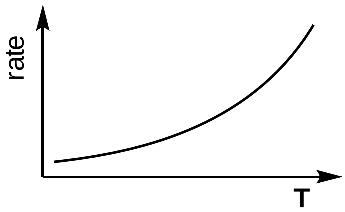
# № 12. TEMPERATURE DEPENDENCE OF REACTION RATE. ACTIVATION ENERGY. ARRHENIUS EQUATION.

**Temperature affects reaction rates of chemical reactions!** **A + B $\rightarrow$ products**

Clearly, if two molecules **A** and **B** are to react, they must approach closely enough to disrupt some of their existing bonds and to permit the creation of any new ones that are needed in the products. Such encounter is called **collision**. There is very specialized theory, **Collision theory**, that is concerned with how exactly reactions happen. Most likely outcome if the reaction between **A** and **B** requires a significant disruption or rearrangement of the bonds between their atoms, is bouncing off each other. In order to effectively initiate a reaction, **collisions must be sufficiently *energetic*** (in terms of their kinetic energy) to bring about this bond disruption. We could try to dissect the anatomy of a collision: Energetic collisions between molecules cause interatomic bonds to stretch and bend farther, temporarily weakening them so that they become more susceptible to cleavage. Distortion of the bonds can expose their associated electron clouds to interactions with other reactants that might lead to the formation of new bonds. Since the kinetic energy of colliding species is determining factor and this energy is directly proportional to temperature, it is obvious that **higher temperatures mean faster reactions!** And there is often one additional requirement. In many reactions, especially those involving more complex molecules, the **reacting species must be oriented in a manner that is appropriate for the particular process (spatial requirement)**. It is common knowledge that **chemical reactions occur more rapidly at higher temperatures**. Everyone knows that milk turns sour much more rapidly if stored at room temperature rather than in a refrigerator, butter goes rancid more quickly in the summer than in the winter, and eggs hard-boil more quickly at sea level than in the mountains (boiling point of water is higher at lower elevations than in the mountains). For the same reason, cold-blooded animals such as reptiles and insects tend to be noticeably more lethargic on cold days. An increase of body temperature of ~0.5$^oC$ increases the metabolic rate by > 7%, thus more intake of $O_2$ is needed and therefore heartbeat increases. **Thermal energy relates directly to motion at the molecular level**. As the temperature rises, molecules move faster and collide more vigorously, greatly increasing the likelihood of bond cleavages and rearrangements, i.e. chemical transformation. As a rough rule of thumb, an increase of only 10$^oC$ can be expected to double or triple reaction rate (an old rule named after Van't Hoff for homogeneous system at 0-100$^oC$).



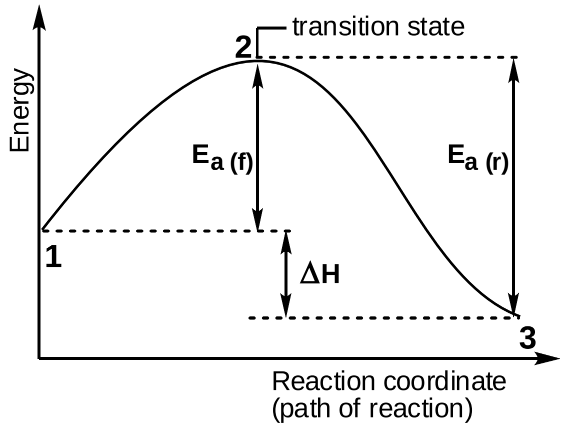
The kinetic energy of motion of colliding molecules is transformed into increased internal molecular kinetic energy and into potential energy of distorted electron clouds. Following more violent collisions, reactant particles, during the very short time of deformation, go through a rearrangement of their electrons' and nuclei configuration (connectivities). As the system relaxes into a more permanent state, product particles form and that determines the **collision as effective** (successful for a reaction).

Most reactions involving neutral molecules cannot take place at all until they have acquired the energy needed to stretch, bend, or otherwise distort one or more bonds. This critical energy is known as the *activation energy* of the reaction.

**The activation energy ($E_a$) of a reaction is the minimum collision energy necessary to proceed to products**.

(*Notice!* Activation energy is characteristic not of molecules but of a particular reaction.) All molecules that have at least activation energy (**$E_a$**) or more can cause effective collisions, and cause a reaction. They are called **active molecules**. *Where does the activation energy come from?* In most cases, the activation energy is supplied by thermal energy, through intermolecular collisions. Activation can be achieved also by absorption of light by a molecule (photoexcitation); by electrochemical activation; by ultrasound (form of heat).

