



CATALYSTS IN PETRO-REFINING PROCESSES

December 2016



Applied Catalysis



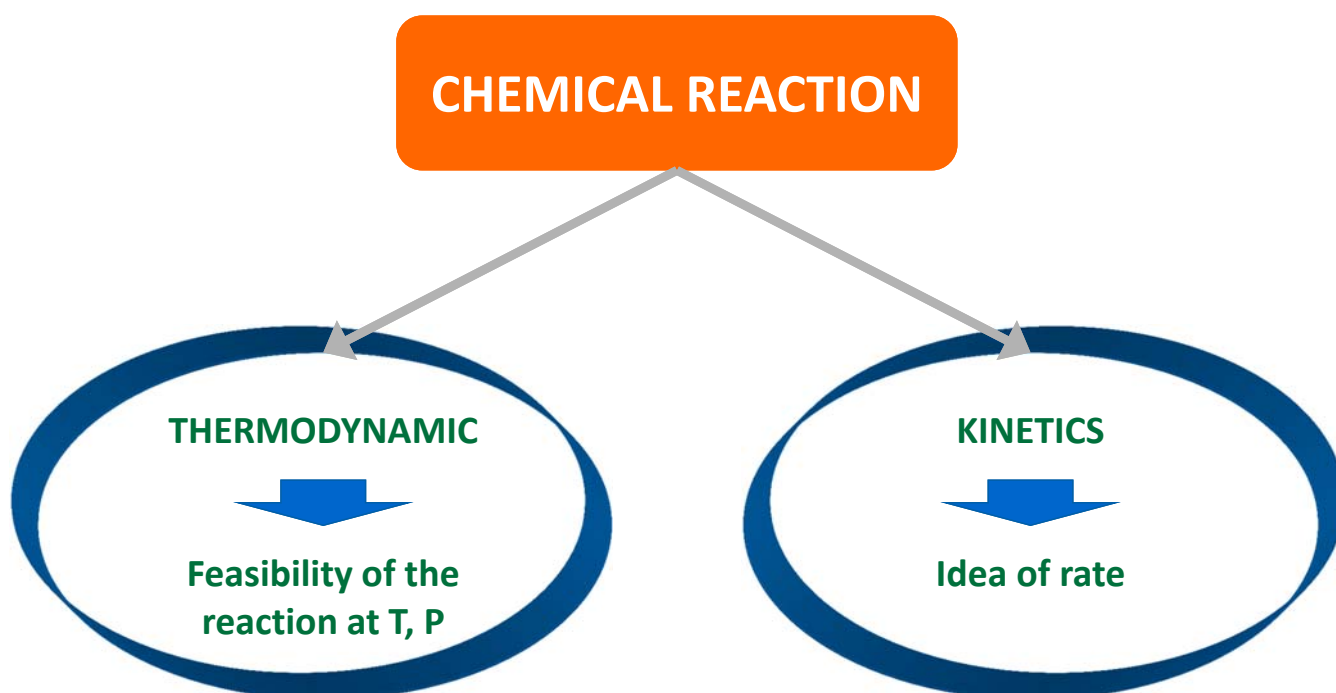
RC - 09121 - RA HDT - 09121_A - DE16 - Ver 1.0

Outline

- ▶ **The chemical reaction: thermodynamics and kinetics**
- ▶ **Definition, role and classification of the catalysts**
- ▶ **Preparation of the industrial catalyst**
- ▶ **Catalyst properties**

Outline

- ▶ **The chemical reaction: thermodynamics and kinetics**
- ▶ Definition, role and classification of the catalysts
- ▶ Preparation of the industrial catalyst
- ▶ Catalyst properties



