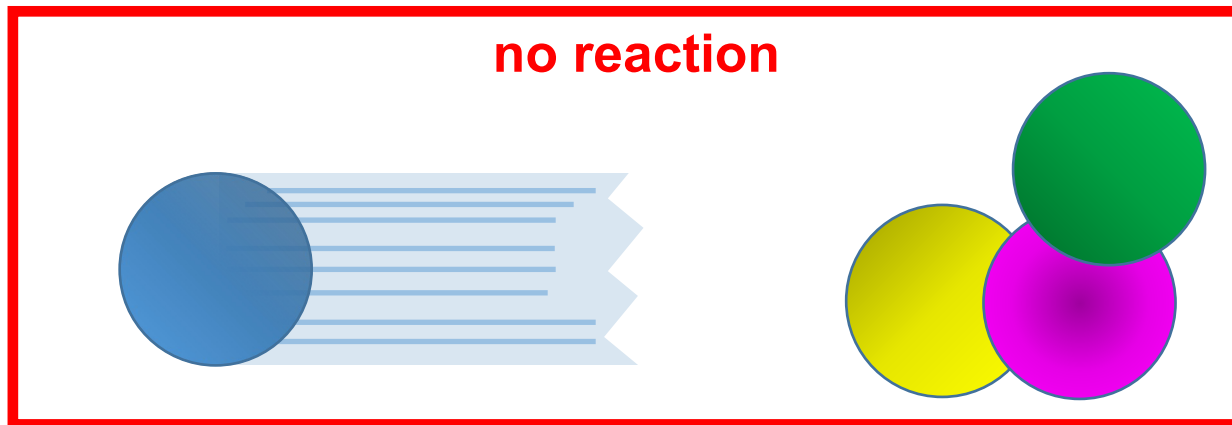
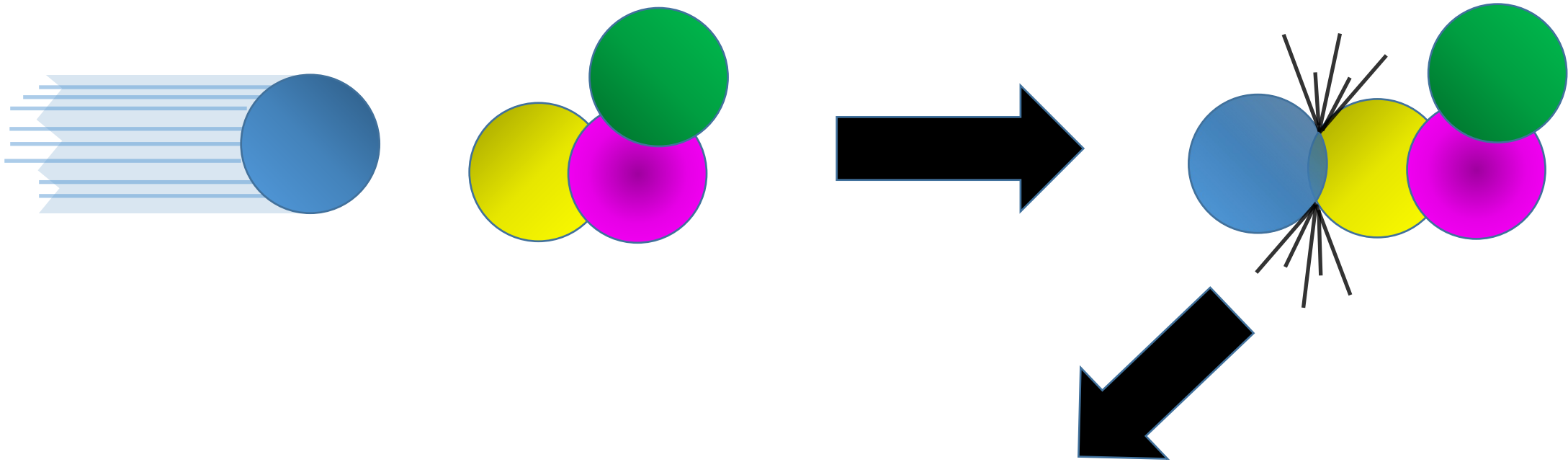
In order for a reaction between two molecules to happen, three things must occur:

1. Both molecules must collide with each other.
2. The molecules need to collide with enough energy for the reaction to happen; in other words, to get over the **activation energy** (E_a) barrier for the reaction.
3. The molecules need hit each other with the correct **three-dimensional orientation**.

What does “Correct Orientation” Mean?



What does “Correct Orientation” Mean?