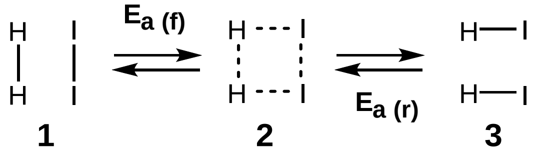
**Activation energy diagrams** Graphics that represent the energy changes in a reaction system as it proceeds from reactants to products by necessity include the activation energy barrier, as illustrated in the next Figure.



*Take special note:* On the Y-axis are plotted **relative values of the potential energy** of substances (reactants or products), on the X-axis – the "**reaction coordinate**" is rather abstract concept that is not tied to any single measurable quantity. This axis simply shows the direction of a chemical change – "path of reaction". The symbols $\mathbf{E_{a\,(f)}}$ and $\mathbf{E_{a\,(r)}}$ designate the activation energy for forward and reverse reaction, respectively, and **ΔH** is enthalpy change (thermal effect). At the maximum is the energy of «transition state». This elusive state has nothing in common with «intermediate» which can be studied experimentally.

The state of the system when the existing bonds are not entirely broken and the new are not completely formed is termed **transition state** *or active complex*. It is at the highest energy point and hence unstable (it can exist on timescale of a picosecond, $1\text{x}10^{-12}$ s). The active complex spontaneously goes either to form the products or returns back to reactants. It does *not* correspond to an identifiable intermediate structure. For the reaction:

$$H_{2\,(g)} + I_{2\,(g)} \longrightarrow 2\,HI\,(g) + Q$$

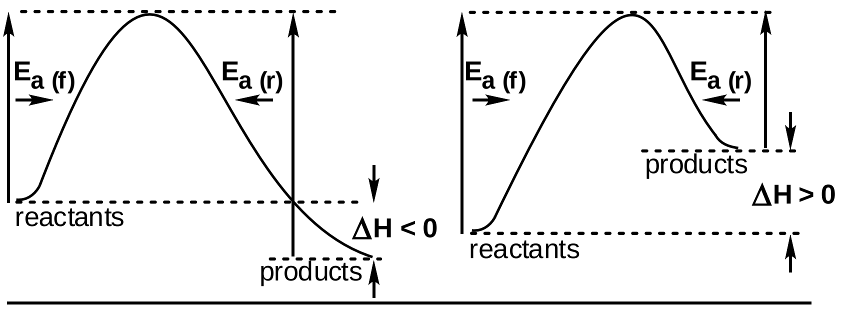


the initial state includes molecules $H_2$ and $I_2$ at point 1 of the Figure, the final state – molecules HI at point 3, and the transition state is at point 2 where original bonds in $H_2$ and $I_2$ are not broken yet and bonds H–I are not completely formed.

In short: **TRANSITION STATE ≠ INTERMEDIATE STATE or intermediate**.

Activation energy diagrams always incorporate the energetics (**ΔH** or **ΔU**) of the net reaction, but it is important to understand that these quantities depend solely on the thermodynamics of the process which are always **independent of the reaction pathway**. This means that the same reaction can exhibit different activation energies if it can follow alternative pathways, such as: $\mathbf{\Delta H = H_{(final)} - H_{(initial)}}$ or $\mathbf{\Delta H = H_{(3)} - H_{(1)}}$; and this difference signifies an endothermic reverse reaction, **Q** = – **ΔH**, *therefore since the forward reaction is exothermic, the reverse reaction is endothermic*; $\mathbf{E_{a\,(f)} = (2) - (1)}$, $\mathbf{E_{a\,(r)} = (3) - (2)}$, and $\mathbf{E_{a\,(r)} = E_{a\,(f)} + Q}$.

