Energy in Chemical Kinetics

The Effect of Temperature

High temperature means faster molecules. (The kinetic molecular theory states that kinetic energy, $K_E = \frac{1}{2} mv^2$, of molecules is directly related to temperature.)
Higher temperature means greater K_E, which means faster molecules (the mass of the molecules does not change, only the velocity factor of the kinetic energy.)

Faster molecules lead to MORE COLLISIONS and the collisions will have more energy, i.e faster bumps and bigger bumps!!

Generally, an increase in temperature speeds up a reaction considerably.

Sometimes, an increase of only 10 ^{0}C will DOUBLE the reaction rate of some chemical reactions. Why is this?

Activation Energy and Reaction Rate

(1) MOST MOLECULAR COLLISIONS ARE INEFFECTIVE AND DO NOT RESULT IN REACTION.

(2) ONLY HIGH-ENERGY COLLISIONS ARE EFFECTIVE AND CAN LEAD TO REACTION.

(3) At low temperature, very few collisions are effective and the reaction does not proceed.

(4) At higher temperature, there is an increase in the number of effective collisions and the reaction proceeds.

ACTIVATION ENERGY is and energy "passport" for a given reaction, this is the minimum or the "threshold" energy needed to have a reaction. Only molecules that have at least the activation energy can lead to effective collisions. The activation energy is a constant for a particular reaction. The activation energy gives clues as to what is happening during effective collisions.

A LOW ACTIVATION ENERGY means that the molecules can react easily.

A HIGH ACTIVATION ENERGY means that the molecules may not have enough energy to form effective collisions and the reaction will not proceed, suggesting that a lot of bond breaking is going on as this is a very endothermic process.

The activation energy will be different for the forward and the reverse reaction. Based on this, which will be favoured to happen more often, an exothermic or an endothermic reaction? Why?

The kinetic energy diagrams shows where the activation energy is a factor in reactions, (see your text-book)

ACTIVATION ENERGY

For any quantity of molecules, the kinetic energy will vary from zero to very high values. The energy distribution forms a “bell curve”, called the The Maxwell Boltzmann Distribution of Energies, of the shape shown below:

<u>The molecules with energy greater than the activation energy are most likely to lead to reaction,</u> to form the unstable, highly energised arrangement – the “**Activated Complex**”, and the energy necessary to overcome this arrangement is called the activation energy. The second diagram shows the effect of higher temperature, T_2, on the energy distribution of the molecules, ($T_2 > T_1$)

The distribution curve moves to the right at the higher temperature. (There are more molecules with higher kinetic energy.)

(Note: A small rise in temperature, say 10^0C, often doubles the rate of reaction.)

<u>REASON:</u> While there may not be a great increase in the average molecular kinetic energy, the number BEYOND THE ACTIVATION ENERGY may have doubled. Since it is <u>these</u> molecules that have the ability to form activated complexes leading to reaction, the rate may well double <u>for only a small increase</u> in temperature.

<u>Specifically</u>, suppose 5% of the molecules were beyond the activation energy, then 95% of them do not have enough energy to lead effective collisions. Say the temperature is 25^0C (298 K). At 35^0C (308 K), the energy distribution may be 10% of the molecules beyond the activation energy and 90% below the activation energy.
Statistically, there does not seem to be a great difference, but the 95% and 90% don’t matter. It’s the 5% becoming 10% that matters for possible reaction. Now, 10% is **TWICE** 5% so the molecules with the possibility of effective collisions have been doubled. (These numbers are arbitrarily chosen to demonstrate the concept.)

<u>In all reactions there is a high-energy intermediate state between reactants and products.</u>
(Otherwise, ALL EXOTHERMIC REACTIONS would be spontaneous)

This intermediate state or “molecule” is called the ACTIVATED COMPLEX.
The energy needed to reach the activated complex is called the ACTIVATION ENERGY for the reaction.
(The activation energy in the potential energy diagram corresponds to the Activation energy in the kinetic energy diagrams shown previously.)

If the reactant molecules do not have enough energy to reach the activation energy “hump”, the reaction does not go forward.

A HIGH ACTIVATION ENERGY means reaction will be difficult.
A LOW ACTIVATION ENERGY means reaction will be easy.

Take as an example the reaction between carbon monoxide and nitrogen dioxide to form carbon dioxide and nitric oxide. The heat of reaction (Δ H) for this reaction is -226 kJ mol^{-1}. This is an EXOTHERMIC REACTION that gives out 226 kJ mol^{-1}.

$$CO + NO_2 \longrightarrow \text{" ONCOO"} \longrightarrow CO_2 + NO \qquad \Delta H = -226 \text{ kJ mol}^{-1}$$

The activation energy for the reaction is 134 kJmol^{-1}. (Activation energy is ENDOTHERMIC) Since the reaction is Exothermic, the reaction will be self-sustaining once the activation energy is overcome. The energy put in to reach the activated complex (134 kJmol^{-1}) is recovered as the activated complex goes on to become reactants.

The reverse reaction is an endothermic reacion, $\Delta H = +226$ kJ mol^{-1}.
The activation energy for the reverse reaction is 360 kJ mol^{-1}. (226 + 134 = 360 kJ mol^{-1})

Thus, endothermic reactions always have high activation energies.

If an activation energy is too large, a reaction will not occur.
If an activation energy it too low, the reaction will easily occur.

THE EFFECT OF CATALYSTS – CATALYSIS

Positive catalysts speed up a reaction. Catalysts are substances that help the reaction go forward more easily. They do not appear as products of the reaction.

Example: $KClO_{3(s)} + \text{heat} \longrightarrow KCl(s) + 1\tfrac{1}{2} O_2(g)$ Very SLOW

$KClO_{3(s)} + \text{heat} \xrightarrow{MnO_2} KCl(s) + 1\tfrac{1}{2} O_2(g)$ Very FAST

The manganese dioxide is not used up, nor does it change to any new product, Is seems that catalysts act as reaction sites for the reactants to more easily get together.
Catalysts are essential in the chemical and petro-chemical industries. Palladium and platinum are excellent catalysts and are widely used, If a reaction can take place more easily and faster, it will be a less costly process. See notes on Catalytic Cracking of alkanes
Catalysts are expensive, but they are re-cycled in most petrochemical processes.

<u>Chemical Catalysts</u>

Catalysts provide a lower energy pathway from reactants to products. The reactants combine with the catalyst to form a different activated complex where is easier for effective collisions to take place.
The diagram shows how the activation energy is lower in the catalysed reaction. The heat of reaction, ΔH, is the same in both cases.

In the case of the kinetic energy diagram showing molecular distribution, the activation energy is moved to the left (lowered) in the catalysed case.

The number of active collisions is increased because the activation energy E_A (catalysed) for the catalysed situation is lower.