

Lecture 14 “Chemical reactions under changing external conditions: the influence of temperature and pressure”

Goal of the lecture: To understand how external factors, particularly **temperature** and **pressure**, affect the rate, equilibrium, and direction of chemical reactions; to apply thermodynamic and kinetic principles such as the **Arrhenius equation** and **Le Chatelier’s principle** to explain the behavior of reactions under varying conditions.

Brief lecture notes: In real chemical and industrial processes, reactions rarely occur under constant conditions. Variations in **temperature** and **pressure** can significantly alter the **reaction rate**, **equilibrium composition**, and even **reaction pathways**. Understanding these effects allows chemists and engineers to **control product yield and efficiency**, design optimal reactors, and ensure safety in large-scale production.

The two main aspects influenced by external conditions are:

- **Kinetic effects** – how fast a reaction proceeds.
- **Thermodynamic effects** – to what extent a reaction proceeds and in which direction equilibrium shifts.

1. Influence of Temperature on Reaction Rate

Temperature has a strong effect on how quickly reactions occur. According to **collision theory**, as temperature increases, molecules move faster and collide more frequently with higher energy, increasing the number of **effective collisions**.

The quantitative relationship between the **rate constant (k)** and temperature (T) is given by the **Arrhenius equation**:

$$k = Ae^{-E_a/RT}$$

where

- A = frequency factor (collision frequency and orientation),
- E_a = activation energy,
- R = gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$),
- T = absolute temperature (K).

Taking the logarithm:

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$$

A plot of $\ln k$ vs $1/T$ gives a straight line with slope $-E_a/R$, allowing calculation of activation energy.

For example, In the decomposition of hydrogen peroxide, increasing the temperature from 20 °C to 40 °C doubles the rate constant because the fraction of molecules with sufficient energy to overcome the activation barrier increases exponentially.

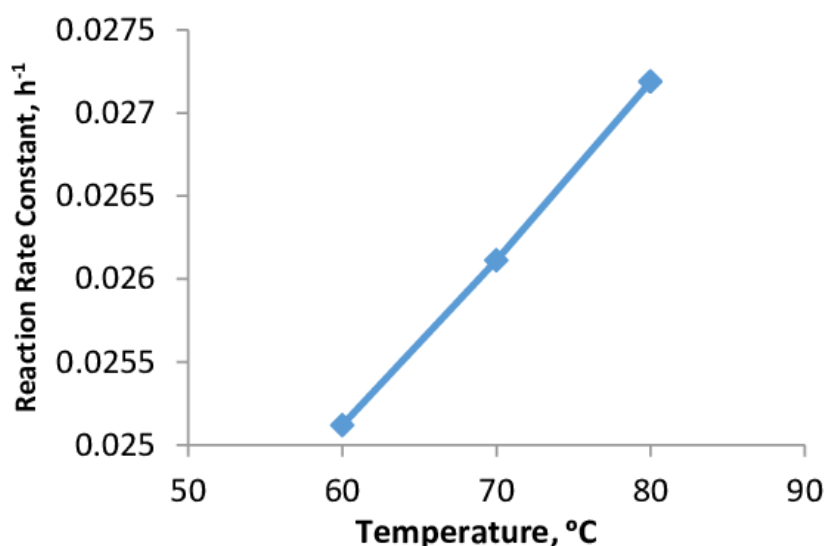


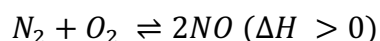
Figure 1 – Effect of temperature on reaction rate

2. Influence of Temperature on Chemical Equilibrium

Temperature not only changes the rate but also shifts the **equilibrium position** according to **Le Chatelier's Principle**:

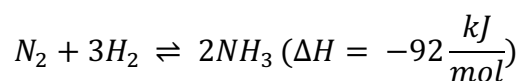
When a system at equilibrium is disturbed by a change in temperature, the equilibrium shifts in the direction that counteracts that change.

- For **endothermic reactions** ($\Delta H > 0$): increasing temperature shifts equilibrium **toward products**.
Example:



Higher temperature favors the formation of NO.

- For **exothermic reactions** ($\Delta H < 0$): increasing temperature shifts equilibrium **toward reactants**.
Example:



In ammonia synthesis, lower temperature favors product formation, but too low a temperature slows the reaction. Therefore, a **compromise temperature** (≈ 450 °C) is used in the Haber process.

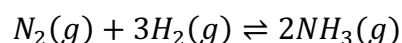
3. Influence of Pressure on Chemical Equilibrium

Pressure mainly affects reactions involving **gaseous reactants and products**. According to **Le Chatelier's principle**:

An increase in pressure shifts the equilibrium toward the side with fewer gas molecules, while a decrease shifts it toward the side with more gas molecules.

Examples:

1. Ammonia synthesis (Haber process):



4 moles of gas $\rightarrow$ 2 moles of gas.

Increasing pressure shifts equilibrium toward ammonia formation.

2. Decomposition of $CaCO_3$:



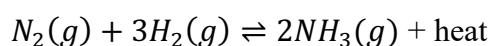
Here, an increase in pressure shifts equilibrium **toward reactants**, reducing CO_2 release.

Pressure changes have **no effect** on reactions where the number of gas molecules is the same on both sides.

4. Combined Effect of Temperature and Pressure

In industrial practice, both parameters must be optimized simultaneously.

For example, in the **Haber–Bosch process**, the reaction:



is **exothermic** and involves a **reduction in gas volume**.

- **Low temperature** favors equilibrium yield but slows the reaction.
 - **High pressure** increases yield but raises equipment cost.
- Hence, the process is operated at **moderate temperature (450 °C)** and **high pressure (150–200 atm)** with an **iron catalyst**, balancing yield and rate efficiently.

5. Thermodynamic Relationships

The effect of temperature on equilibrium constant K is described by the **van't Hoff equation**:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

This equation allows prediction of how the equilibrium constant changes with temperature, using the enthalpy of reaction (ΔH°).

Table 1 – Influence of External Conditions on Chemical Reactions

Condition	Effect on Rate	Effect on Equilibrium	Example
Increase in Temperature	Increases rate (via k)	Shifts endothermic reactions forward	Formation of NO
Decrease in Temperature	Decreases rate	Shifts exothermic reactions forward	Ammonia synthesis
Increase in Pressure	Little effect on liquids/solids; increases gas-phase rate	Shifts equilibrium toward fewer gas moles	Haber process
Decrease in Pressure	Opposite effect	Shifts toward more gas moles	Decomposition reactions

6. Role of Catalysts

While catalysts **do not change the position of equilibrium or the thermodynamic favorability** of a reaction, they play a crucial role in determining **how quickly equilibrium is reached**. A catalyst provides an **alternative reaction pathway** with a **lower activation energy (E_a)** than the uncatalyzed reaction. As a result, a greater fraction of molecules possess enough energy to react at a given temperature, significantly increasing the rate of both forward and reverse reactions equally.

Catalysts are especially important in processes that must operate under **mild or controlled conditions**, where high temperatures or pressures would be costly or unsafe. By reducing the required activation energy, catalysts help **save energy, increase product yield, and improve process selectivity** without being consumed in the reaction.

Questions for self-control:

1. How does temperature affect both the rate and direction of a chemical reaction?
2. State and explain the Arrhenius equation.
3. What is Le Chatelier's principle, and how does it apply to pressure changes?
4. Describe how temperature and pressure are optimized in the Haber–Bosch process.
5. What is the van't Hoff equation, and what information does it provide about equilibrium constants?

Literature:

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