- ▶ Thermodynamics is the science of initial and final states
- ▶ It allows to predict the spontaneous evolution of a system, knowing the thermodynamical values

$$\Delta G = G_{\text{final}} - G_{\text{initial}} = \Delta H - T\Delta S$$

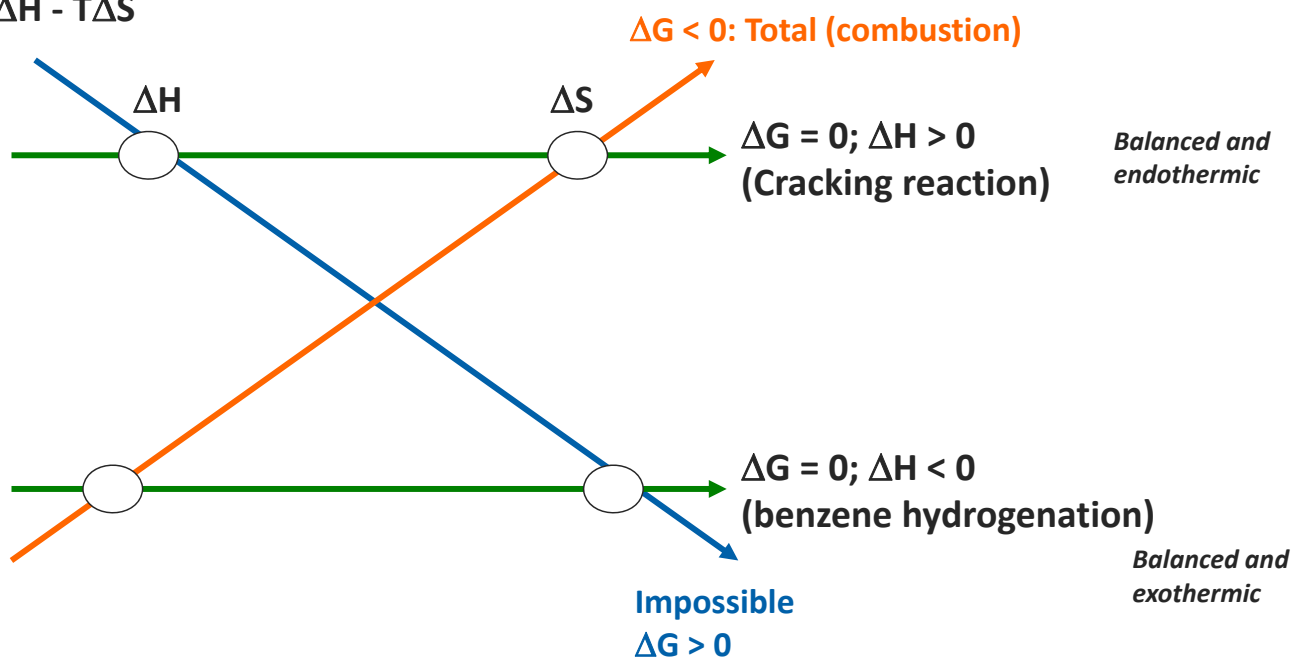
ΔH : enthalpy of the reaction

ΔS : entropy of the reaction

- ▶ It is essential to consider very early the thermodynamic aspect to determine whether the reaction is feasible or not

