Introduction:

Catalyst design for synthesis

Prof. Xile Hu

Catalysis: some history

When is catalysis first mentioned? In what context?

Nobel Prize in Chemistry

1909

Wilhelm Ostwald

Born: 2 September 1853, Riga, Russian Empire (now Latvia)
Died: 4 April 1932, Leipzig, Germany
Affiliation at the time of the award: Leipzig University, Leipzig, Germany
Prize motivation: "in recognition of his **work on catalysis** and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction"

Nobel Prize in Chemistry

1912

Paul Sabatier

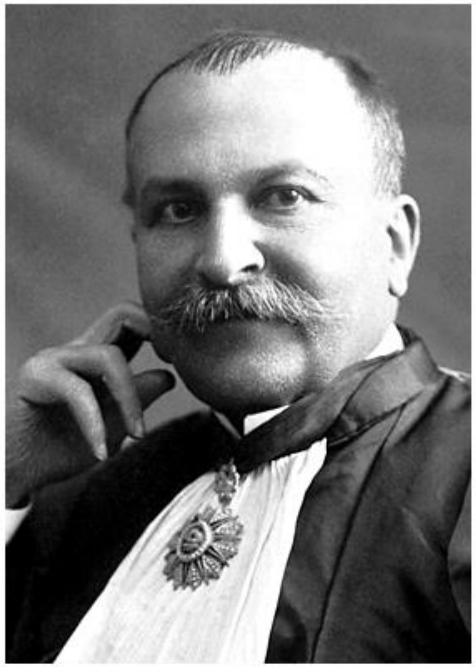
Born: 5 November 1854, Carcassonne, France

Died: 14 August 1941, Toulouse, France

Affiliation at the time of the award: Toulouse University, Toulouse, France

Prize motivation: "for his method of hydrogenating organic compounds in the presence of finely disintegrated metals whereby the progress of organic chemistry has been greatly advanced in recent years"

Field: Organic chemistry



1918

Fritz Haber

Born: 9 December 1868, Breslau (now Wroclaw), Prussia (now Poland)

Died: 29 January 1934, Basel, Switzerland

Affiliation at the time of the award: Kaiser-Wilhelm-Institut (now Fritz-Haber-Institut) für physikalische Chemie und Electrochemie, Berlin-Dahlem, Germany

Prize motivation: "for the synthesis of ammonia from its elements"

Field: Inorganic chemistry, industrial chemistry

Fritz Haber received his Nobel Prize one year later, in 1919.

Nobel Prize in Chemistry 1931

Carl Bosch

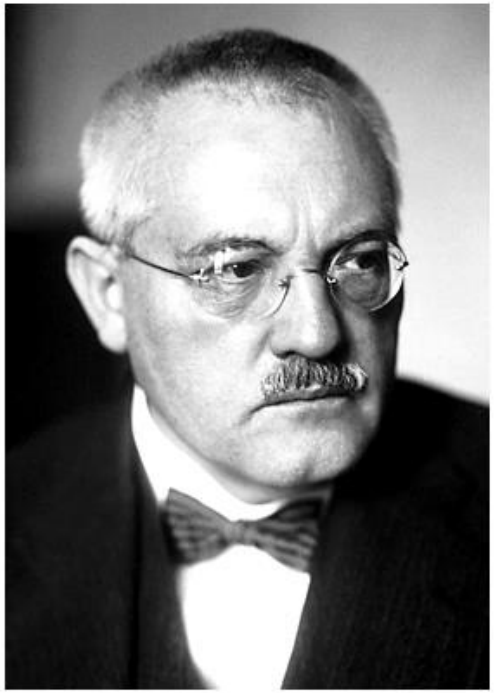
Born: 27 August 1874, Cologne, Germany

Died: 26 April 1940, Heidelberg, Germany

Affiliation at the time of the award: University of Heidelberg, Heidelberg, Germany, I.G. Farbenindustrie A.G., Heidelberg, Germany

Prize motivation: "in recognition of their contributions to the invention and development of chemical high pressure methods"