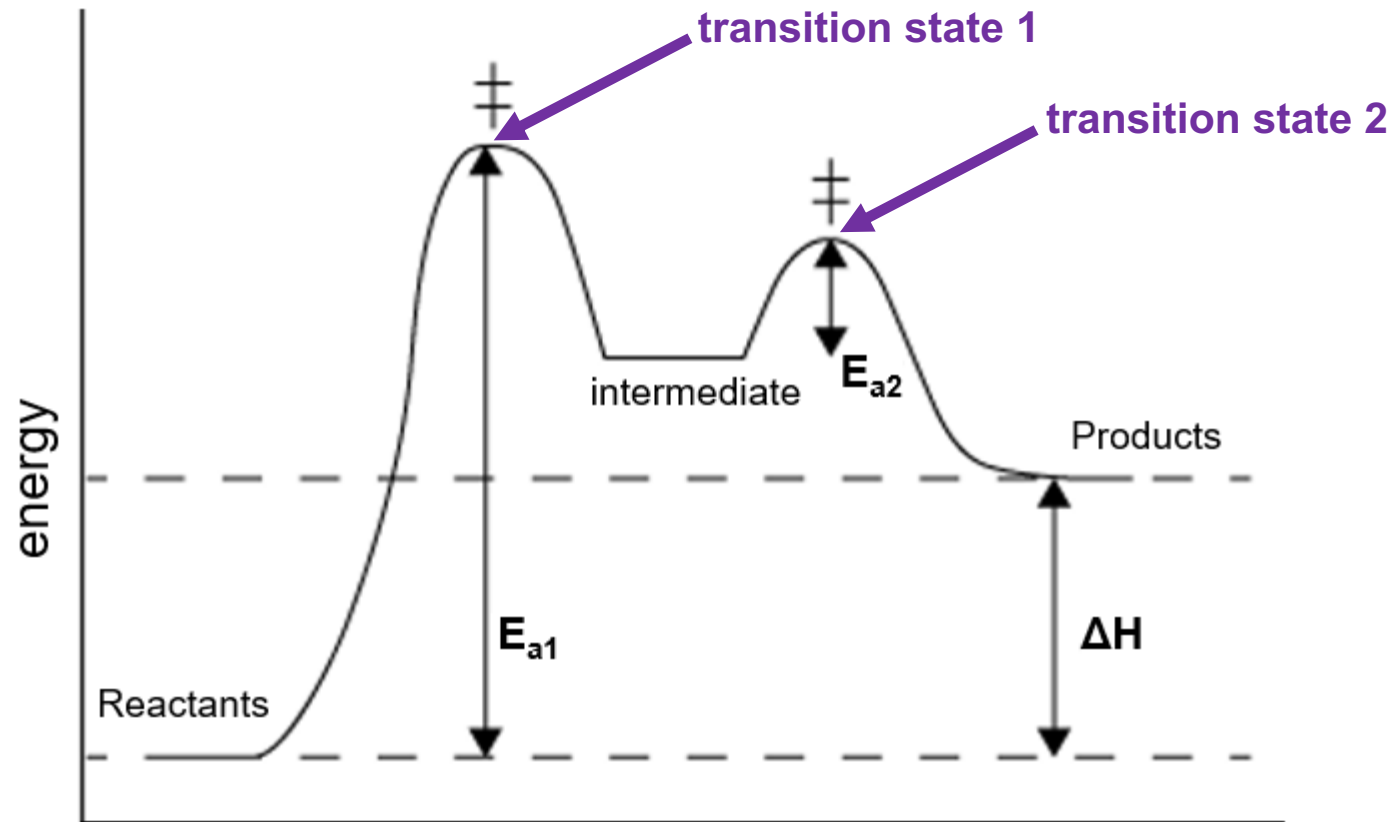
Collision Theory

In order for a reaction between two molecules to happen, three things must occur:

1. Both molecules must collide with each other.
2. The molecules need to collide with enough energy for the reaction to happen; in other words, to get over the **activation energy** (E_a) barrier for the reaction.
3. The molecules need hit each other with the correct **three-dimensional orientation**.

Back to Activation Energy

In a prior video, I introduced you to *reaction coordinate diagrams*, with their various components: *transition states*, *intermediates*, ΔH , and *activation energies* (E_a).



The Arrhenius Equation

Like everything else in chemistry, there exists an equation we can use to calculate **activate energy** (E_a). This equation is called the **Arrhenius Equation**:

$$k = Ae^{-E_a/RT}$$

... Where:

- k is the rate constant.
- R is the ideal gas constant (8.314 J/mol-K, and yes, for this equation, we have to use this value of R , instead of 0.0821 L-atm/mol-K).
- T is the reaction temperature.
- E_a is the reaction's activation energy.
- A is something called a **frequency factor**.

The Arrhenius Equation

You do NOT need to memorize this equation. What you do need to know is that a reaction's rate is directly related to its *rate constant*, ***k***. Mathematically, then:

$$k = Ae^{-E_a/RT}$$

... As ***T*** goes up, ***k*** goes up, and so does the reaction's speed or rate.

$$\uparrow T \approx \uparrow k \approx \uparrow \text{reaction rate}$$

Why?

Why would increasing temperature increase a reaction's rate?

- Increasing temperature increases molecules' speed, which increases the number of collisions they experience.
- Increasing temperature increases molecules' average ***kinetic energy***, so the molecules will hit each other with greater energy, which increases their ability to overcome (E_a).

The Arrhenius Equation

The *Arrhenius Equation* also tells us that k is inversely proportional to E_a .

