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

I. Equilibrium in chemical reactions — concepts and conditions

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

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I. Equilibrium in chemical reactions — concepts and conditions

- The „<u>direction</u>": 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 <u>extent of reaction</u> is important.
- Two approaches (two different levels) used:
  - **macroscopic**: $0 < \xi < 1$ 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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I. Equilibrium in chemical reactions — concepts and conditions

- ξ = 0 at the beginning of the reaction, only the reactants are present
- ξ = 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 v_j coefficient.
  - $d\xi = dn_j/v_j$
  - for reactant A, $v_j < 0$, so ξ decreases: $dn_A/v_A = -d\xi$,
  - for product B, $v_j > 0$, so ξ increases: $dn_B/v_B = +d\xi$.

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II. Equilibrium constant

- Based on the measurement of equilibrium concentrations in numerous systems (Guldberg and Waage, 1863):
- The stoichiometry of the process: $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

$$K = \frac{[\text{C}]^c_{\text{equilibrium}}[\text{D}]^d_{\text{equilibrium}}}{[\text{A}]^a_{\text{equilibrium}}[\text{B}]^b_{\text{equilibrium}}} \qquad K = \frac{[\text{C}]^{v_C}_e[\text{D}]^{v_D}_e}{[\text{A}]^{v_A}_e[\text{B}]^{v_B}_e} \text{ (in general)}$$

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

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II. 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.

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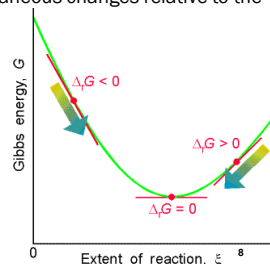
IV. The connection between standard reaction Gibbs energy and chemical potentials

- $\Delta_r G$: 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:

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

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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: $K_p = \dfrac{p_{B,\,equilibrium}}{p_{A,\,equilibrium}}$
- **Thermodynamic** description:
  - $\Delta_r G = \mu_B - \mu_A =$
  $= \left(\mu_B^{\ominus} + RT \ln \dfrac{p_B}{p^{\ominus}}\right) - \left(\mu_A^{\ominus} + RT \ln \dfrac{p_A}{p^{\ominus}}\right) =$
  $= \Delta_r G^{\ominus} + RT \ln \dfrac{p_B}{p_A}$
  - $\Delta_r G^{\ominus} = \mu_B^{\ominus} - \mu_A^{\ominus}$ (the difference in standard chemical potentials)
  - Let $p_B/p_A = Q_p$ called reaction quotient:
  $\boxed{\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q_p}$

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

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

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

  - 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: $v_A A + v_B B \rightleftharpoons v_C C + v_D D$
- after $d\xi$ change: $dn_A = v_A d\xi \ldots dn_C = v_C d\xi$
  in general: $dn_J = v_J d\xi$
- Change in G: $dG = \left(\sum_J v_J \mu_J\right) d\xi$
- The reaction Gibbs energy is the slope of $G = f(\xi)$:

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \sum_J \mu_J v_J$$

- As $\mu_J = \mu_J^{\ominus} + RT \ln a_J$, where $a_J = f_J/p^{\ominus}$, so
$\boxed{\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q}$, where $\Delta_r G^{\ominus} = \sum_J v_J \mu_J^{\ominus}$

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

- The reaction quotients Q in equilibrium: $Q = \dfrac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}} = \prod_J a_J^{\nu_J}$

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

$$K = Q_{equilibrium} = \left(\frac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}}\right)_{equilibrium} = \prod_J \left(a_J^{\nu_J}\right)_{I,s}$$

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

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

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VI. Other expressions for the equilibrium constant

- In gas phase (fugacity or pressure): $K = \prod_J \left(\dfrac{f_J}{p^\theta}\right)^{\nu_J}$

  - For an ideal gas: $K_p = \prod_J \left(\dfrac{p_J}{p^\theta}\right)^{\nu_J}$

- Based on molality (or mole fractions):

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

  - γ can be determined with „iteration".