- ▶ Enthalpic and entropic balances for chemical reactions

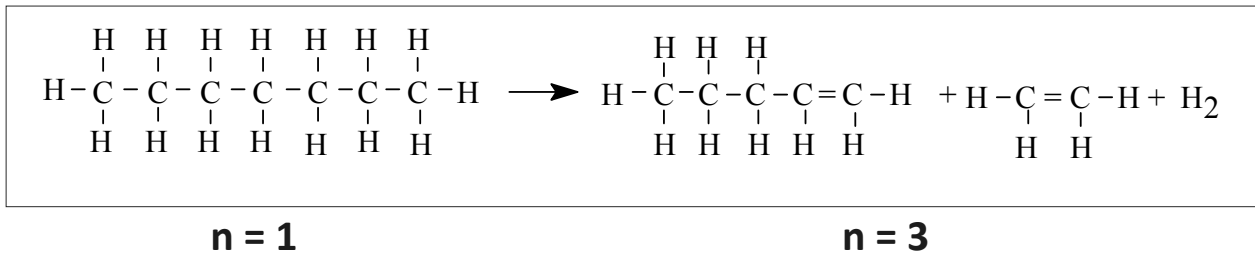
$$\Delta G = \Delta H - T\Delta S$$



Evolution of a reaction with the pressure

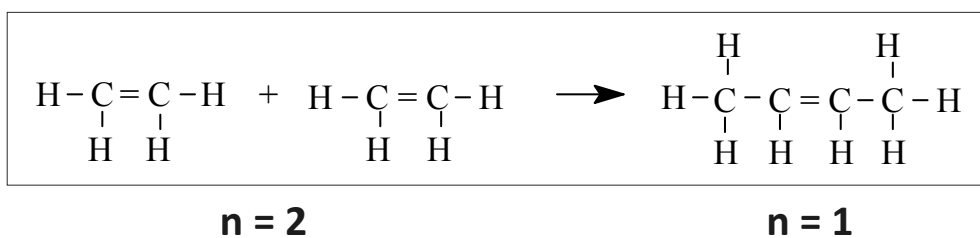
- ▶ If there is a decrease of the number of moles, the reaction is favored by an increase of pressure (and vice versa)

▶ Examples: **CRACKING**



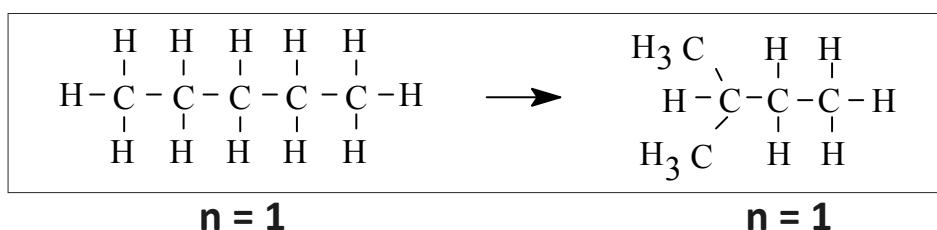
- ➔ Reaction favored at low pressure

▶ **DIMERIZATION**



- ➔ Reaction favored at high pressure

▶ **ISOMERIZATION**



- ➔ The reaction is not influenced by a variation of pressure

Evolution of a reaction with the temperature

- ▶ An endothermic reaction is favored at high temperature
- ▶ An exothermic reaction is favored at low temperature

▶ Examples:

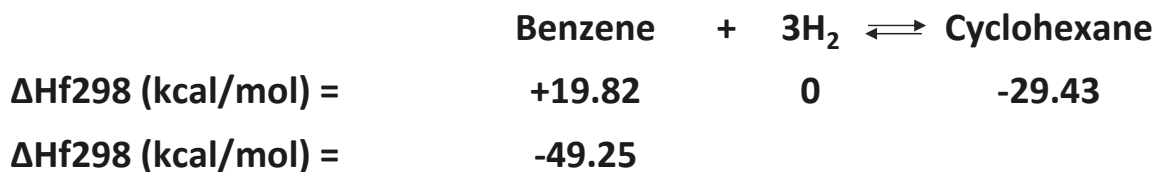
- Cracking $\Delta H > 0 \Rightarrow$ reaction favored at high temperature