Field: Industrial chemistry

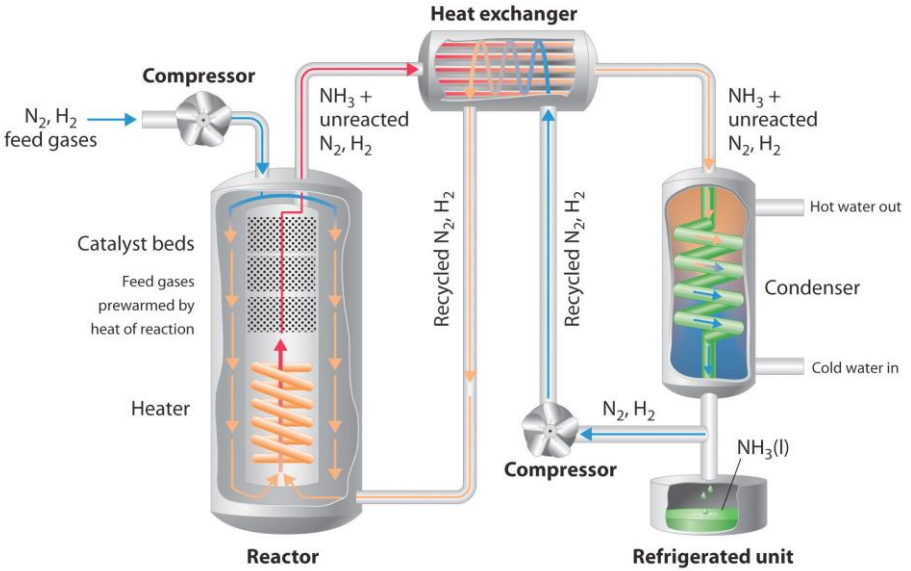


The Haber-Bosch process - catalysis that changed the world

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Heterogeneous iron catalyst ($Fe^{(III)}$), aluminium oxide (Al_2O_3) and potassium oxide (K_2O) promoters. 250 atmospheres (atm), 450-500°C; yield of 10-20%:

The process was patented by Fritz Haber in 1908. In 1910 Carl Bosch, at BASF, commercialized the process.



Fritz Haber

Carl Bosch

What is Catalysis

What is Catalysis

Catalysis is the increase in the rate of a chemical reaction due to the participation of an additional substance called a catalyst.

With a catalyst, reactions occur faster and with less energy.

