

Thermodynamic equilibrium in reactive systems

- I. Equilibrium in chemical reactions – concepts and conditions
- II. Equilibrium constant
- III. The concept of reaction Gibbs energy, exergonic and endergonic processes
- IV. Standard reaction Gibbs energy and its connection with chemical potentials
- V. Connection between the formal and thermodynamic description of an equilibrium
- VI. Other expressions for the equilibrium constant: K_p , K_x , K_a
- VII. Determination of the equilibrium constant from other thermodynamic data

II. Equilibrium in chemical reactions – concepts and conditions

- ∞ Application of thermodynamics for chemical changes (a.k.a. reactive systems)
- ∞ Three important questions:
 - the direction: What is produced? What is consumed?
 - the quantity: Where does the reaction „stop”? Where does the equilibrium lie?
 - the course of the change – in time and space. Not investigated in thermodynamics: reaction kinetics and reaction mechanism.

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II. Equilibrium in chemical reactions – concepts and conditions

- ∞ The „direction”: the spontaneous process under the given conditions (T , p , x_i) (the reverse may be forced externally). Chemically: What is produced? What is consumed?
- ∞ For quantification: the extent of reaction is important.
- ∞ Two approaches (two different levels) used:
 - **macroscopic**: $0 < \zeta < 1$ **small Greek XI letter**
 - **molecular**: more commonly called reaction coordinate, which gives a spatial and temporal measure of the reactant molecules → product molecules process.

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II. Equilibrium in chemical reactions – concepts and conditions

- $\zeta = 0$ at the beginning of the reaction, only the reactants are present
- $\zeta = 1$ if the reaction is complete and only the products are present
- Can also be obtained from the studying the individual substances: the ratio of the amount of substance n_j consumed or produced in the reaction and the stoichiometric ν_j coefficient.
 - $d\zeta = dn_j/\nu_j$
 - for reactant A, $\nu_j < 0$, so ζ decreases: $dn_A/\nu_A = -d\zeta$,
 - for product B, $\nu_j > 0$, so ζ increases: $dn_B/\nu_B = +d\zeta$.

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III. Equilibrium constant

- ∞ Based on the measurement of equilibrium concentrations in numerous systems (Guldberg and Waage, 1863):
- ∞ The stoichiometry of the process: $aA + bB \rightleftharpoons cC + dD$

$$K = \frac{[C]_{\text{equilibrium}}^c [D]_{\text{equilibrium}}^d}{[A]_{\text{equilibrium}}^a [B]_{\text{equilibrium}}^b} \quad K = \frac{[C]_e^c [D]_e^d}{[A]_e^a [B]_e^b} \quad (\text{in general})$$

- ∞ Obviously:
 - if the value of K is large, the equilibrium is shifted to the right, the conversion is high, ζ is close to 1,
 - if the value of K is small, the equilibrium is shifted to the left, the conversion is low, ζ is close to 0.

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III. Equilibrium constant

- ∞ The simple observation-based rule was...
 - backed up by general thermodynamic laws,
 - connected precisely to other thermodynamic data of the reaction,
 - complemented by the introduction of activities to deal with „deviations” in real systems,
 - was connected to electrochemistry by setting up an exact equation between K and the cell potential of the reaction carried out in an electrochemical cell.

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III. The concept of reaction Gibbs energy

- Simple example react ion: $A \rightleftharpoons B$ (e.g. isomerization)
 - change in the amount of substance of A: $dn_A = -d\xi$
 - change in the amount of substance of B: $dn_B = +d\xi$
 - change in G for the entire system:
 $dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi$
 - A rearrangement yields the $\Delta_r G$ reaction Gibbs energy:

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A = \Delta_r G$$

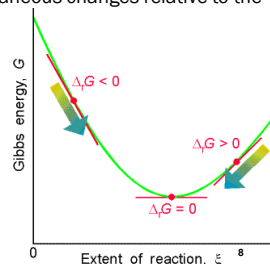
- This property controls the advance of the process.

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III. The concept of reaction Gibbs energy

- Thermodynamics (universal experience):
 - G decreases (p, T are constant) in spontaneous processes, this indicates the direction of spontaneous changes relative to the initial composition.

- Initial composition:
 - reactants only
 - products only
 - both reactants and products
- Interpretation of $\Delta_r G$: the slope of the curve shown on right in a given point.