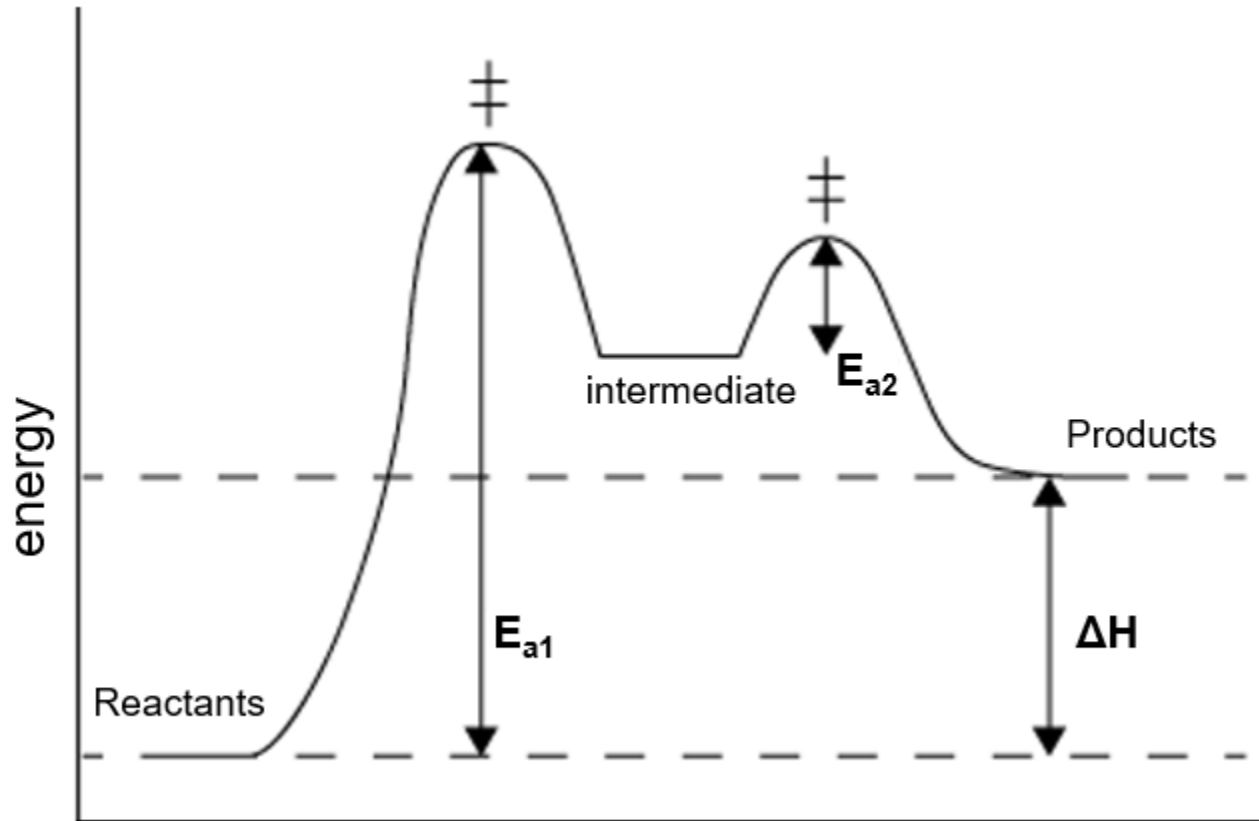
$$k = Ae^{-E_a/RT}$$

. . . This means that as E_a goes down, k goes up, and so does the reaction's speed or rate.

$$\downarrow E_a \approx \uparrow k \approx \uparrow \text{reaction rate}$$

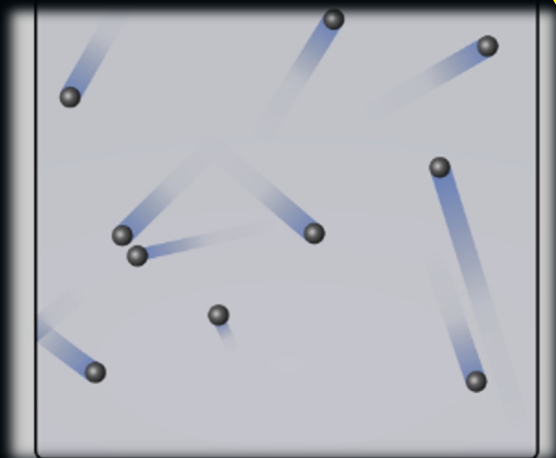
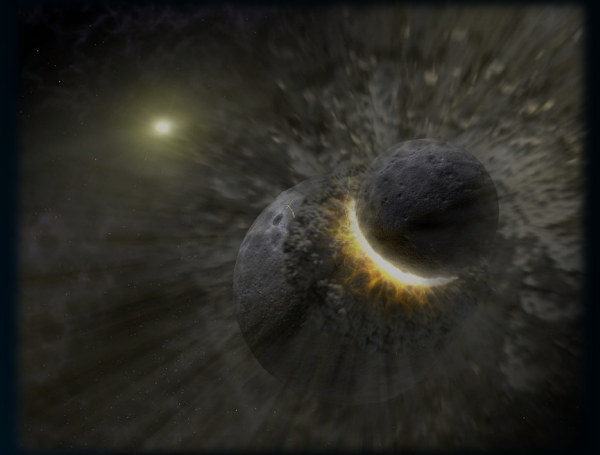
The Arrhenius Equation

$$\downarrow E_a \approx \uparrow k \approx \uparrow \text{reaction rate}$$



Chemical Kinetics

(Reaction Mechanisms)



Reactions Are Complex

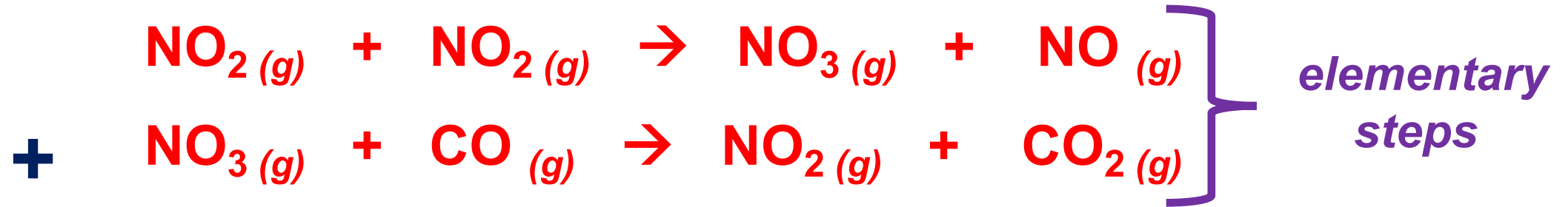
When learning chemistry, we often write chemical equations like this:



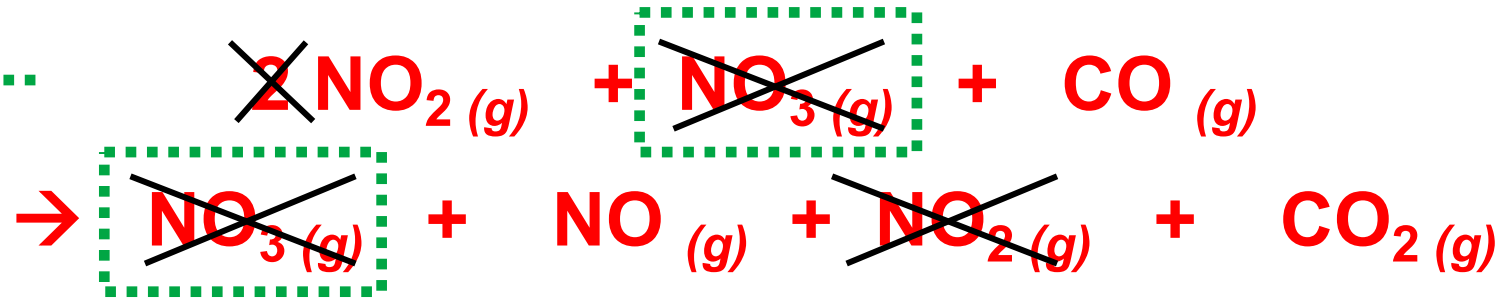
. . . Without giving much thought into what actually transpires when these reactants interact with each other to produce these products. In real life, however, sometimes reactions like this one actually happen over multiple steps. This one, for instance, actually transpires over the following two steps:



Reactions Are Complex



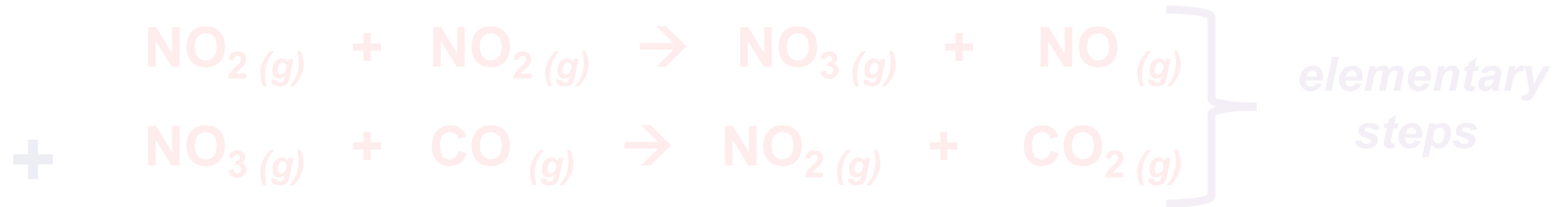
intermediate



Overall:



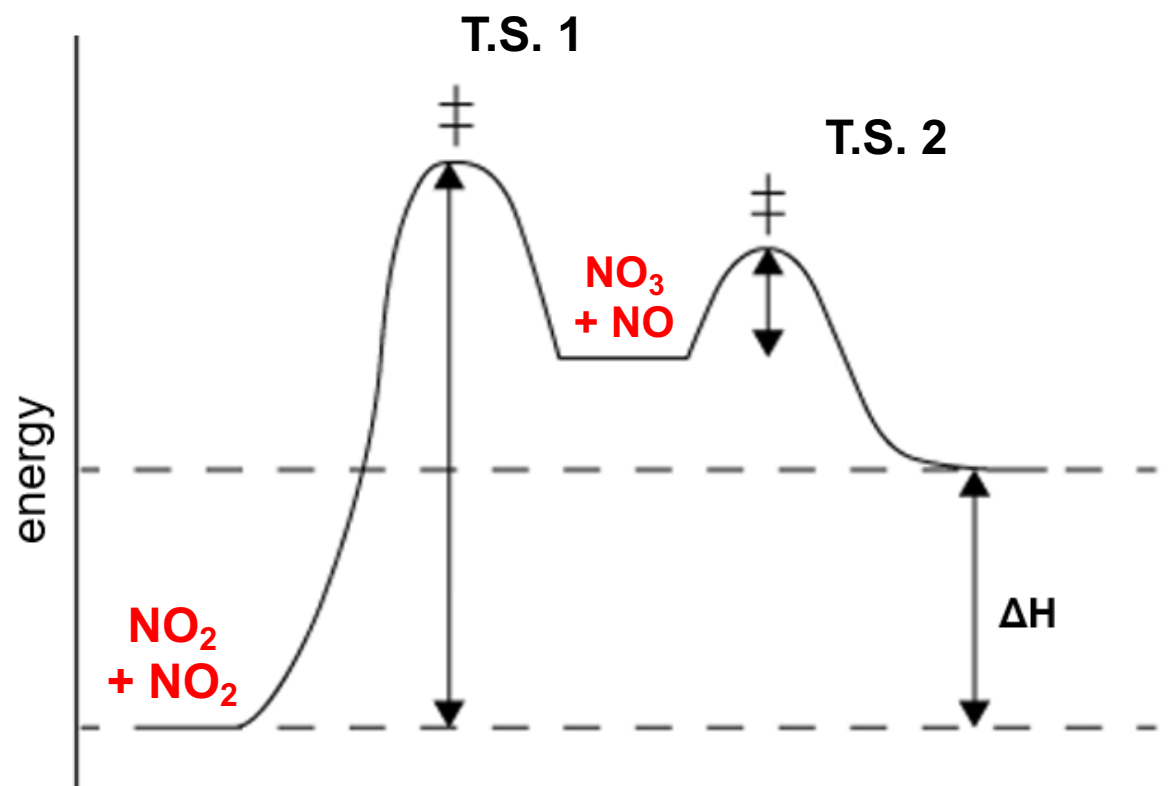
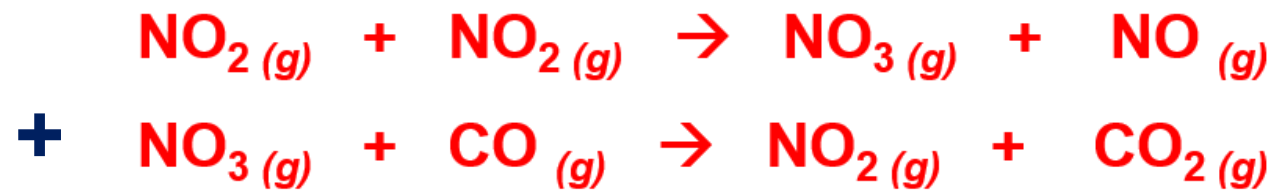
Reactions Are Complex