- Dimerization
- Isomerization

} $\Delta H < 0 \Rightarrow$ reaction favored at low temperature

Enthalpic balances

▶ Benzene hydrogenation



Hydrogenation = exothermic reaction

➔ Favored at low temperature

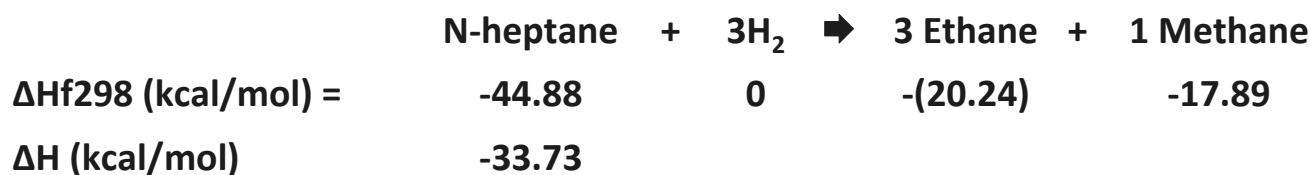
► N-Heptane aromatization



Aromatization = endothermic reaction

➔ Favored at high temperature

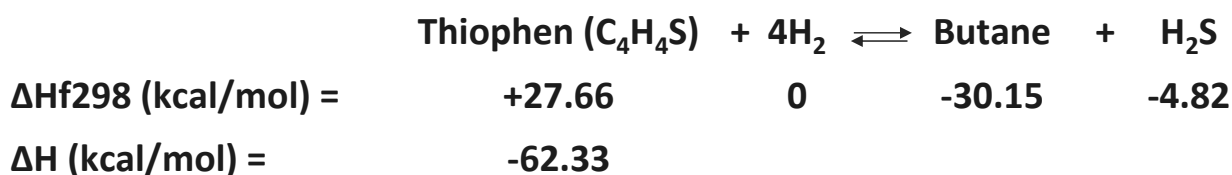
► N-Heptane hydrogenolysis



Hydrogenolysis = exothermic reaction

➔ Favored at low temperature

► Desulfurization



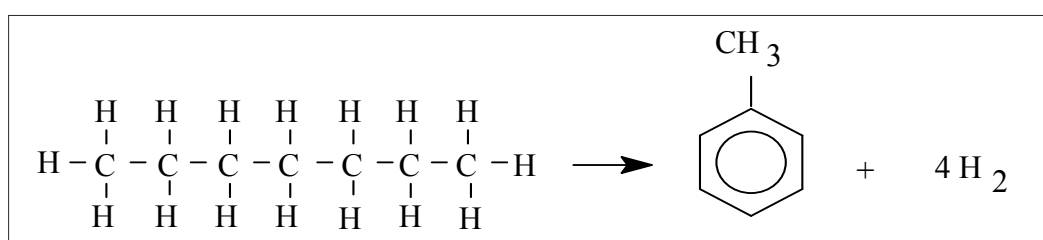
HDS = exothermic reaction

➔ **Favored at low temperature**

Example: n-heptane dehydrocyclization



1. Write the equation of the reaction



2. The reaction is endothermic ($\Delta H = 250$ kJ/mol)

► What is the influence of temperature and pressure on the evolution of this reaction?

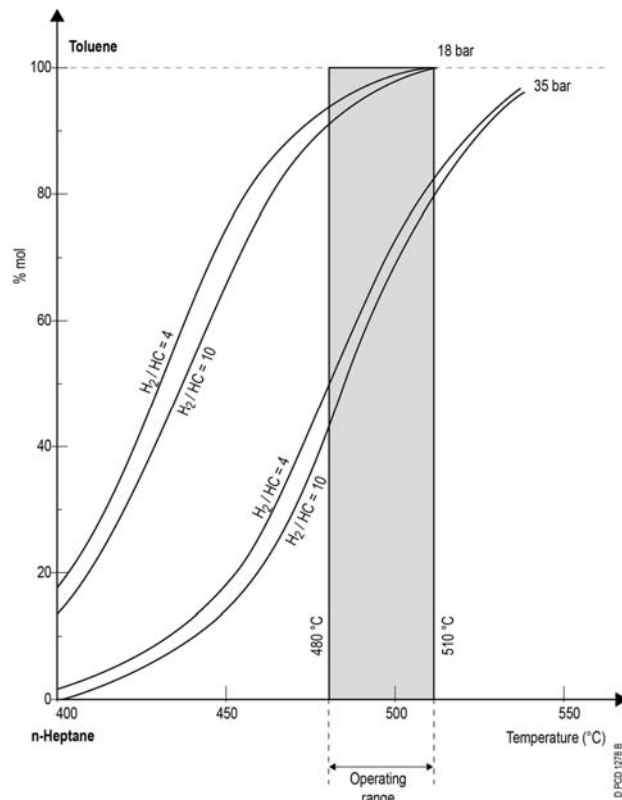
- The number of moles increases ➔ The reaction is favored at low pressure
- $\Delta H > 0$ ➔ The reaction is favored at high temperature

3. Check your answer on the figure

at $T = 480^\circ\text{C}$ and $\text{H}_2/\text{HC} = 4$ } % Tol = 50% for 35 bars
 % Tol = 92% for 18 bars

at $p = 35$ bars and $\text{H}_2/\text{HC} = 4$ } % Tol = 50% for 480°C
 % Tol = 82% for 510°C