IV. The connection between standard reaction Gibbs energy and chemical potentials

- $\Delta_r G$: reaction Gibbs energy
 - the slope of $G = f(\xi)$ at a given composition.
 - The change in G if 1 mol of reactant is transformed into 1 mol of product without a change in the composition (large system). *The difference in the chemical potentials:*

$$\Delta_r G = \mu_B - \mu_A = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

- $\Delta_r G^\ominus$: standard reaction Gibbs energy
 - The change in G if 1 mol of reactant in the **standard state** is transformed to 1 mol of product **the standard state**. The difference in **standard chemical potentials**:

$$\Delta_r G^\ominus = \mu_B^\ominus - \mu_A^\ominus = \Delta_r G^\ominus(B) - \Delta_r G^\ominus(A)$$

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V. Connection between the formal and thermodynamic description of an equilibrium

- A simple example: $A(g) \rightleftharpoons B(g)$ equilibrium gas reaction.

- The **formal** description: $K_p = \frac{p_{B, \text{equilibrium}}}{p_{A, \text{equilibrium}}}$

- Thermodynamic** description:

- $\Delta_r G = \mu_B - \mu_A =$

$$= \left(\mu_B^\ominus + RT \ln \frac{p_B}{p^\ominus}\right) - \left(\mu_A^\ominus + RT \ln \frac{p_A}{p^\ominus}\right) =$$

$$= \Delta_r G^\ominus + RT \ln \frac{p_B}{p_A}$$
- $\Delta_r G^\ominus = \mu_B^\ominus - \mu_A^\ominus$ (the difference in standard chemical potentials)
- Let $p_B/p_A = Q_p$ called reaction quotient:

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q_p$$

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V. Connection between the formal and thermodynamic description of an equilibrium

- $\Delta_r G = \Delta_r G^\ominus + RT \ln Q_p$ equation in **equilibrium**:
 - If $\Delta_r G = 0$, Q_p is identical to the equilibrium constant K_p :

$$Q_{p, \text{equilibrium}} = K_p = \frac{p_{B, \text{equilibrium}}}{p_{A, \text{equilibrium}}}$$

- Result: $\Delta_r G^\ominus = -RT \ln K_p$
- The negative sign is important!
 - negative $\Delta_r G^\ominus \rightarrow K$ is higher than 1 (product-dominance)
 - positive $\Delta_r G^\ominus \rightarrow K$ is lower than 1 (reactant-dominance)

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V. Connection between the formal and thermodynamic description of an equilibrium

General sequence of thought:

- The reaction: $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$

- after $d\xi$ change: $dn_A = \nu_A d\xi \dots dn_C = \nu_C d\xi$
 in general: $dn_j = \nu_j d\xi$

- Change in G: $dG = \left(\sum_j \nu_j \mu_j\right) d\xi$

- The reaction Gibbs energy is the slope of $G = f(\xi)$:

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \sum_j \mu_j \nu_j$$

- As $\mu_j = \mu_j^\ominus + RT \ln a_j$, where $a_j = f_j/p^\ominus$, so

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q, \text{ where } \Delta_r G^\ominus = \sum_j \nu_j \mu_j^\ominus$$

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V. Connection between the formal and thermodynamic description of an equilibrium

∞ The reaction quotients Q in equilibrium: $Q = \frac{a_C^{v_C} a_D^{v_D}}{a_A^{v_A} a_B^{v_B}} = \prod_J a_J^{v_J}$

- In equilibrium $\Delta_r G = 0$, then

$$K = Q_{\text{equilibrium}} = \left(\frac{a_C^{v_C} a_D^{v_D}}{a_A^{v_A} a_B^{v_B}} \right)_{\text{equilibrium}} = \prod_J (a_J^{v_J})_{l,s}$$

- So the result is again: $\Delta_r G^\ominus = -RT \ln K$
- This is K (in any phase), the thermodynamic equilibrium constant based on **activities**:

$$K = \prod_J a_J^{v_J}$$

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VI. Other expressions for the equilibrium constant

∞ In gas phase (fugacity or pressure): $K = \prod_J \left(\frac{f_J}{p^\ominus} \right)^{v_J}$

- For an ideal gas: $K_p = \prod_J \left(\frac{p_J}{p^\ominus} \right)^{v_J}$

∞ Based on molality (or mole fractions):

$$K = \left(\frac{a_C a_D}{a_A a_B} \right)^v = \left(\frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \right)^v \times \left(\frac{m_C m_D}{m_A m_B} \right)^v = K_\gamma K_m$$

- γ can be determined with „iteration“.