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VI. Other expressions for the equilibrium constant

A commonly used formalism:
- degree of dissociation: $0 < \alpha < 1$
- $HA \rightleftharpoons H^+ + A^-$
- In equilibrium $[H^+]_e = [A^-]_e = \alpha c$ and $[HA]_e = (1-\alpha)c$, so:

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

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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		ΔG^θ (kJ/mol)
$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$	6.8×10^5	-33.2
$0{,}5N_2 + 1{,}5H_2 \rightleftharpoons NH_3$	$K' = \dfrac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$	8.2×10^2	-16.6
$NH_3 \rightleftharpoons 0{,}5N_2 + 1{,}5H_2$	$\bar{K}' = \dfrac{[N_2]^{1/2}[H_2]^{3/2}}{[NH_3]}$	1.2×10^{-3}	$+16.6$
$2NH_3 \rightleftharpoons N_2 + 3N_2$	$\bar{K} = \dfrac{[N_2][H_2]^3}{[NH_3]^2}$	1.5×10^{-6}	$+33.2$

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VII. Determination of the equilibrium constant

- Experimental measurement of equilibrium concentrations
  - without disturbing the equilibrium:
    a) quenching the reaction mixture,
    b) 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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VII. Determination of the equilibrium constant

Calculating K and/or $\Delta_r G^\theta$ and/or E^θ:
- from thermodynamic data ($\Delta_r H^\theta$ and $\Delta_r S^\theta$):
  - $\Delta_r G^\theta = \Delta_r H^\theta - T \Delta_r S^\theta$ (standard enthalpy and entropy of reaction)
  - $\Delta_r G^\theta = \sum_J \nu_J \Delta_r G^\theta (J)$ (standard free energies of formation)
  - the connection to the equilibrium constant K:
    $\Delta_r G^\theta = -RT \ln K$
- electrochemical measurements: $\Delta_r G^\theta = -zFE^\theta$
- These are of course reciprocal conversions.

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Ⅶ. Determination of the equilibrium constant

What does the value of ΔG^θ depend on?

ΔG^θ =	ΔH^θ –	$T\Delta S^\theta$	
–	–	+	spontaneous
+ or –	–	–	T-dependent
+ or –	+	+	T-dependent
+	+	–	non-spontaneous

- ✍ ΔH^θ: reflects the change in bonding
- ✍ ΔS^θ: 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 <u>direction</u> of processes:
  - o G increases,
  - o 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 → B and *vice versa*.
  - o The system always moves toward equilibrium.
- ✍ <u>Quantification</u> (equilibrium composition):
  - o Minimum of G: where the slope of the $G = f(\xi)$ function is 0: $\left(\partial G / \partial \xi\right)_{p,T} = 0$
  - o where the μ_J chemical potentials are the same: $\mu_A = \mu_B$
  - o no macroscopic change in equilibrium.

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Summary:

ΔG^θ =	ΔH^θ –	$T\Delta S^\theta$	
–	–	+	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:
  - o $\Delta_r G < 0$: exergonic;
  - o $\Delta_r G > 0$: 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:
  - o 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.]
  - o According to formal thermodynamics, there is no more change in equilibrium, which means that no macroscopic changes are detectable.
  - o In reality, equilibrium is <u>dynamic</u>: the forward ad 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 <u>addition or removal of a reactant or product</u> 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)...
  - o on the value of the equilibrium constant K
  - o 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 $\Sigma\nu \neq 0$).
  - 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.

  o An increase in (external) pressure is relieved by a decrease of internal pressure (decrease in number of moles).
  o An increase in (external) temperature is relieved by a decrease in internal temperature (endothermic direction).
  o The addition of a substance is relieved by its consumption.
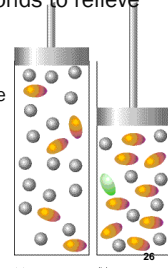
(a)   (b)   26

II. 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 $\Delta_r G^\theta$ 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:**

  o $\left(\dfrac{\partial \ln K}{\partial p}\right)_T = \dfrac{-\Delta_r V^\theta}{RT}$

  o $\Delta_r V^\theta$ is the standard molar volume change for the reaction.