Various activation energy diagrams can describe both **exothermic and endothermic reactions**, as in the next Figure:

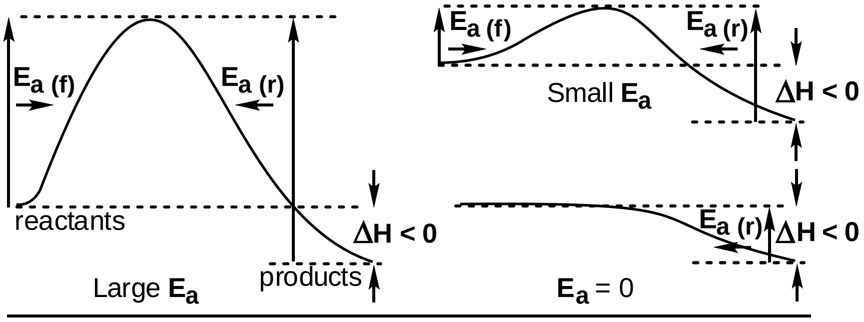


Q > 0 exothermic Q < 0 endothermic

*Important to remember*: **For an exothermic reaction $\mathbf{E_{a\,(r)} > E_{a\,(f)}}$** and **for an endothermic reaction $\mathbf{E_{a\,(r)} < E_{a\,(f)}}$.**

**The thermal effects of the forward and of the reverse reaction are equal in magnitude, but have opposite signs.**

The activation energy magnitudes vary widely and can be large, small, or zero (independently, of course, of the value of $\Delta$**H**):



*Notice*: in all three cases above, the $\Delta$**H** value is the same.

The activation energy $\mathbf{E_a}$ is often called **"energy barrier"**.

It is obvious that **high $\mathbf{E_a}$ means lower rate**; only a few molecules can pass the barrier. The $\mathbf{E_a}$ is included in the rate constant of a kinetic equation. **The activation energy is a characteristic quantity of each reaction**.

Since the strength of chemical bonds that are rearranged is related to $\mathbf{E_a}$, it depends on the nature of the substances. **$\mathbf{E_a}$ does not depend on temperature.**

### The Arrhenius law

By 1890 it was common knowledge that higher temperatures speed up reactions, often doubling the rate for a 10-degree rise, but the reasons for this were not clear. Finally, in 1899, the Swedish chemist Svante Arrhenius (1859-1927) combined the concepts of activation energy and the Boltzmann distribution law into one of the most important relationships in physical chemistry. The law connects the rate constant with activation energy:

$$k = A.e^{-\frac{E_a}{RT}}$$

IMPORTANT!

Where ***k*** is the rate constant, **A** is a pre-exponential factor whose meaning will become clear later, $\mathbf{E_a}$ is the activation energy, and **RT** is related to temperature energy term.

This equation seems similar to the exponential decay law we discussed earlier . $[A]_t = [A]_o.e^{-kt}$

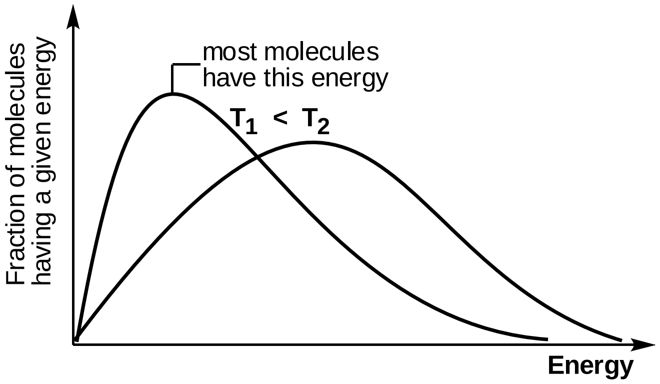
What is "decaying" here is not the concentration of a reactant with time, but the magnitude of the rate constant as a function of the exponent $\mathbf{E_a / RT}$. If you recall that **RT** is the *average kinetic energy*, it will be apparent that the exponent is just the ratio of the activation energy $\mathbf{E_a}$ to the average kinetic energy. The larger this ratio, the smaller the rate (hence the negative sign). This means that **high temperature and low activation energy favor larger rate constants, and thus speed up the reaction**. Because these terms occur in an exponent, their effects on the rate are quite substantial.

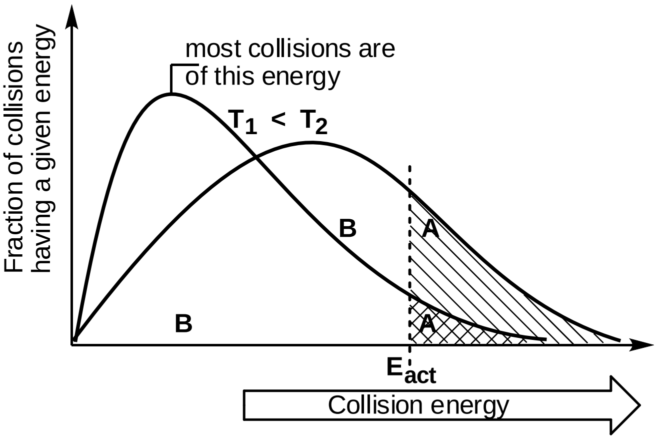
### Temperature and kinetic energy

In the vast majority of cases, a chemical reaction depends on thermal activation, so the major factor we need to consider is what fraction of the molecules possesses enough kinetic energy to react at a given temperature.