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VI. Other expressions for the equilibrium constant

A commonly used formalism:

∞ degree of dissociation: $0 < \alpha < 1$

∞ $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

∞ In equilibrium $[\text{H}^+]_e = [\text{A}^-]_e = \alpha c$ and $[\text{HA}]_e = (1-\alpha)c$, so:

$$K_d = \frac{[\text{H}^+]_e [\text{A}^-]_e}{[\text{HA}]_e} = \frac{\alpha^2 c}{1-\alpha}$$

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VI. Other expressions for the equilibrium constant

The connection between the reaction equation and K :

∞ Definite stoichiometry and exactly defined standard states are needed.

Reaction	Equilibrium constant	$\Delta_r G^\ominus$ (kJ/mol)
$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$	$K = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3}$	6.8×10^5 -33.2
$0,5\text{N}_2 + 1,5\text{H}_2 \rightleftharpoons \text{NH}_3$	$K' = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}}$	8.2×10^2 -16.6
$\text{NH}_3 \rightleftharpoons 0,5\text{N}_2 + 1,5\text{H}_2$	$\bar{K} = \frac{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}}{[\text{NH}_3]}$	1.2×10^{-3} +16.6
$2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$	$\bar{K} = \frac{[\text{N}_2] [\text{H}_2]^3}{[\text{NH}_3]^2}$	1.5×10^{-6} +33.2

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VIII. Determination of the equilibrium constant

- ∞ Experimental measurement of equilibrium concentrations
 - without disturbing the equilibrium:
 - quenching the reaction mixture,
 - measurement of quantities proportional to the concentration, e.g. photometry, electrode potential, pressure etc.
- ∞ Measuring the cell potential of a Voltaic cell
- ∞ From thermodynamic data
- ∞ Calculations base on statistical mechanics
 - from spectroscopic data

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VIII. Determination of the equilibrium constant

Calculating K and/or $\Delta_r G^\ominus$ and/or E^\ominus :

∞ from thermodynamic data ($\Delta_r H^\ominus$ and $\Delta_r S^\ominus$):

- $\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$ (standard enthalpy and entropy of reaction)
- $\Delta_r G^\ominus = \sum_J \nu_J \Delta_f G^\ominus (J)$ (standard free energies of formation)
- the connection to the equilibrium constant K :
 $\Delta_r G^\ominus = -RT \ln K$

∞ electrochemical measurements: $\Delta_r G^\ominus = -zFE^\ominus$

∞ These are of course reciprocal conversions. 18

VII. Determination of the equilibrium constant

What does the value of ΔG° depend on?

ΔG°	=	ΔH°	-	$T\Delta S^\circ$	
-		-		+	spontaneous
+ or -		-		-	T-dependent
+ or -		+		+	T-dependent
+		+		-	non-spontaneous

- ∞ ΔH° : reflects the change in bonding
- ∞ ΔS° : reflects the change in order (increase in T important!)
- ∞ It is possible to couple reactions, an exergonic process may „drive“ an endergonic reaction (e.g. the hydrolysis of ATP can drive the biosynthesis of proteins).

Summary

- ∞ The spontaneous direction of processes:
 - G increases,
 - μ_i chemical potentials converge to the same values,
 - some μ_i 's decrease, others increase!
 - if $\mu_A > \mu_B$, then the reaction proceeds $A \rightarrow B$ and *vice versa*.
 - The system always moves toward equilibrium.
- ∞ Quantification (equilibrium composition):
 - Minimum of G : where the slope of the $G = f(\xi)$ function is 0: $(\partial G / \partial \xi)_{p,T} = 0$
 - where the μ_j chemical potentials are the same: $\mu_A = \mu_B$
 - no macroscopic change in equilibrium.

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Summary:

ΔG°	=	ΔH°	-	$T\Delta S^\circ$	
-		-		+	spontaneous
+ or -		-		-	T-dependent
+ or -		+		+	T-dependent
+		+		-	non-spontaneous

- ∞ **Thermodynamics: exergonic** processes, i.e. those with a decrease in free energy ($\Delta_r G < 0$) are spontaneous. *Exact!*
- ∞ The thermodynamic classification of reactions:
 - $\Delta_r G < 0$: exergonic;
 - $\Delta_r G > 0$: endergonic.