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

- **In gas reaction**s, a pressure increase causes a decrease in the number of moles following Le-Chatelier's principle.

  o Reaction: $A \rightleftharpoons 2B$
  o In the beginning $n_A = n$, $n_B = 0$
  o At α conversion in equilibrium: $n_A = (1-\alpha)n$, $n_B = 2\alpha n$.

- Connection between equilibrium mole fractions and K:

  $x_A = \dfrac{(1-\alpha)n}{(1-\alpha)n + 2\alpha n} = \dfrac{1-\alpha}{1+\alpha}$ and $x_B = \dfrac{2\alpha}{1+\alpha}$

- Consequence: $K = \dfrac{p_B^2}{p_A} = \dfrac{x_B^2 p^2}{x_A p} = \dfrac{4\alpha^2 p}{1-\alpha^2}$ and $\alpha = \dfrac{1}{(1+4p/K)^{1/2}}$
- so K does not depend on the pressure, but α does! 28

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

The influence of p in general:
- In earlier considerations, $K_p = \prod_J \left(\dfrac{p_J}{p^\theta}\right)^{\nu_J}$
- and $p_J = x_J\, p$,

- so: $K_p = \prod_J \left(\dfrac{x_J p}{p^\theta}\right)^{\nu_J} = \prod_J x_J^{\nu_J} \left(\dfrac{p}{p^\theta}\right)^{\Sigma\nu} = K_x \left(\dfrac{p}{p^\theta}\right)^{\Sigma\nu}$

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

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

  o Endothermic reaction: increase in $T \rightarrow$ more products
  o 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

- ꙮ The derivation of the van't Hoff equation:
  - ○ earlier: $\ln K = \dfrac{-\Delta_r G^{\ominus}}{RT}$
  - ○ differentiation with respect to T and using the Gibbs–Helmholtz equation:

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

- ꙮ The endothermic/exothermic contrast is better seen in a different form:
  $$\frac{d\ln K}{d(1/T)} = -\frac{\Delta_r H^{\ominus}}{R}$$

- ꙮ *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
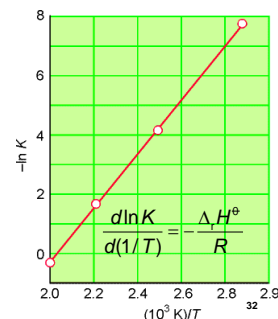
- ꙮ *Determination of $\Delta_r H^{\ominus}$ by integration:*

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

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

- ꙮ 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!

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

(axes: $-\ln K$ vs $(10^3\,K)/T$, values 2.0 2.2 2.4 2.6 2.8 2.9)

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IV. Influence of substance addition or removal on the equilibrium

- ꙮ A change in the x_J concentration of reactants or products only <u>influences the equilibrium composition</u>, but <u>not the value of K</u>.
- ꙮ 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 form the reactant and *vice versa*.

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V. Practical applications

- ꙮ 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".

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

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V. Practical applications
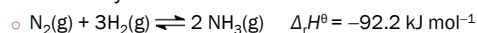
- ꙮ Ammonia synthesis:
  - ○ $N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$ $\Delta_r H^{\ominus} = -92.2$ kJ mol^{-1}
- ꙮ Ammonia formation is favored by:
  - ○ high pressure ≡ high initial concentrations of N_2 and H_2,
  - ○ low temperature.
- ꙮ **Problem**: at low temperature, the rate of the reaction is also low (kinetics!), so the reaction takes too long.
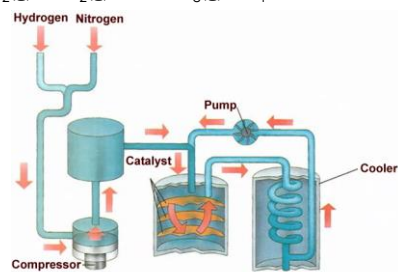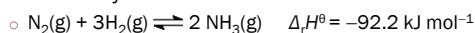- ꙮ INDUSTRIAL PROCESS: moderately high temperature (450 °C) and very high pressure (250 bar)
  - ○ compromise that ensures reasonable conversion and reaction time at the same time.

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V. Practical applications

- ꙮ Ammonia synthesis:
  - ○ $N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$ $\Delta_r H^{\ominus} = -92.2$ kJ mol^{-1}

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