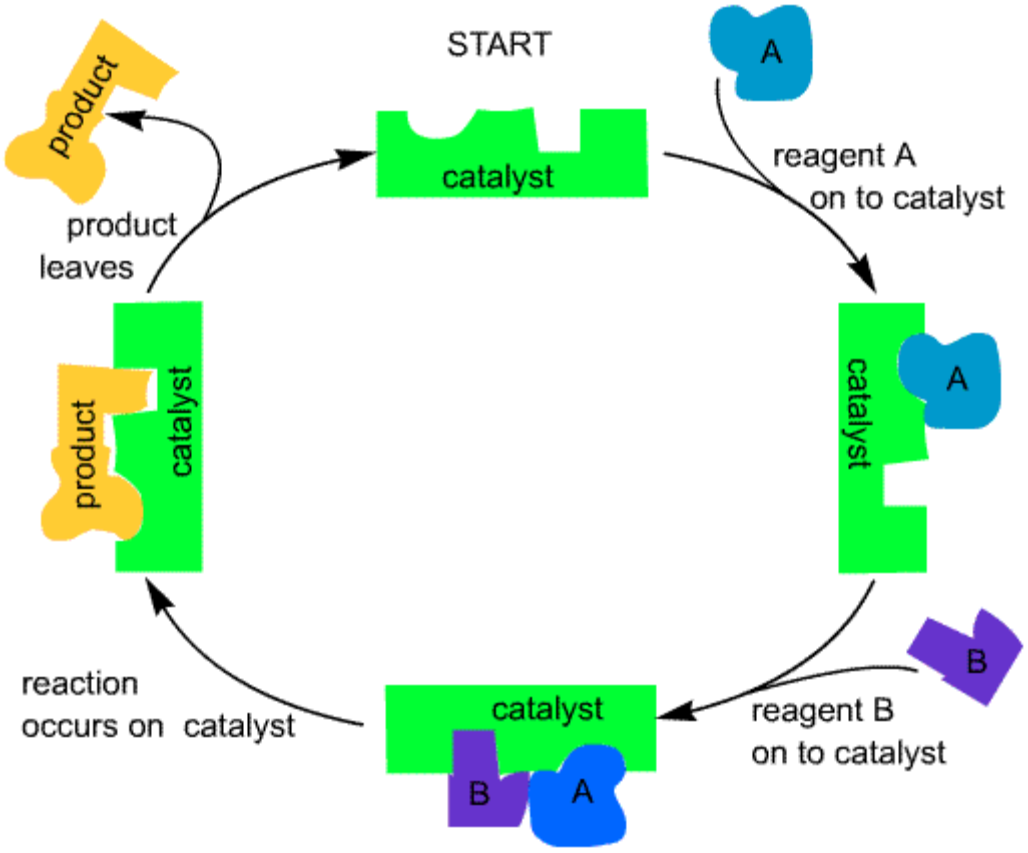
Catalyst

Catalyst

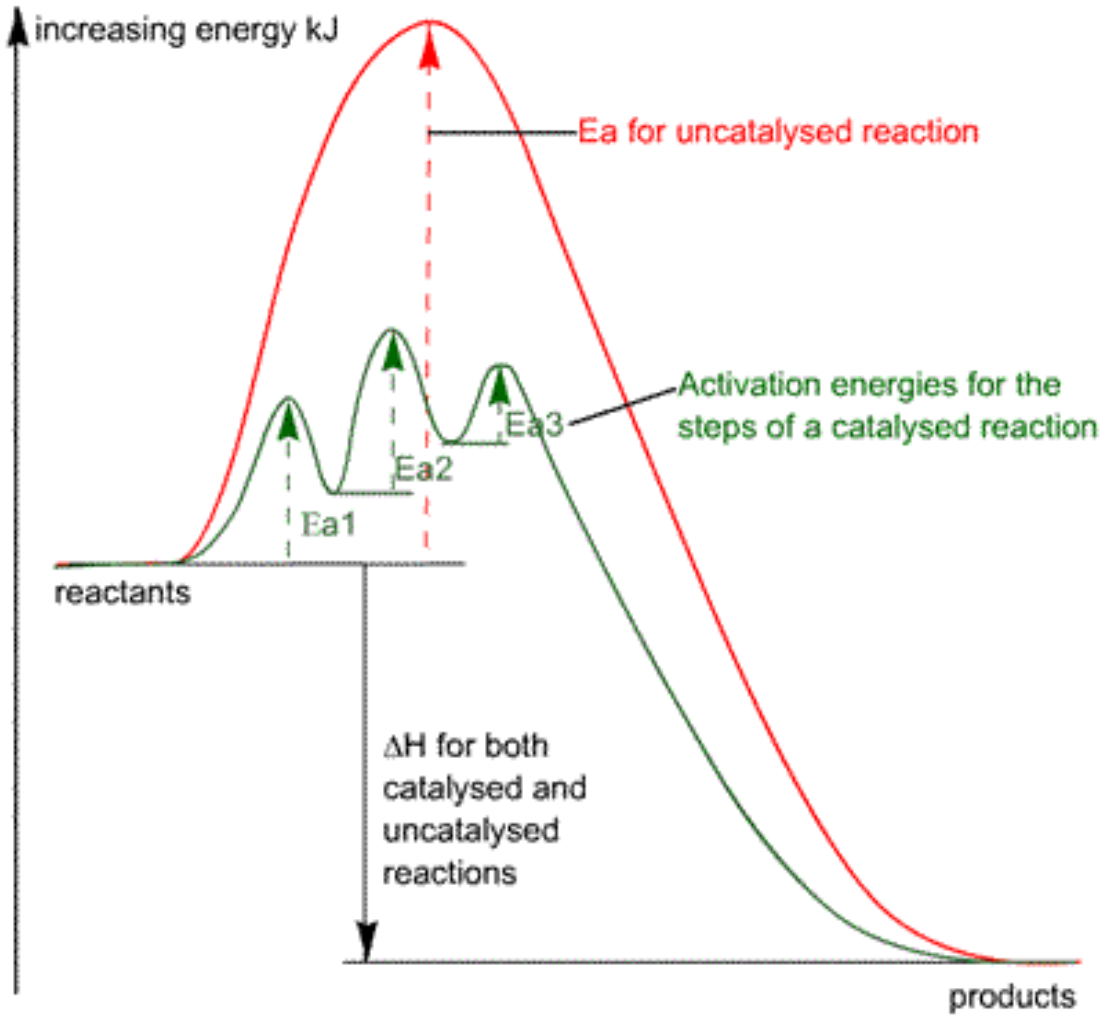
Catalysts are substances which,when added to a reaction, increase the rate of reaction by providing an alternate reaction pathway with a lower activation energy(Ea).

They do this by promoting proper orientation between reacting particles.