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Summary:

- ∞ The thermodynamic equilibrium is primarily characterized by the maximum of S entropy. The K equilibrium constants (and the equilibrium composition) can be described by the $\Delta_r G$ Gibbs free energy, that is, by the μ chemical potential.
- ∞ Three remarks:
 - The system (or the reaction) can only proceed until equilibrium is established, cannot go further (it is NOT like a pendulum!). [Chemical oscillation always occurs far from equilibrium.]
 - According to formal thermodynamics, there is no more change in equilibrium, which means that no macroscopic changes are detectable.
 - In reality, equilibrium is dynamic: the forward and reverse reactions do not stop, but their rates are identical. This can be proved experimentally, e.g. by isotopic labelling!

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Influence of external conditions on the chemical equilibrium

- I. The dynamic nature of equilibrium. Le Chatelier's principle.
- II. The influence of **pressure change** on the equilibrium constant and equilibrium composition.
- III. The influence of **temperature change** on the equilibrium constant and equilibrium composition (van't Hoff equation).
- IV. The influence of the **addition or removal of a reactant or product** on the equilibrium composition.
- V. Practical applications.

I. The dynamic nature of equilibrium. Le Chatelier's principle.

- ∞ The effect of three important intensive variables (p, T, x_j)...
 - on the value of the equilibrium constant K
 - on the equilibrium composition).
- ∞ A preliminary summary:
 - a) Pressure p does not influence K , $(\partial K / \partial p)_T = 0$, but may influence the composition (if $\sum \nu \neq 0$).
 - b) Temperature T : influences both!
 - c) Addition or removal of a substance: only influences the equilibrium composition, never the value of K .

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I. The dynamic nature of equilibrium. Le Chatelier's principle.

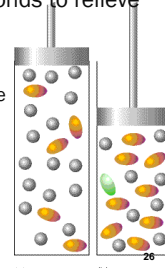
General experience:

- ∞ Equilibrium can be reached from both directions (reactant and product).
- ∞ A change in p , T and x_j may move the equilibrium compositions in both directions
- ∞ It can be returned to the original state.
- ∞ A system in macroscopic equilibrium seems unchanged but involves continuous forward and reverse reactions on the molecular level. The rate of these processes is measurable (see later in reaction kinetics).

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I. The dynamic nature of equilibrium. Le Chatelier's principle.

- ∞ **Le Chatelier' principle:** the response of the system to external stress.
- ∞ A system in equilibrium always responds to relieve the external stress.
 - An increase in (external) pressure is relieved by a decrease of internal pressure (decrease in number of moles).
 - An increase in (external) temperature is relieved by a decrease in internal temperature (endothermic direction).
 - The addition of a substance is relieved by its consumption.



III. Influence of pressure change on the equilibrium constant and the equilibrium composition

- ∞ In gas reactions, equilibrium constant K does not depend on pressure p as $\Delta_r G^\ominus$ is pressure-independent (actually defined at a standard pressure): $(\partial K / \partial p)_T = 0$
- ∞ The equilibrium composition is changed by a pressure change following **Le Chatelier's principle** – if the gas reaction involves a change in volume...

∞ **Solution reactions have a special situation:**

$$\left(\frac{\partial \ln K}{\partial p} \right)_T = \frac{-\Delta_r V^\ominus}{RT}$$

- $\Delta_r V^\ominus$ is the standard molar volume change for the reaction.

III. Influence of pressure change on the equilibrium constant and the equilibrium composition

- ∞ In gas reactions, a pressure increase causes a decrease in the number of moles following **Le-Chatelier's principle**.
 - Reaction: $A \rightleftharpoons 2B$
 - In the beginning $n_A = n$, $n_B = 0$
 - At α conversion in equilibrium: $n_A = (1-\alpha)n$, $n_B = 2\alpha n$.
- ∞ Connection between equilibrium mole fractions and K :

$$x_A = \frac{(1-\alpha)n}{(1-\alpha)n + 2\alpha n} = \frac{1-\alpha}{1+\alpha} \quad \text{and} \quad x_B = \frac{2\alpha}{1+\alpha}$$
- ∞ Consequence: $K = \frac{p_B^2}{p_A} = \frac{x_B^2 p^2}{x_A p} = \frac{4\alpha^2 p}{1-\alpha^2}$ and $\alpha = \frac{1}{(1+4p/K)^{1/2}}$
- ∞ so K does not depend on the pressure, but α does! ⁸⁸

III. Influence of pressure change on the equilibrium constant and the equilibrium composition

The influence of p in general:

$$\begin{aligned} \text{∞ In earlier considerations, } K_p &= \prod_j \left(\frac{p_j}{p^\ominus} \right)^{\nu_j} \\ \text{∞ and } p_j &= x_j p, \\ \text{∞ so: } K_p &= \prod_j \left(\frac{x_j p}{p^\ominus} \right)^{\nu_j} = \prod_j x_j^{\nu_j} \left(\frac{p}{p^\ominus} \right)^{\sum \nu_j} = K_x \left(\frac{p}{p^\ominus} \right)^{\sum \nu_j} \end{aligned}$$

∞ As K_p is independent of p , K_x and ν are in a reverse connection:

- if $\sum \nu > 0$, an increase in p causes the decrease of K_x and the formation of more reactants,
- if $\sum \nu = 0$, then $K_x = K_p$, so the equilibrium composition is independent of pressure,
- if $\sum \nu < 0$, an increase in p causes the increase of K_x and the formation of more products.