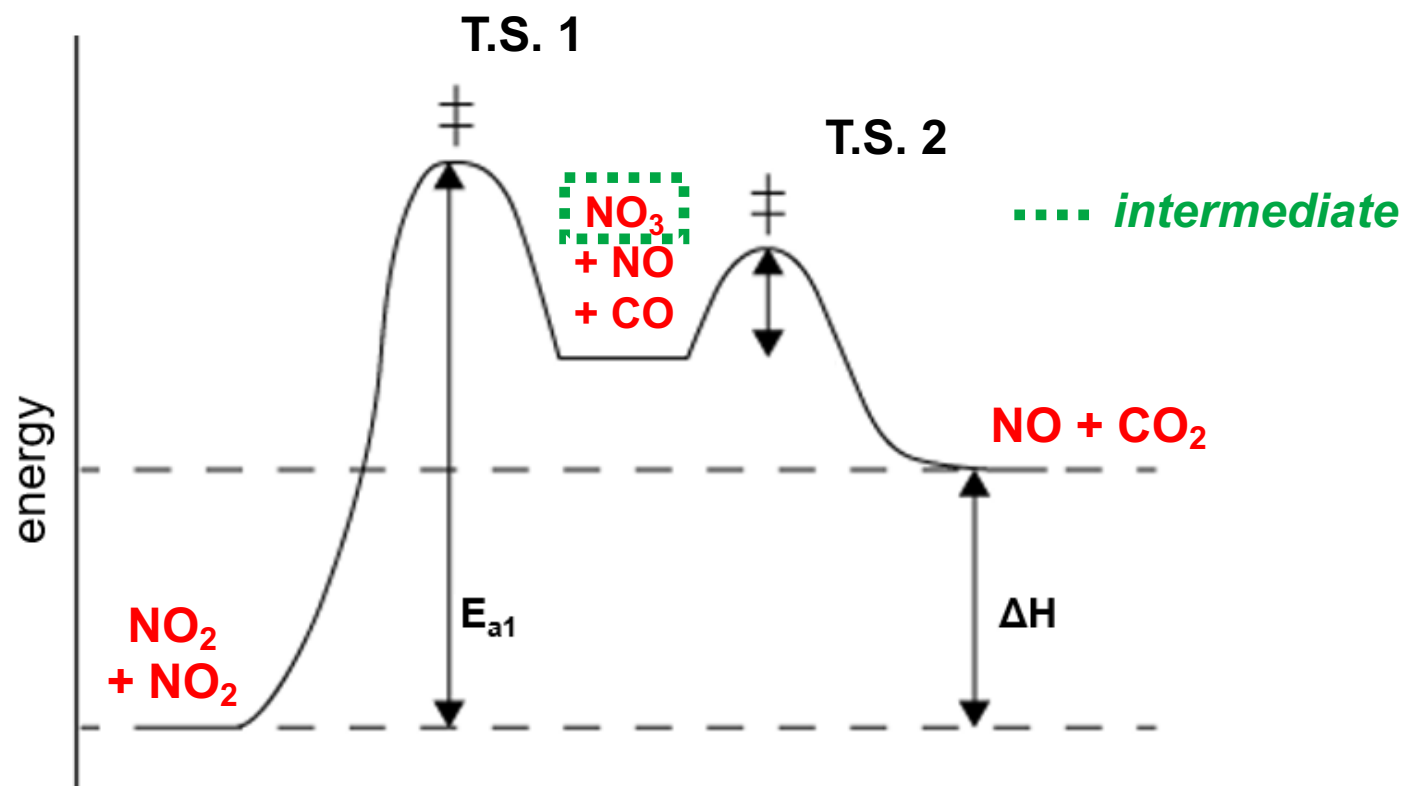
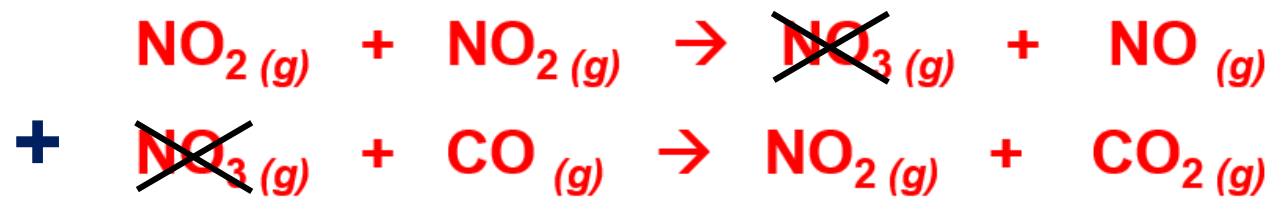