Catalytic Cycle



Energy Profile



Catalyst Parameters

Activity

The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst to become active.

Selectivity

The selectivity of a catalyst is its ability to direct a reaction to yield a particular product.

For example -:

$$CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$$

$$CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO\text{-}Cr_2O_3} CH_3OH(g)$$

$$CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$$

Stability

The number of reactions performed by each active site before it decays or becomes inactive.

Catalyst Parameters

Catalysts *cannot* make energetically unfavorable reactions possible — they have *no* effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are equally affected.

The degree of activity of a catalyst can be described by the turnover number (TON) and the catalytic efficiency by the *turnover frequency* (TOF).

Turnover number: the number of moles of substrate that a mole of catalyst has been converted**.**

Turnover frequency is used to refer to the turnover number per unit time.

Types of catalysis

Homogeneous Catalysis

The catalyst and reactants are in the same phase, usually liquid.

Heterogeneous catalysis

Catalyst and reactants are in different phases.

Enzymatic Catalysis

Catalyst is an enzyme (macromolecules made of amino acids).

Homogeneous *versus* heterogeneous catalysis

Property	Homogeneous	Heterogeneous
Activity	High	Variable
Selectivity	High	Variable
Reaction conditions	Mild	Generally harsh
Reaction temperature	Often low	Often high
Mechanistic understanding	Can be ascertained	Difficult to obtain
Catalyst tuning	By ligand modification	Difficult
Catalyst separation	Difficult	Easy
Catalyst recycling	Difficult	Easy
Active site	All metal atoms	Surface atoms only
Diffusion problems	Rare	Existing
Mixing	Easy	May be difficult

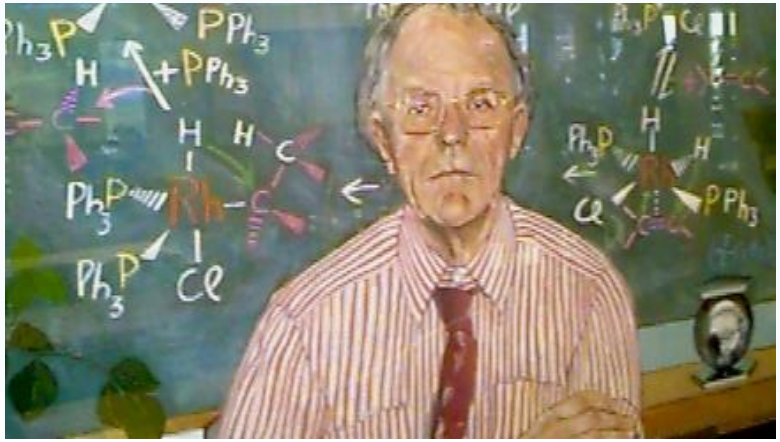
The origins of homogeneous catalysis

Modern homogeneous catalysis, which has transformed the chemical industry, started in the 1950s.

Ziegler and Natta developed Ti and Zr metallocene catalysts for making polyethylene and related polymers.

Wilkinson made a Rh compound that catalyses the addition of a wide range of substrates across unsaturated bonds.

Within a short time their catalysts were used on an industrial scale.



Polymerization catalysis

Karl Ziegler prepared linear polyethylene with a catalyst he discovered and Giulio Natta used similar catalysts to polymerize 1-alkenes.

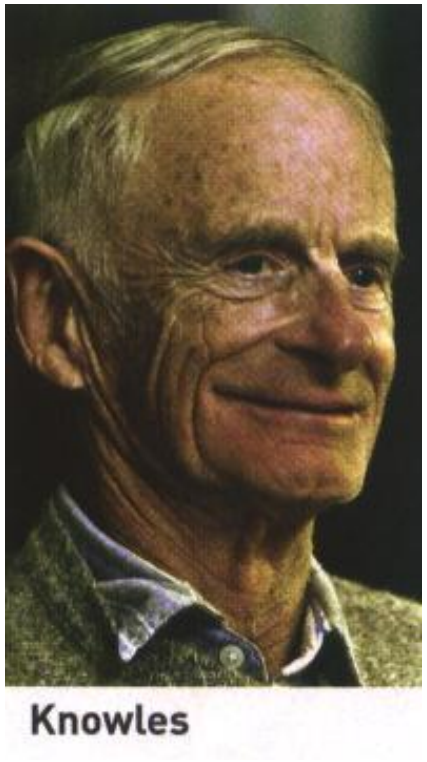
They were awarded the Nobel Prize in Chemistry in 1963.