➔ The reaction is favored at low pressure and high temperature



n-heptane-toluene equilibrium under hydrogen pressure

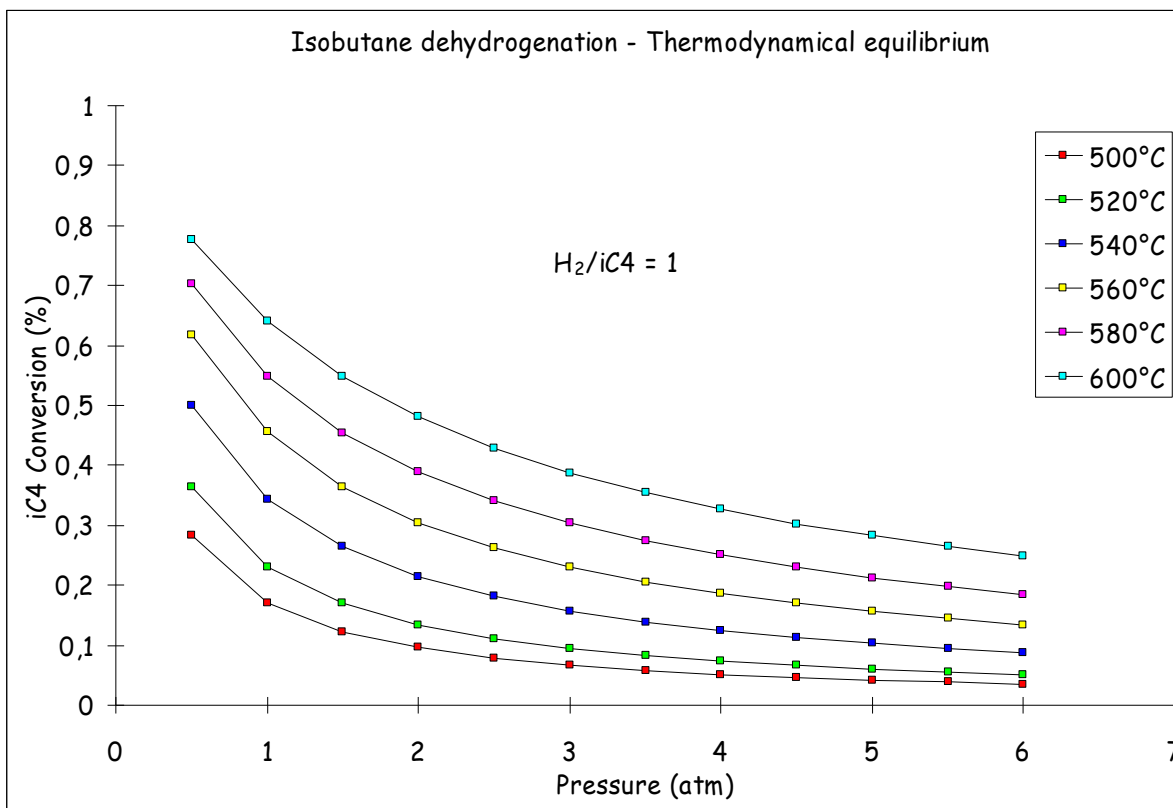
4. The notion of H_2/HC ratio, is very important because it allows to have access to the H_2 partial pressure

Determine the H_2 partial pressure for a total pressure of 18 bars and H_2/HC (molar) of 10

$$p_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{H}_2} + n_{\text{HC}}} \times p_t$$

$$n_{\text{H}_2} = 10 \cdot n_{\text{HC}} \rightarrow \frac{10 \cdot n_{\text{HC}}}{10 \cdot n_{\text{HC}} + n_{\text{HC}}} \times p_t = p_{\text{H}_2}$$

$$p_{\text{H}_2} = \frac{10}{11} \times p_t = \frac{10}{11} \times 18 = 16.35 \text{ bar}$$



Kinetics

The aim of kinetics is to study the course of the chemical transformation versus time



IDEA OF THE REACTION RATE
[A] → [B]

$V = k [A]$ for a 1 order reaction
 $k =$ rate constant
 $k = k_0 e^{-E_a/RT}$ (Arrhénius Law)
 $E_a =$ Activation energy

Activation energy: energy to provide to the system to transform the reactants into products