**According to kinetic molecular theory, a population of molecules at a given temperature is distributed over a variety of kinetic energies that is described by the Maxwell-Boltzmann distribution law.**

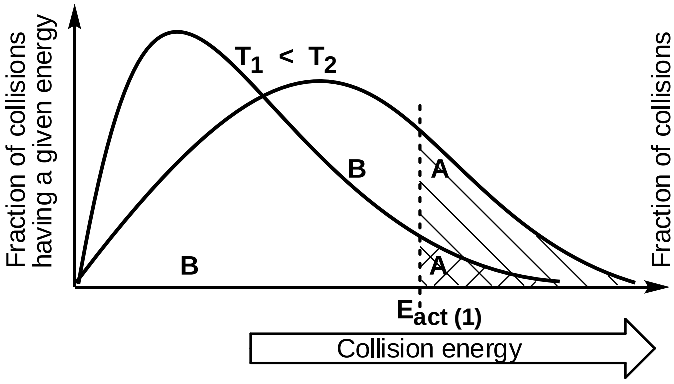
The distribution of an ensemble of molecules according their kinetic energy is presented in the left Figure:

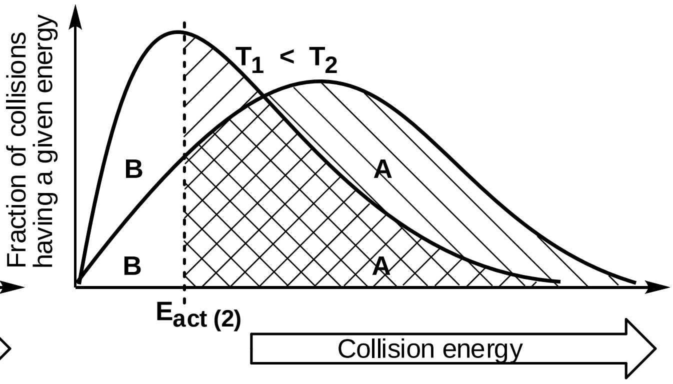




When two molecules collide, their energy is combined and the distribution plots are similar as shown on the right Figure. The two distribution plots shown here are for a **lower temperature $T_1$** and a **higher temperature $T_2$. The shaded regions indicate the number of molecules which are sufficiently energetic to meet the requirements dictated by the value of $E_a$**. It is clear from these plots that the fraction of molecules whose kinetic energy exceeds the activation energy increases quite rapidly as the temperature is raised. This is the reason that virtually all chemical reactions (and all elementary reactions) are more rapid at higher temperatures.

The rate of a reaction is the number of **successful collisions** that occur each second in each unit of volume in a reaction mixture. Generally, only a small fraction of the collisions have enough energy to be successful. The ratio of shaded area **A** to the total area under the curve (**A+B**) represents this small fraction, i.e. **A/(A+B)** that can climb up the energy barrier. In other words, a high energy of activation (**$E_{act(1)}$**) means a small fraction of successful collisions and a slow rate of reaction. On the contrary – small **$E_{act(2)}$** means large area **A**, approaching (**A+B**), and hence almost instantaneous reaction. Compare left and right plots showing similar energy distributions but different **$E_{act}$** (**$E_{a(1)} > E_{a(2)}$**).





**Determining the activation energy**

The Arrhenius equation: $\boldsymbol{k = A.e^{-\frac{E_a}{RT}}}$

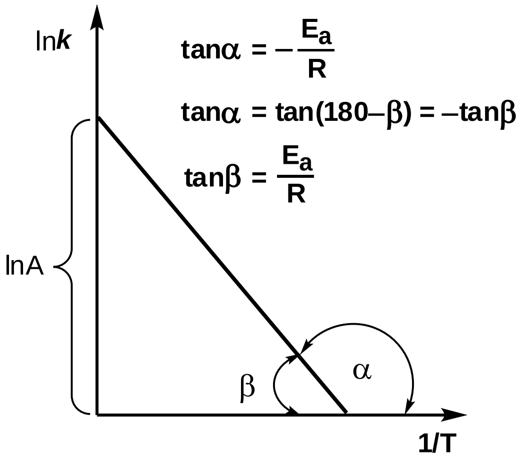
can be written in a non-exponential form which is often more convenient to use and to interpret graphically. Taking the logarithms of both sides and separating the exponential and pre-exponential terms yields:

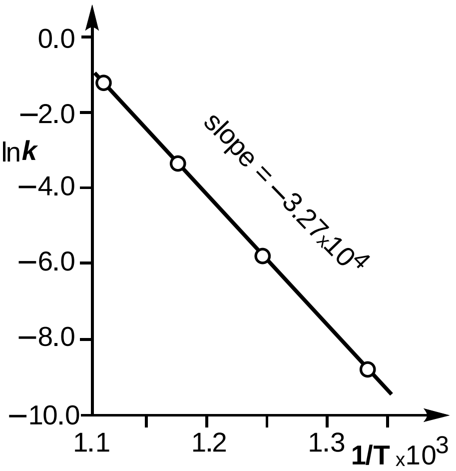
$$\ln k = \ln(A.e^{-\frac{E_a}{RT}}) = \ln A + \ln(e^{-\frac{E_a}{RT}}) \quad \text{and} \quad \boldsymbol{\ln k = \ln A - \frac{E_a}{RT}}$$

IMPORTANT!

where: ***k*** – rate constant; **A** – Arrhenius constant for a particular reaction (frequency factor or pre-exponential factor); **e** – natural logarithm base; **$E_a$** – energy of activation; **R** – ideal gas constant; **T** – absolute temperature. (**A**, **$E_a$** and **R** do not depend on the temperature.)

The Arrhenius equation in a slightly modified form: $\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$ is an equation of a straight line presenting the change of **ln*k*** with respect to **1/T** whose slope is **$-E_a/R$**. This affords a simple way of determining the activation energy from values of ***k*** observed at different temperatures. We just plot **ln*k*** as a function of **1/T** and determine the slope as shown in the Figures: (from the right graph seems high $E_a$ for C–C bond breakage reaction)





**You don't always need a plot** (... if you are willing to live a bit dangerously!). Since the **ln*k*** vs. **1/T** plot yields a straight line, it is often convenient to estimate the activation energy from experiments at only two temperatures (such correlations using *only* two points to build a line are not advisable). To see how this is done, consider that we can measure the rate constants at two different temperatures, ***$k_1$*** at **$T_1$** and ***$k_2$*** at **$T_2$** , write the Arrhenius law equations, and subtracting latter from the first: (as a matter of fact, we have made the lnA term "disappear" in the result by subtracting the expressions for the two ln*k* terms.) Solving the resulting expression on the right for the activation energy yields:

$$\begin{array}{l} \ln k_1 = \cancel{\ln A} - \frac{E_a}{R}\frac{1}{T_1} \\ - \\ \ln k_2 = \cancel{\ln A} - \frac{E_a}{R}\frac{1}{T_2} \\ \hline \ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \end{array}$$

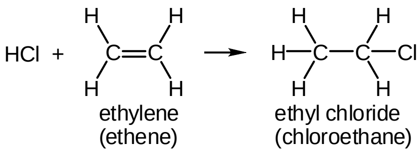
$$E_a = \frac{R.\ln\frac{k_1}{k_2}}{\frac{1}{T_2} - \frac{1}{T_1}}$$

**The pre-exponential factor** (A) **in Arrhenius equation** $k = A . e^{-\frac{E_a}{RT}}$

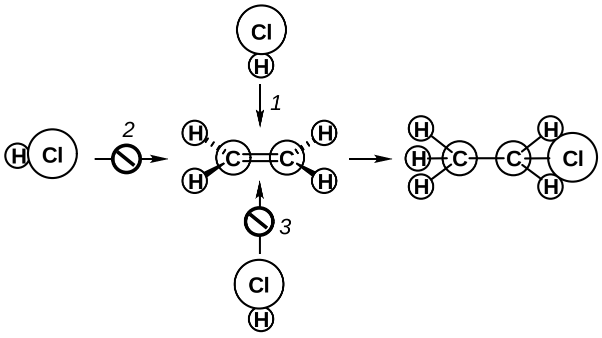
We have been neglecting **A** in the Arrhenius equation because it is not directly involved in relating temperature and activation energy, which is the main practical use of the equation. But since **A** multiplies the exponential term, its value clearly contributes to the value of the rate constant and thus of the rate. Recall that the exponential part of the Arrhenius equation expresses the fraction of reactant molecules that possess enough kinetic energy to react, as governed by the Maxwell-Boltzmann law. This fraction can run from zero to nearly unity, depending on the magnitudes of **$E_a$** and of the temperature. If this fraction were unity, the Arrhenius law would reduce to ***k* = A** . In other words, **A** is the fraction of molecules that would react if either the activation energy was zero, or if the kinetic energy of all molecules exceeded **$E_a$** – admittedly, an uncommon scenario.

