

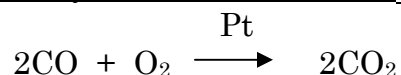
## CATALYSTS

A catalyst is a substance which speeds up a reaction without being used up itself. It speeds up the reaction by changing the reaction mechanism to one which requires less activation energy. The actual mechanisms of some catalytic reactions are not well understood. However, many are understood and these can be grouped into two general categories:

### Heterogeneous Catalysts

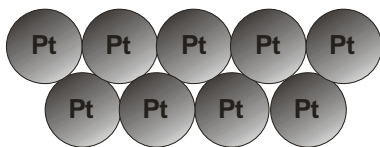
Heterogeneous catalysts are in a different phase than the reactants. Some solid catalysts are classified as surface catalysts because they have large surface areas and are capable of adsorbing the reactants on their surfaces which makes it easier for the reaction to occur. Adsorption refers to the binding of molecules to a surface, in contrast to absorption which refers to the uptake of molecules into the interior of another substance. In other cases, one of the reactant molecules may readily react with the atoms of the catalyst and form an intermediate species which undergoes subsequent reactions. This results eventually in the formation of the desired products and the regeneration of the catalyst.

#### Platinum Catalyzed Formation of CO<sub>2</sub> From CO and O<sub>2</sub>

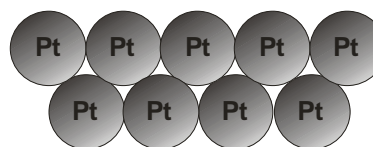


Platinum acts as a surface catalyst when increases the rate of formation of carbon dioxide from carbon monoxide and oxygen. Platinum acts in this way:

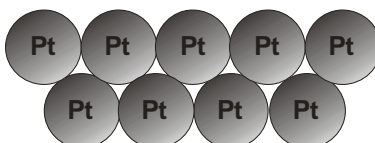
1)



2)

