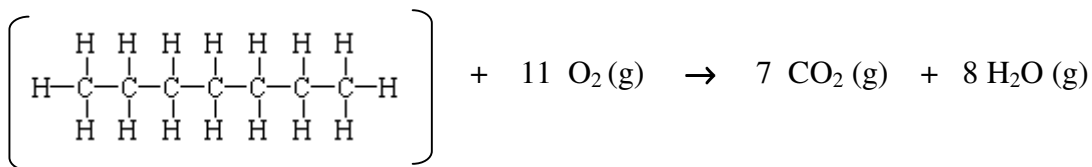## Unit 4, Lesson 04, Reaction Mechanisms

We have considered chemical reactions as happening in one collision or one step. While some reactions do occur this simply, imagine the reaction between heptane and oxygen:

$$\left[ \begin{array}{c} H \ H \ H \ H \ H \ H \ H \\ H-C-C-C-C-C-C-C-H \\ H \ H \ H \ H \ H \ H \ H \end{array} \right] \quad + \quad 11 \ O_2 \,(g) \quad \rightarrow \quad 7 \ CO_2 \,(g) \quad + \quad 8 \ H_2O \,(g)$$

One molecule of heptane and 11 molecules of oxygen are involved in this reaction- a total of 12 molecules. What are the chances that all 12 molecules will collide at the same time, in the correct orientation and with enough energy to make this reaction proceed? Not very good! But we know that all alkanes burn readily and rapidly in air, once a spark is added to provide sufficient activation energy.

Rather than occurring as one massive collision, most reactions proceed as a series of steps, called **elementary reactions** or **elementary steps**, with each step requiring one collision between two or three molecules.

The series of elementary steps that take place as a reaction proceeds from reactants to products is called the "**reaction mechanism**".

The number of particles (molecules, atoms or ions) that collide in an elementary reaction is called the **molecularity** of that step.
- if a single molecule breaks down, then the molecularity of that step is 1, or it is unimolecular
- if two particles collide, molecularity of that step is 2, or it is bimolecular
- if three particles collide, molecularity of that step is 3, or it is termolecular ("ter" from **ter**tiary) Termolecular reactions are very rare.

The molecules that form during the elementary steps are called the "**reaction intermediates**".
- reaction intermediates are produced in one elementary step and used up in a subsequent elementary step, so they do NOT appear in the overall chemical equation.

Every elementary step in the reaction mechanism has its own activation energy- the minimum amount of energy that must be present in order for the elementary step to proceed, so each elementary step will occur at a different rate. The elementary step that has the highest activation energy will have the slowest rate, and it will determine the rate of the overall chemical reaction. The slowest elementary step is called the "**rate determining step**" (RDS).

Let's look at an analogy- you are washing the dishes and your brother (or sister, or friend- whatever) is drying. Your mom is putting the clean, dry dishes away. The overall reaction is:

> dirty dishes    →    clean, dry, put-away dishes
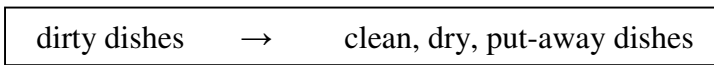
But, this reaction occurs in several steps:
1. the dishes are put in soapy water and scrubbed (a medium reaction)
2. the dishes are rinsed in clean water (a very fast reaction)
3. the dishes are dried by your partner (a slow reaction), and
4. mom puts the dishes away (a medium-fast reaction).