**It's all about collisions!** So what would limit the rate constant if there were no activation energy requirements? The most obvious factor would be the rate at which reactant molecules come into contact.

**The pre-exponential factor (A) includes contributions related to the frequency of collisions and relative orientation of the molecules at the point of collision**. The latter is important, so we can also define a geometrical or **steric factor**. **Direction makes a difference!** The more complicated the structures of the reactants, the more likely that the value of the rate constant will depend on the trajectories at which the reactants approach each other. Let's consider addition of HCl to ethylene:



Experiments have shown that the reaction only takes place when the HCl molecule approaches the alkene with its hydrogen-end, and in a direction that is approximately perpendicular to the double bond, as shown at approach *1* in the next graph. Clearly, **direction makes a difference**. If, instead, the HCl approaches with its chlorine end leading as in *3*, electrostatic repulsion between the like charges (on Cl and $\pi$-electrons of the double bond) causes the two molecules to bounce away from each other before any reaction can take place. The same thing happens in *2*, even worse from steric repulsion between chlorine and two ethylene hydrogens.

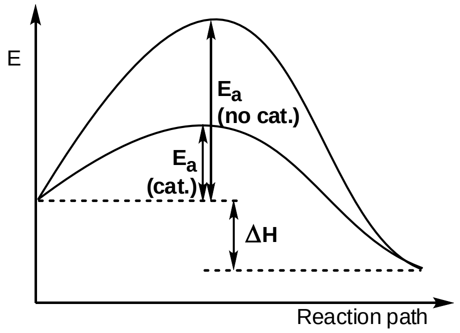


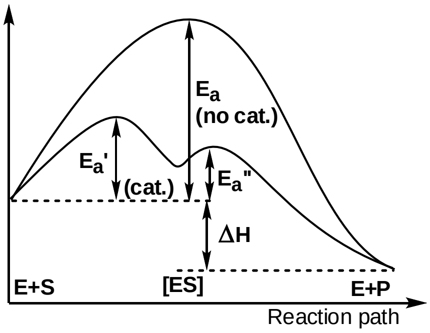
Just to recall: **The rate of a chemical reaction is affected by:**

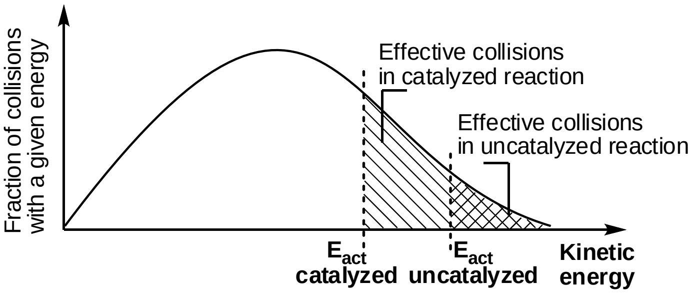
- **The nature of the reactants;**
- **Physical state; interacting area (contact area);**
- **Concentration (pressure) of substances;**
- **Temperature;**
- **The presence of catalyst**.

**Catalysts can reduce activation energy.**

A **catalyst** is usually defined as a substance that speeds up a reaction without being consumed by it. More specifically, a catalyst provides an alternative, lower activation energy pathway between reactants and products. As such, they are vitally important to chemical technology; approximately 95% of industrial chemical processes involve catalysts of various kind. In addition, most biochemical processes that occur in living organisms are mediated by **enzymes**, which are catalysts made of proteins. It is important to understand that a **catalyst affects only the kinetics** of a reaction; it does *not* alter the thermodynamic tendency for the reaction to occur. Thus there is only a single value of **ΔH** (Q) for the two pathways depicted in the next plots on activation energy diagrams. **A catalyst alters the reaction path**, indicated on the upper Figures, left – laboratory reaction; right – enzyme catalyzed, biochemical reaction.







Lowering the activation barrier (**E$_a$**) increases effectively the number of molecules with enough energy to jump over the barrier, as shown on the left.