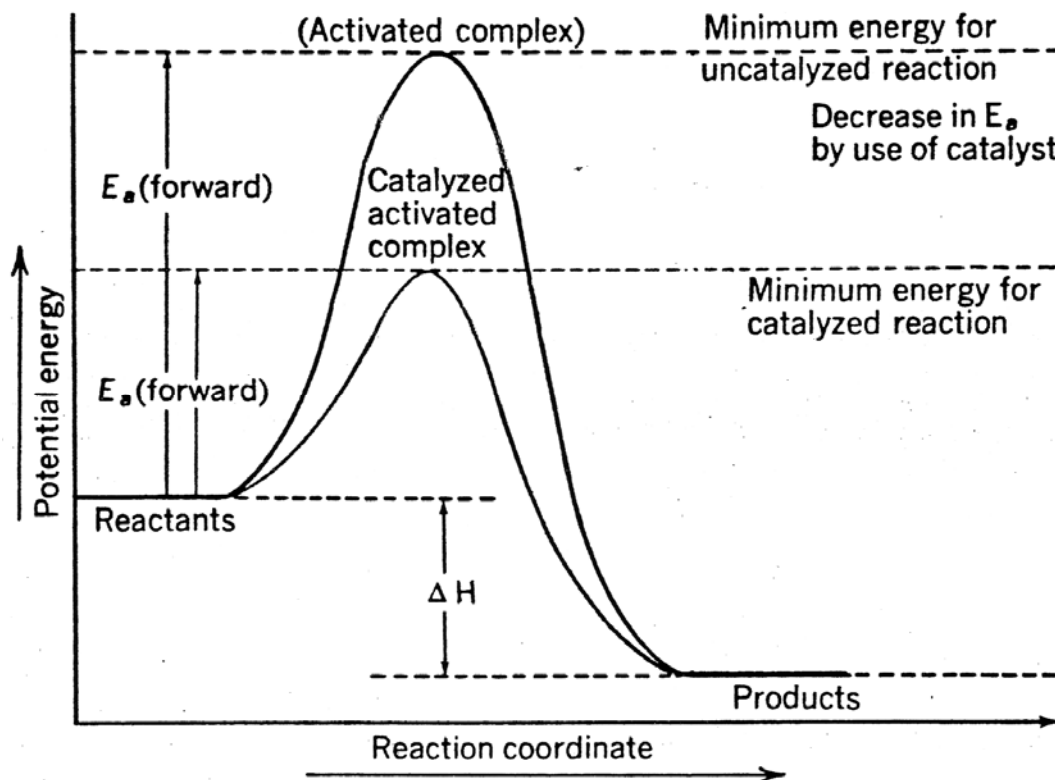


3)



## Effect of Catalysts of Reaction Mechanisms

Catalysts act by lowering the energy barrier or activation energy for a reaction. By creating a lower energy pathway, a greater fraction of the reactant molecules possess the required energy, thereby increasing the rate of reaction.



### Notes:

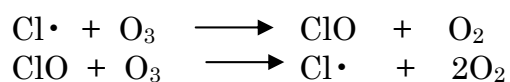
- 1) The catalyst acts by altering the reaction mechanism but not the net reaction,
- 2) The activation energy ( $E_a$ ) for the catalyzed reaction is less than the activation energy of the uncatalyzed reaction.
- 3) The catalyst is regenerated, so it has not been consumed or permanently changed.
- 4) The reactants and products are the same for catalyzed and uncatalyzed reactions..
- 5) The enthalpy of reaction ( $\Delta H$ ) is unchanged.
- 6) The amount of products obtained from the uncatalyzed reaction are the same as with the catalyzed reaction, but they are obtained more rapidly.

## Homogeneous Catalysts

Homogenous catalysts are in the same phase as the reactants. Homogenous catalysts act by forming an intermediate species. By creating a multi-step reaction, the activation energy of the net reaction is lower. For example, the decomposition of ozone in the atmosphere was greatly accelerated by CFCs (chlorofluorocarbons) in the atmosphere.



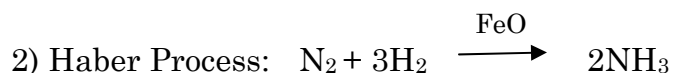
CFCs speed up the reaction by producing a new pathway. CFCs are degraded by UV radiation to produce chlorine free radical ( $\text{Cl}\cdot$ ). This free radical reacts with ozone in a 2-step reaction to produce oxygen and regenerate the chlorine catalyst:



**Net:**

## The Importance of Catalysts

Catalysts provide a simple and efficient means of increasing the rate of a reaction. There is an added advantage in that the catalyst is regenerated so that it can be used over and over. Other means of increasing reaction rates are often unsuitable. For example, increasing the temperature of a reaction system can cause the decomposition of the reactants before they can react. In addition, increased temperature may result in the formation of unwanted (side) products. Thus, much of the industrial chemical research that is carried out is devoted to the search for new and more effective catalysts for reactions of commercial importance. The following is a list of important catalyzed reactions that you should be aware of:



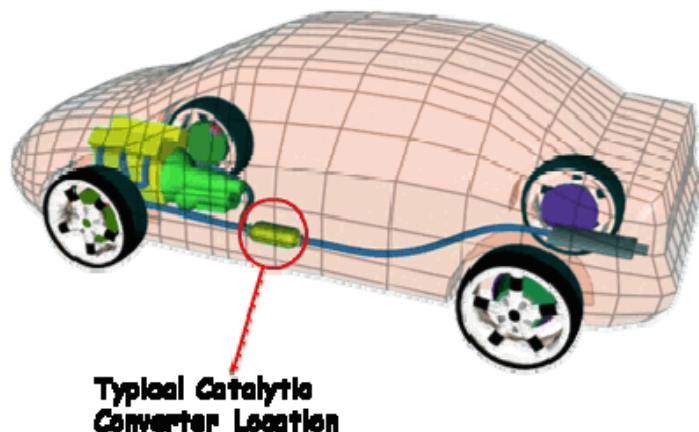
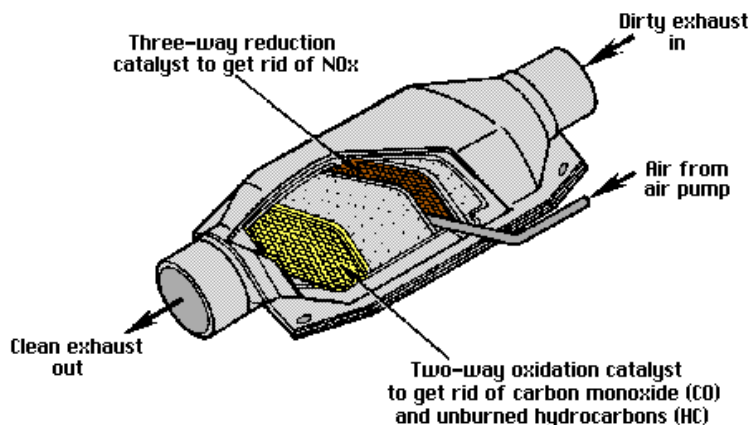
The ammonia that is produced by this reaction is used to make fertilizer, explosives and other important chemicals.

3) Nickel catalyzes the hydrogenation of oils to form fats such as those in margarine.

4) In the petroleum industry, platinum and other catalysts are used to break down or "crack" the large hydrocarbon molecules in crude oil into smaller fragments and reform them into the more useful hydrocarbon molecules which are found in gasoline, jet fuel, heating oil, etc.

5) Automobiles contain catalytic converters. These converters contain platinum (or palladium) which catalyzes the conversion of pollutant gases into relatively harmless gases. Internal combustion engines produce harmful gases such as CO, NO<sub>x</sub> and well as unburned hydrocarbons (C<sub>x</sub>H<sub>y</sub>). These are either oxidized to produce CO<sub>2</sub> (complete the combustion) or converted to harmless N<sub>2</sub>.

### CATALYTIC CONVERTER



6) There are numerous (approx. 150 000) biological catalysts in the human body called enzymes which catalyze biochemical processes such as the digestion of foods. Enzymes are natural polymers of amino acids (polypeptides) that fold into conformations that bind reactant molecules. By altering the conformation of the reactant, enzymes can precisely control the rate of the cellular reactions. For example, rhodopsin in the cell membrane of the retina catalyzes the light-sensitive phosphorylation of intracellular proteins. This leads to a cascade of reactions resulting in a nerve impulse that is transmitted to the brain.

### Inhibitors

These are substances which slow down reactions. They can be grouped into two categories. An inhibitor may remove one of the products of an elementary step in a mechanism so that the next step cannot proceed. In other cases, an inhibitor may combine with the surface atoms of the catalyst, thus preventing the reactants from being adsorbed. Extensive research efforts are devoted to finding means of inhibiting or removing certain catalysts that promote undesirable reactions such as corrosion of metals, aging and tooth decay. Inhibitors can cause problems, too. For example, if an automobile equipped with a catalytic converter uses leaded gasoline, the lead combines with the platinum catalyst and prevents it from working. Thus, the lead "poisons" the catalyst. That is one of the reasons why such automobiles use unleaded gasoline.