Now, imagine that your mom is in a hurry, so she wants to go faster. She tells you to rinse the dishes more quickly. Will this speed up the overall process? No- rinsing the dishes happens quickly anyway. What if you wash the dishes more quickly, will this speed things up? No. The bottleneck step in this process is your partner drying the dishes- they are slow. The only way to speed up the reaction is to speed up this step. For this analogy, drying the dishes is the rate-determining step (RDS). If we looked at a reaction pathway for this reaction, we would see:
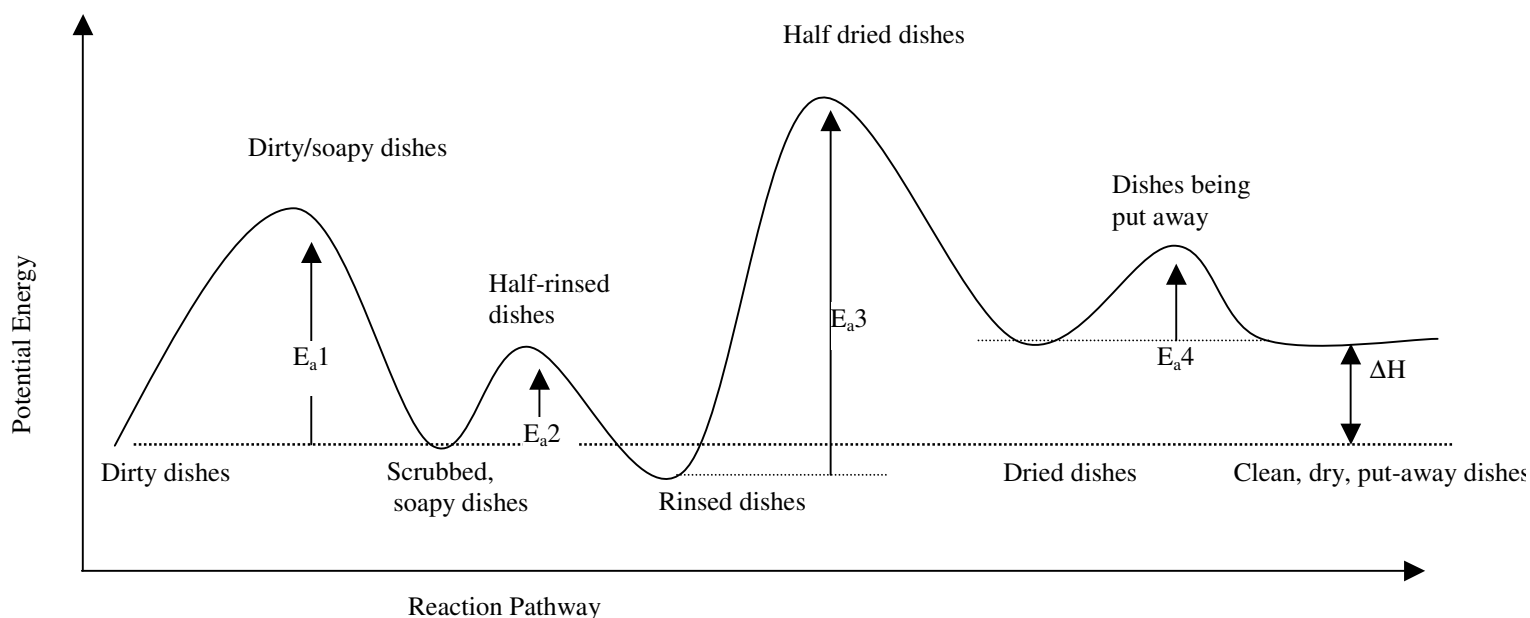


During this reaction, each elementary step in the reaction forms an **activated complex**: which is a transition state that is half way between the two intermediates, for example:
- dishes that are both dirty and soapy as they are being scrubbed
- dishes that are being rinsed that still have soap on them
- dishes that are both wet and dry while they are being dried
- dishes that are half put-away

After each elementary step, there is a **reaction intermediate** which is the product of that elementary step, for example:
- scrubbed, soapy dishes
- rinsed dishes
- dried dishes
- clean, dry, put-away dishes

We do not see the activated complexes or reaction intermediates mentioned anywhere in the overall reaction, but they are part of the process. To get the overall reaction, we sum up the elementary steps (just like Hess's Law):

| | | |
|---|---|---|
| dirty dishes | → | ~~scrubbed soapy~~ dishes |
| ~~scrubbed soapy~~ dishes | → | ~~rinsed dishes~~ |
| ~~rinsed dishes~~ | → | ~~dry dishes~~ |
| ~~dry dishes~~ | → | clean, dry, put-away dishes |
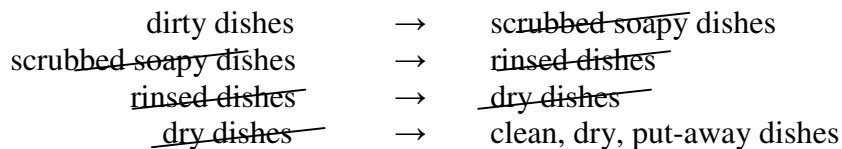
Cancel out any intermediates that appear on both sides of the equations (remember, intermediates are produced in one elementary step and then used up in a later step)