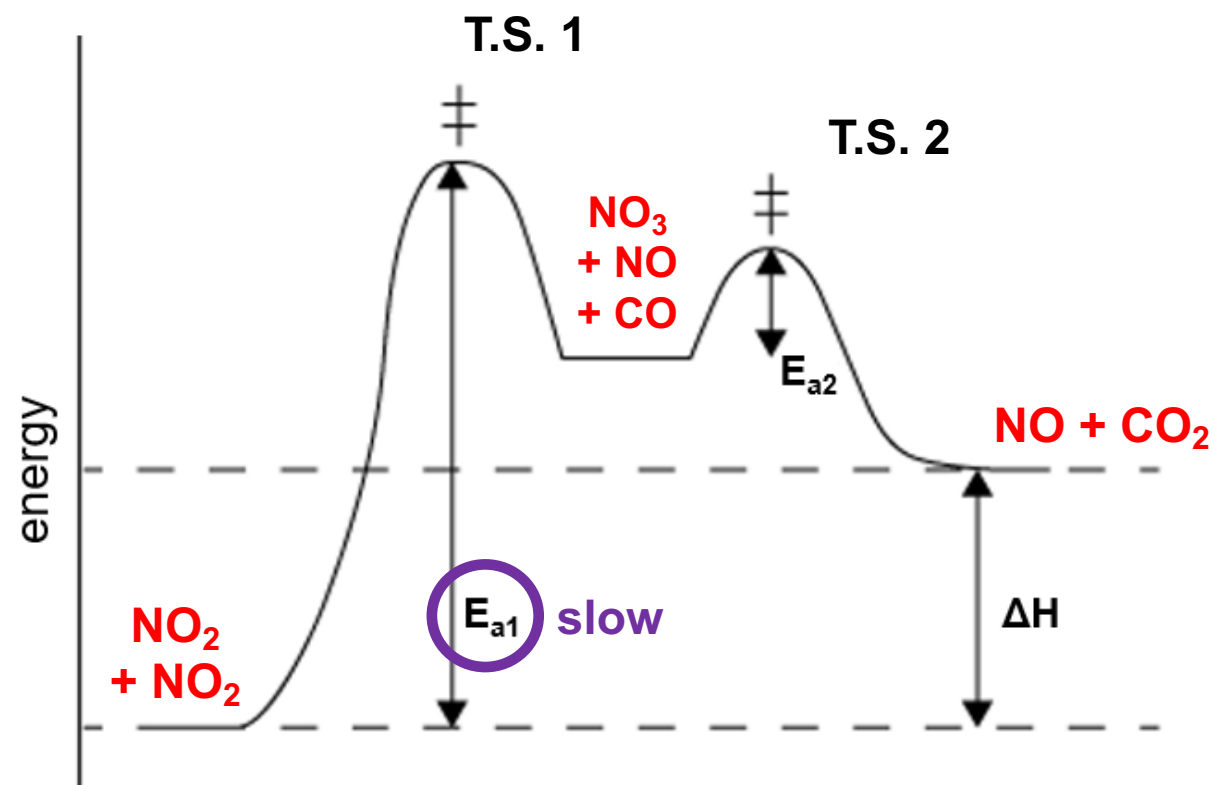
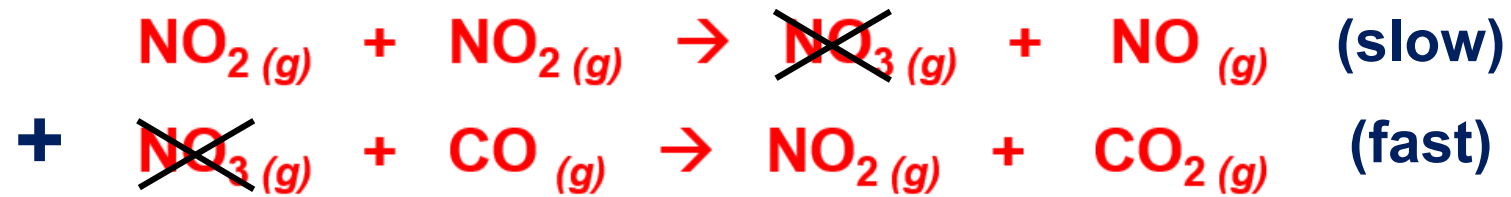
The fully-accurate description, with all the ***elementary steps*** (***elementary reactions***) listed, of how a reaction proceeds, is called that reaction's ***mechanism***.