Their catalysts are more active than the most efficient enzymatic catalysts in nature.

Our epoch has witnessed the gradual replacement of traditional materials by synthetic ones. We have all seen that plastics can often substitute glass, porcelain, wood, metals, bones, and horn, the substitutes being frequently lighter, less fragile, cheaper and easier to shape and work. It has in fact been said that we live in the Age of Plastics.

Nobel Prize in Chemistry 2001


Noyori

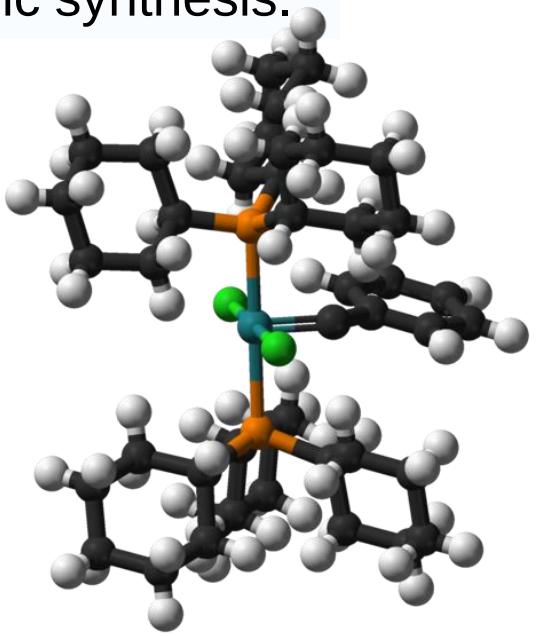

Knowles

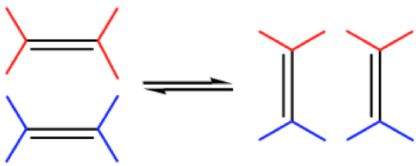
The Nobel Prize in Chemistry 2001 was divided, one half jointly to William S. Knowles and Ryoji Noyori *"for their work on chirally catalysed hydrogenation reactions"* and the other half to K. Barry Sharpless *"for his work on chirally catalysed oxidation reactions"*.

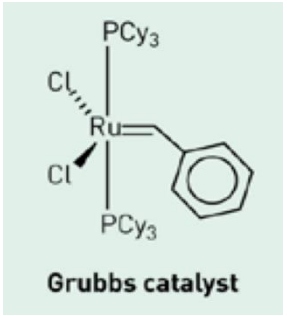
Nobel prizes for homogeneous catalysis

2005 Yves Chauvin, Robert H. Grubbs, Richard R. Schrock

for the development of the metathesis method in organic synthesis.







The Nobel Prize in Chemistry 2010

Richard F. Heck, Ei-ichi Negishi, Akira Suzuki

«C-C coupling reactions
with palladium catalysts»

The Nobel Prize in Chemistry 2018
Biocatalysis: Direct Evolution
Francis Arnold

“for the directed evolution of enzymes”

The Nobel Prize in Chemistry 2021

"for the development of asymmetric organocatalysis "

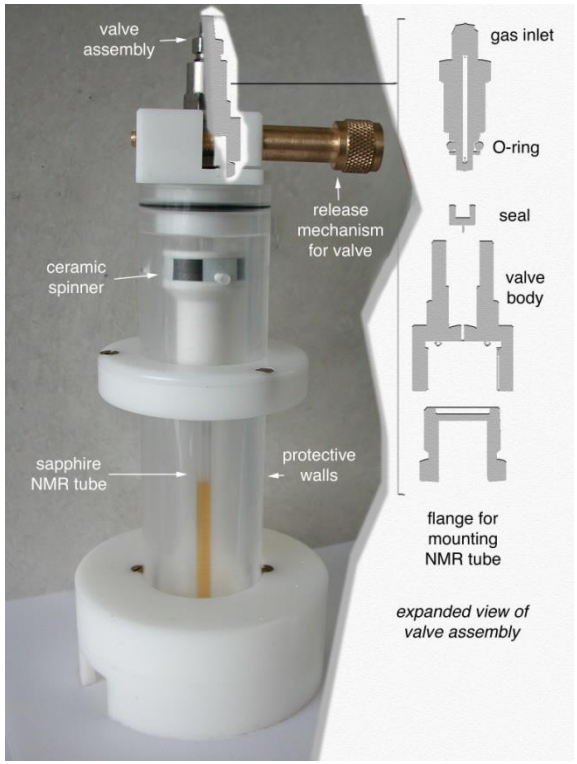
Benjamin List **David W.C. MacMillan**

How are catalysts improved?