Sum up the remaining reactants and products, and we get our overall reaction:

dirty dishes  →  clean, dry, put-away dishes
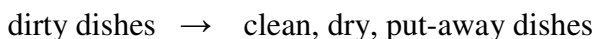
For the overall reaction:
- the Ea for the reaction is the same as the Ea for the rate determining step. This step determines the rate of the overall reaction
- the $\Delta H$ for the reaction is the $\Delta H$ between the initial reactants and final products. It doesn't matter what happens to the enthalpy in between. Remember, $\Delta H$ is a state function.
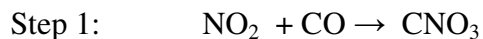
Let's look at an example for a chemical reaction:   $NO_2 + CO \rightarrow NO + CO_2$

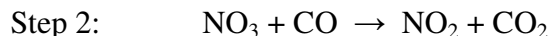There is no way to know what the elementary steps are except by experiment.

It could be a single, bimolecular collision:
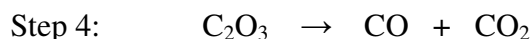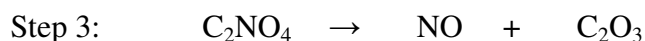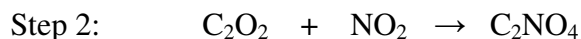Step 1:          $NO_2 + CO \rightarrow NO + CO_2$
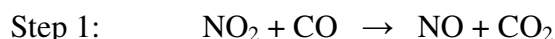
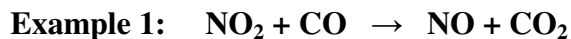It could be a bimolecular collision followed by a unimolecular step:
Step 1:          $NO_2 + CO \rightarrow CNO_3$
Step 2:          $CNO_3 \rightarrow NO + CO_2$

It could be two bimolecular collisions:
Step 1:          $2 NO_2 \rightarrow NO + NO_3$
Step 2:          $NO_3 + CO \rightarrow NO_2 + CO_2$

It could be a very complex series of elementary reactions:
Step 1:          $CO + CO \rightarrow C_2O_2$
Step 2:          $C_2O_2 + NO_2 \rightarrow C_2NO_4$
Step 3:          $C_2NO_4 \rightarrow NO + C_2O_3$
Step 4:          $C_2O_3 \rightarrow CO + CO_2$

Or, it could be any other series of elementary steps that give the final overall equation. The actual mechanism must be determined empirically (by experiment). Once the mechanism is determined, the rate determining step and energy change for each step can be found. This allows chemists to find ways to control or speed up reactions.

**Example 1:** $NO_2 + CO \rightarrow NO + CO_2$

The actual mechanism is:

Step 1: $2\ NO_2 \rightarrow NO + NO_3$

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$
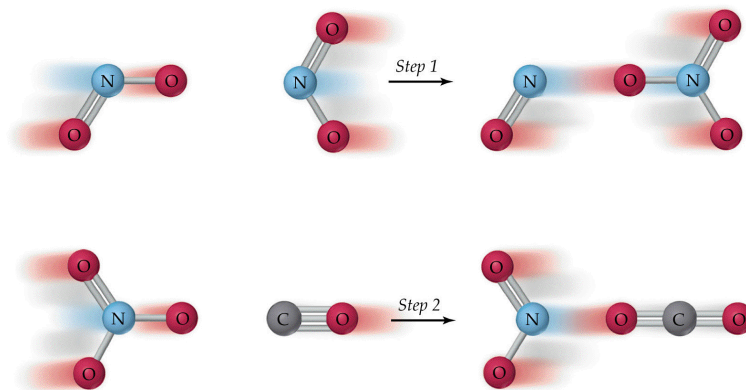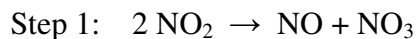


The potential energy diagram for this reaction mechanism is shown to the left.

**Answer the following questions by referring to the potential energy graph of the reaction:**

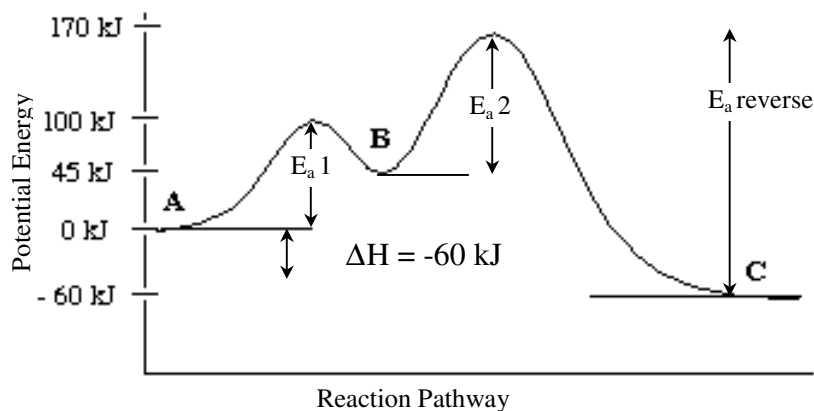i) How many elementary steps are in the reaction mechanism? 2 elementary steps (2 "bumps")