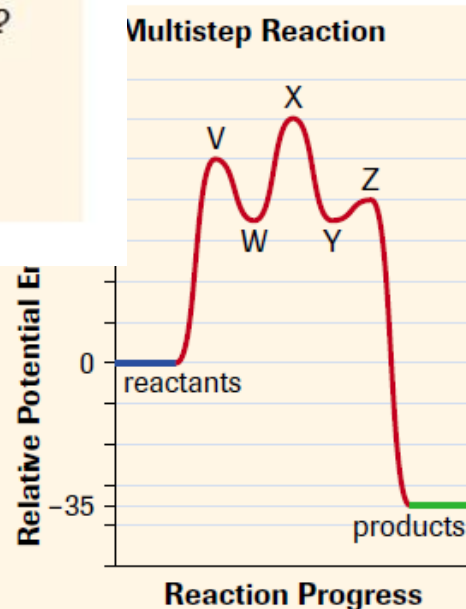
# Catalyst Worksheet

## Part 1:

1. Identify five different factors that are likely to affect the rate of a reaction. Give a practical example of each.
2. Which of the five factors that affect the rate of reactions applies only to heterogeneous systems? Give an example of such a system.
3. What would happen to the rate of a reaction if the temperature were raised from 20°C to 40°C? Explain qualitatively and make a quantitative prediction.
4. A match can be applied to a lump of coal with little effect. However, the ignition of coal dust has caused many fatal mining explosions. Explain.
5. Signs warn about the dangers of having sparks or open flames near oxygen tanks or near flammable fuels. Which of the five factors that affect reaction rate are involved in each of these warnings?

## Part 2:

3. (a) What is the (overall) activation energy for the following reaction in the potential energy diagram in **Figure 9**?  
reactants  $\rightarrow$  products
- (b) What is the reaction enthalpy ( $\Delta H$ ) for the reaction?
- (c) What is the rate-determining step for the reaction?
- (d) Is the reaction exothermic or endothermic?
- (e) Which letters represent activated complexes?
- (f) Which letters represent reaction intermediates?



**Figure 9**  
Potential energy diagram

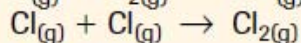
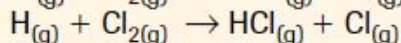
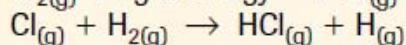
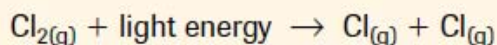


### Part 3:

- Which of the five factors that affect rate of reaction do so by
  - increasing the collision frequency?
  - increasing the fraction of collisions that are effective?
- The reaction of hydrogen and oxygen is exothermic and self-sustaining.
  - Write the equation for this reaction, and provide a reason why it is not likely that the reaction occurs as a single step.
  - This reaction is catalyzed by platinum metal, which provides a surface on which hydrogen gas splits to form Pt-H units that react readily with oxygen molecules. Suggest a possible mechanism for this process, given that a catalyst must be regenerated in any change.
- Identify each of the following as examples of the action of homogeneous or heterogeneous catalysts:
  - Rhodium and platinum metals are used in an automobile catalytic converter to convert exhaust gases into safer gases.
  - Gaseous chlorofluorocarbons (CFCs) have been shown to catalyze the breakdown of ozone in the upper atmosphere.
  - Aqueous sulfuric acid catalyzes the decomposition of aqueous formic acid to carbon monoxide and water.
  - Powdered  $\text{TiCl}_4$  is used in the formation of polyethylene polymer from gaseous ethylene.

- Use collision theory to explain each of the following observations.
  - Permanganate ion ( $\text{MnO}_4^-$ ) reacts much more quickly with iron(II) ions ( $\text{Fe}^{2+}$ ) than with oxalate ions ( $\text{C}_2\text{O}_4^{2-}$ ).
  - When heated in a flame, steel wool burns but a steel nail just glows.
  - Liquid nitroglycerin is a dangerous explosive, but people with heart conditions take nitroglycerin tablets.

- The reaction of hydrogen with chlorine at room temperature is so slow as to be undetectable if the container is completely dark, but is explosively fast if sunlight is allowed to fall on the reactants. The following reaction mechanism has been suggested for this reaction:



- Write the overall reaction equation.
- Identify the reaction intermediates.
- Compare the activation energy for the collision of molecular chlorine with molecular hydrogen to the activation energy for the collision of atomic chlorine with molecular hydrogen. Which reaction must have the greater activation energy, and what evidence can be used to support your argument?