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III. Influence of temperature on the equilibrium constant and the equilibrium composition

- ∞ Qualitatively (Le Chatelier's principle): an increase in T shifts the system in the endothermic direction (and vice versa).
 - Endothermic reaction: increase in $T \rightarrow$ more products
 - Exothermic reactions: increase in $T \rightarrow$ more reactants
- ∞ Influence of T on the equilibrium:
 - the value of K changes
 - therefore, the equilibrium composition also changes.
- ∞ Quantitative relationship: **van't Hoff equation**.

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III. Influence of temperature on the equilibrium constant and the equilibrium composition

∞ The derivation of the **van't Hoff equation**:

- earlier: $\ln K = \frac{-\Delta_r G^\ominus}{RT}$
- differentiation with respect to T and using the Gibbs-Helmholtz equation:

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d}{dT} \left(\frac{\Delta_r G^\ominus}{T} \right) = -\frac{1}{R} \left(\frac{-\Delta_r H^\ominus}{T^2} \right) = \frac{\Delta_r H^\ominus}{RT^2}$$

∞ The endothermic/exothermic contrast is better seen in a different form:

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^\ominus}{R}$$

∞ The van't Hoff equation is analogous to the Clausius-Clapeyron equation: both describe equilibria!

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III. Influence of temperature on the equilibrium constant and the equilibrium composition

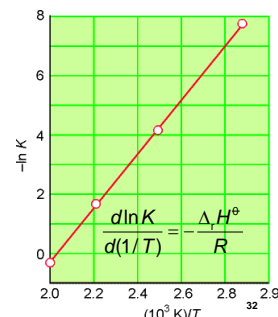
∞ Determination of $\Delta_r H^\ominus$ by integration:

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

- Condition: $\Delta_r H^\ominus$ should be (roughly) constant in the $T_2 - T_1$ range applied.

∞ Measurements are usually made at more than two temperatures and K is obtained from a graph:

- Graph: + or - slope; $\Delta_r H^\ominus$ can be calculated!



IV. Influence of substance addition or removal on the equilibrium

∞ A change in the x_j concentration of reactants or products only influences the equilibrium composition, but not the value of K .

∞ **Le Chatelier's principle** (K remains unchanged):

- addition of more reactants will result in the formation of more product and *vice versa*,
- removal of the product will result in the formation of more product from the reactant and *vice versa*.

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V. Practical applications

∞ The equilibrium can be shifted in a desired direction:

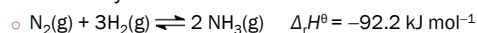
- by a suitable change in T and p ;
- adding the reactant,
- removing the desired product e.g. gas removal, precipitation, product extraction etc.,
- complexing the desired product by an excess of suitable complexing agent: „masking“.

∞ Important: **A catalyst does not influence the equilibrium composition, only the time necessary to reach it.**

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V. Practical applications

∞ Ammonia synthesis:



∞ Ammonia formation is favored by:

- **high pressure** \equiv **high initial concentrations** of N_2 and H_2 ,
- **low temperature**.

∞ **Problem:** at low temperature, the rate of the reaction is also low (kinetics!), so the reaction takes too long.

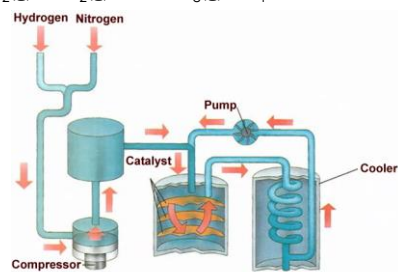
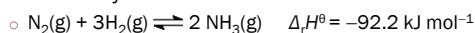
∞ **INDUSTRIAL PROCESS:** moderately high temperature (450 °C) and **very high pressure (250 bar)**

- compromise that ensures reasonable conversion and reaction time at the same time.

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V. Practical applications

∞ Ammonia synthesis:



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