ii) Which step is the rate-determining step? Step 2 (it has a higher $E_a$ so it is slower)

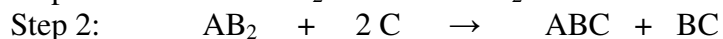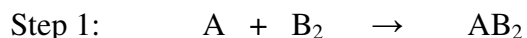iii) Is the overall reaction exothermic or endothermic? exothermic (overall heat is released)

iv) What is the $\Delta H$ for the overall reaction (kJ)? $\Delta H$ = -60 kJ

v) What is the activation energy (kJ) for the reverse reaction? $E_a\ reverse$ = (60 kJ + 170 kJ) = 230 kJ

vi) What is the $E_a$ (kJ) for the rate-determining step? $E_a\ step\ 2$ is from 45 kJ to 170 kJ = 125 kJ



**Example 2:** For the reaction mechanism:

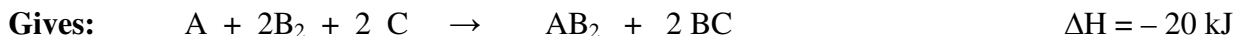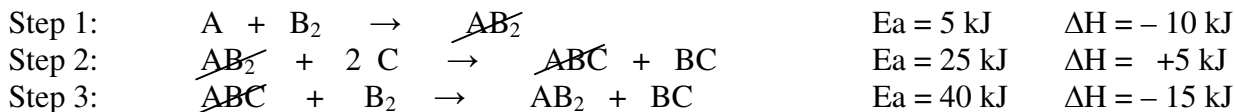| | | | | | Ea | ΔH |
|---|---|---|---|---|---|---|
| Step 1: | A + $B_2$ | → | $AB_2$ | | Ea = 5 kJ | $\Delta H$ = – 10 kJ |
| Step 2: | $AB_2$ + | 2 C | → | ABC + BC | Ea = 25 kJ | $\Delta H$ = +5 kJ |
| Step 3: | ABC + | $B_2$ | → | $AB_2$ + BC | Ea = 40 kJ | $\Delta H$ = – 15 kJ |

**Question Types:**
1. What is the overall equation for this reaction?
2. What is the overall $\Delta H$?
3. Draw the energy profile for the reaction, to scale.
4. What is the overall Ea for the reaction?
5. What it the rate-determining step for the reaction?

**Answers:**
1. To find the overall equation, add up the intermediate steps (just like we did for Hess's Law).
2. To find the overall $\Delta H$, add up the $\Delta H$s for the intermediate steps (as for Hess's Law):

| | | | | |
|---|---|---|---|---|
| Step 1: | A + B$_2$ → ~~AB$_2$~~ | Ea = 5 kJ | $\Delta H$ = – 10 kJ |
| Step 2: | ~~AB$_2$~~ + 2 C → ~~ABC~~ + BC | Ea = 25 kJ | $\Delta H$ = +5 kJ |
| Step 3: | ~~ABC~~ + B$_2$ → AB$_2$ + BC | Ea = 40 kJ | $\Delta H$ = – 15 kJ |