Overall:







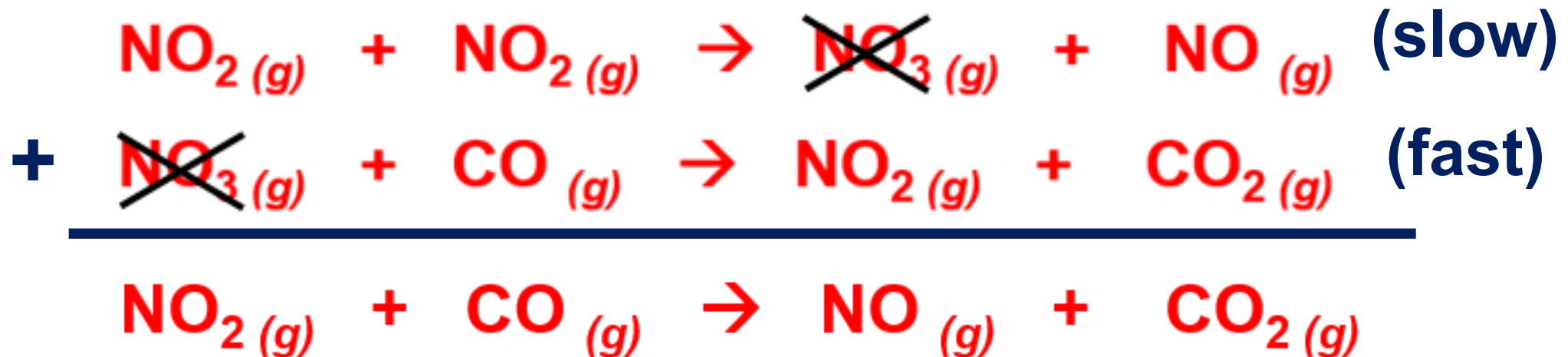


Rate-Determining Steps

The slow step is called the *rate-determining step* (**R.D.S**). Just like on an assembly line, the speed of the entire reaction (process) is equal to the speed of the slowest step. Once again, this is called the *rate-determining step* (**R.D.S**).



assembly line



What You Have to Know

On this subject, for the EXAM, you will likely be given the ***elementary reactions*** (***elementary steps***). You will then have to answer three questions about the reaction's ***mechanism***:

1. What is the ***intermediate***?

(***Intermediates*** are produced in the middle of the reaction and get used up before the end. They get cancelled out along the way.)

2. What is the overall ***rate law***?

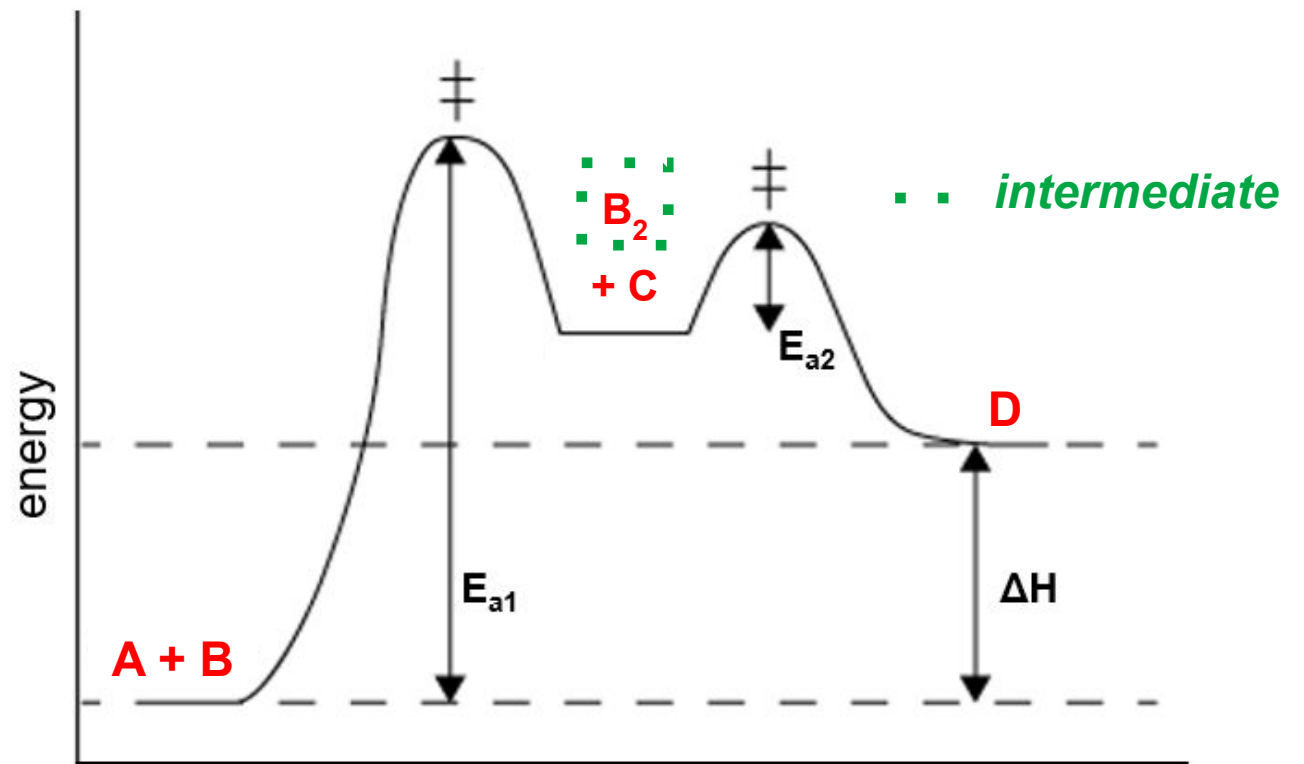
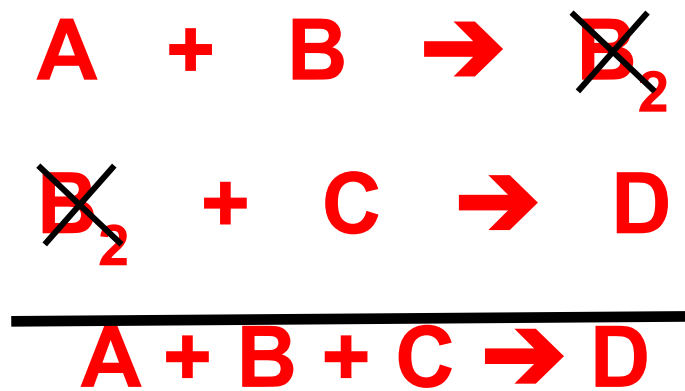
(If you're given a set of ***elementary steps***, then ***rate law*** is:

rate = $k \times$ (concentration of each reactant in the ***slow*** step, multiplied by each other)

3. What is the overall reaction? (Just add up the ***elementary steps*** and cancel out ***intermediates***.)

Intermediate vs. Catalyst

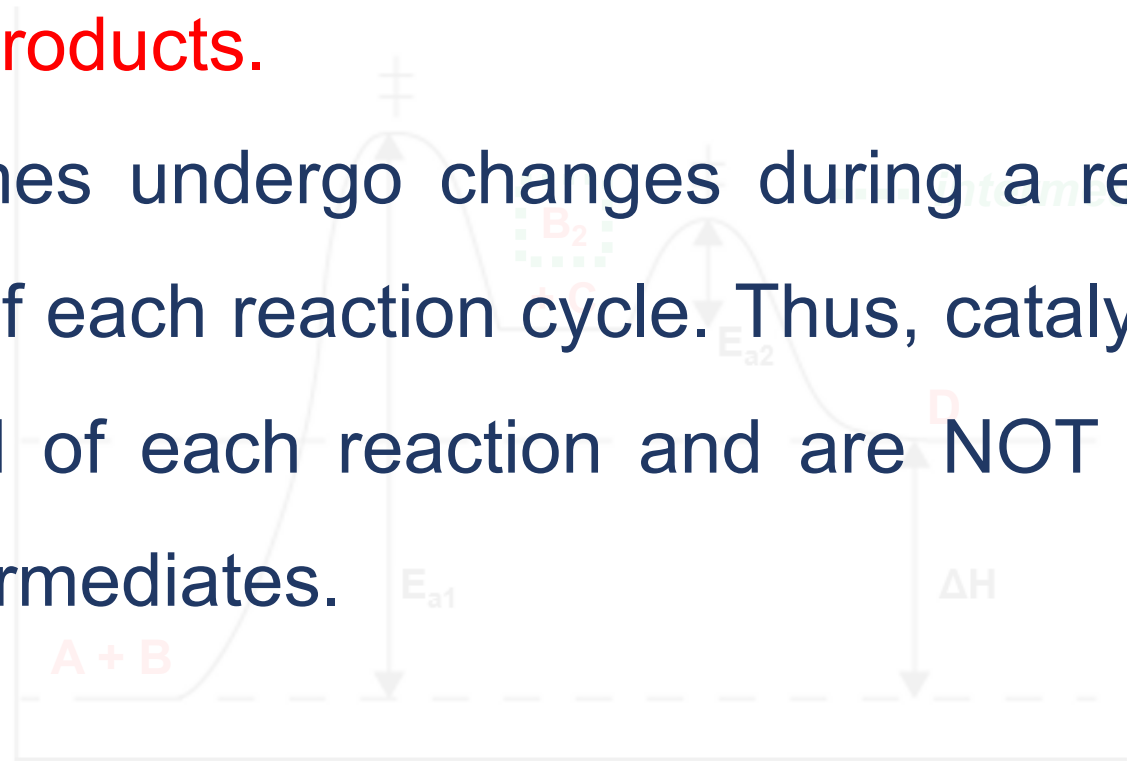
An intermediate is a substance that is not found at the beginning or end of a chemical reaction, but is only produced temporarily along the way:



Intermediate vs. Catalyst

Catalysts are substances that are added, often in a small-percentage amount, at the very *start* of the reaction. Catalysts provide a lower-energy pathway between reactants and products.

Although catalysts sometimes undergo changes during a reaction, they get regenerated at the end of each reaction cycle. Thus, catalysts are present at the start and the end of each reaction and are NOT formed temporarily in the middle, like intermediates.



Questions

A certain chemical reaction has the following elementary steps:



For this reaction, please answer the following:

1. What is the *intermediate*?
2. What is the overall *rate law*?
3. What is the overall reaction?

Questions

For the reaction described by the coordinate diagram below:

1. What are the ***elementary steps***?
2. What is/are the ***intermediate(s)***?
3. What is the overall ***rate law***?
4. What is the overall reaction?