To improve a catalyst it helps to know the mechanism.

Homogeneous catalysts can be studied in solution by high-resolution techniques such as FT-IR and NMR spectroscopy.

By identifying, for example, the rate determining step in the process, it becomes possible to design new systems that facilitate this step and lead to an improved performance of the catalyst.



Challenges in catalysis today

Course objectives

Examples of modern homogeneous catalysis.
- hydrogenation
- C-C and C-N coupling
- Olefin metathesis

Understand how homogeneous catalysts work – catalytic cycles.

Know how to design/modify a homogeneous catalyst with specific properties – ligands/metals.

Quiz - 1

1 - Which phrase does not describe a reaction rate?
A) The change of the concentration of a reactant over time
B) The change of the number of moles of a reactant over time
C) The difference between the concentrations of reactants and products
D) The difference between the initial and final concentrations of one reactant over time

2 - How can chemists collect empirical data necessary for measuring reaction rates?
A) Monitor the mass or volume of gas produced over time
B) Record changes in pH over time
C) Measure electrical conductivity over time
D) All of the above

3 - What type of apparatus can be used to monitor the change in concentration of H_3O^+ ions?
A) A pH meter
B) A thermometer
C) A pressure gauge
D) A spectrophotometer

4 - Which of the following actions would not change the rate of a reaction?
A) Increasing the concentration of the reactants
B) Increasing the available surface area of a reactant
C) Using different reactants
D) None of the above

6 - Which of the following is true, according to the collision theory?
A) Collisions between reactant particles are always elastic.
B) The addition of a catalyst increases the concentration of products at equilibrium.
C) Increasing the concentration of the reactant will increase the number of collisions per second.
D) The greater the surface area of the molecules, the smaller the number of collisions.

7 - Which of the following criteria must a collision between two reactant particles satisfy to result in a reaction?
A) Correct orientation of and sufficient collision energy
B) Sufficient collision energy
C) Correct orientation of reactant particles
D) None of the above

8 - Which of the following does a potential energy diagram not represent?
A) The potential energy change during a chemical reaction
B) The relative amounts of reactants and products involved in a chemical reaction
C) The difference in potential energy between reactants and products in a chemical reaction
D) The activation energy barrier of a reaction

9 - Which statemen is true about potential energy diagrams?
A) They will not have a high activation energy barrier if the reaction is slow.
B) They do not show the transition state.
C) They indicate that a reaction is endothermic if the reactants appear higher than the products.
D) They will have a low activation energy barrier if the reaction is fast.

Quiz - 2

10 - Which of the following is true?
A) In an exothermic reaction, the products are more energetically stable than the reactants.
B) In an endothermic reaction, the products are more energetically stable than the reactants.
C) In an endothermic reaction, the overall difference in potential energy is the amount of energy that is released by the reaction.
D) In an exothermic reaction, the overall difference in potential energy is the amount of energy that is absorbed by the reaction.

11 - Which of the following is true?
A) The chemical species that exists at the transition state is highly stable.
B) The chemical species that exists at the transition state is called the activated complex.
C) Both A and B.
D) Neither A or B.

12 - If Δ E of a reaction is -230 kJ and the activation energy of the forward reaction is 150 kJ, what is the activation energy of the reverse reaction?
A) 80 kJ
B) - 80 kJ
C) - 330 KJ
D) 380 KJ

13 - A single step in a series of steps that makes up an overall reaction is called a(n)
A) reaction mechanism
B) elementary reaction
C) reaction intermediate
D) transitional mechanism

14 - Reaction intermediates are
A) single molecular events
B) series of steps in an overall reaction
C) molecules formed in an elementary reaction and consumed in a subsequent elementary reaction
D) substances that increase the rate of a chemical reaction without being consumed by the reaction

15 - Which is true about the following reaction?

$$C + D \rightarrow CD, \qquad \Delta E = 50 \text{ kJ/mol}$$

A) It is unimolecular.
B) It is exothermic.
C) Both A and B
D) Neither A or B

17 - The rate-determining step
A) has an activation energy barrier that is greater than the activation energy barrier of the other steps in a reaction
B) is the fastest step in a reaction
C) is always the last step in a series
D) all of the above

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