**Gives:**     A + 2B$_2$ + 2 C → AB$_2$ + 2 BC        $\Delta H$ = – 20 kJ

3. To draw the energy profile:
a) Step 1:
- use the lines on lined paper or graph paper to represent 5 or 10 kJ of energy (whatever is appropriate for the reaction)
- draw a horizontal line to represent potential energy = 0 kJ about halfway up the "y" axis. This is where you label "reactants"
- from the zero line (reactants), the first step has an Ea of 5 kJ, so the first bump is 5 kJ above the reactants
- the first step has $\Delta H$ = – 10 kJ, so it will end up 10 kJ below the zero line (reactants). This is the starting place for your second step
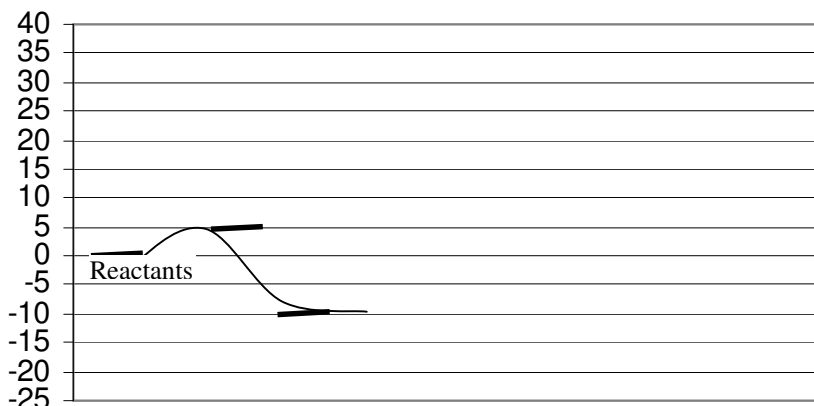


b) Step 2:
- the second step has an Ea of 25 kJ, so the second bump is 25 kJ above the ending point for the first step
- the second step has $\Delta H$ = +5 kJ, so it will end up 5 kJ above the ending point for the first step. This is the starting place for your third step.
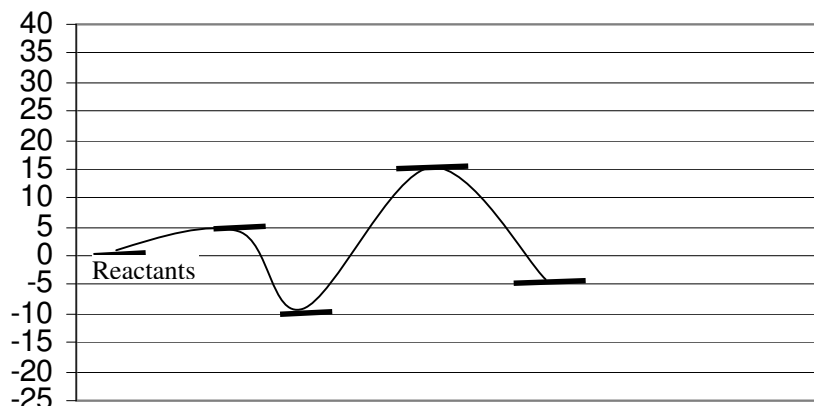


c) Step 3:
- the third step has an Ea of 40 kJ, so the third bump is 40 kJ above the ending point for the second step
- the third step has $\Delta H$ = – 15 kJ, so it will end up 15 kJ below the ending point for the second step
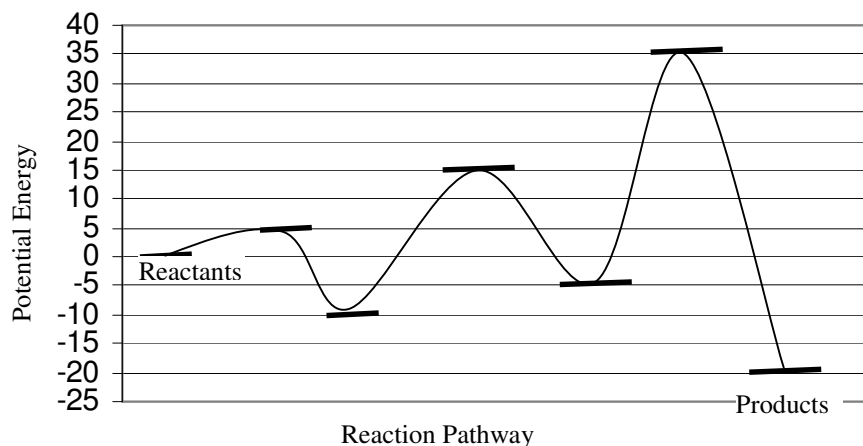


Reaction Pathway

4. The overall Ea for the reaction is the difference in energy between the reactants (zero) and the highest energy point in the reaction pathway (step 3). The overall Ea for this reaction is 35 kJ.

5. The rate determining step is the step with the highest Ea, in this case, the third step. That is, the third step in the reaction mechanism is the slowest step, so it will determine the rate of the overall reaction.

Note: you may be given a value for the original potential energy of the reactants. If so, in step 1, begin your graph with the reactants at this energy level.