

# 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

# I. Equilibrium in chemical reactions – concepts and conditions

- ∞ Application of thermodynamics for chemical changes (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: reaction kinetics and reaction mechanism.

# I. 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.
  - $0 < \xi < 1$       small Greek **Xi** letter

# I. Equilibrium in chemical reactions — concepts and conditions

- $\xi = 0$  at the beginning of the reaction, only the reactants are present
- $\xi = 1$  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  $\nu_j$  coefficient.

# III. Equilibrium constant

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

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

Obviously:

- if the value of  $K$  is large, the equilibrium is shifted to the right, the conversion is high,  $\xi$  is close to one 1,
- if the value of  $K$  is small, the equilibrium is shifted to the left, the conversion is low,  $\xi$  is close to 0.

# 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.

# III. The concept of reaction Gibbs energy

∞ Simple example reaction:  $A \rightleftharpoons B$  (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.

# III. The concept of reaction Gibbs energy

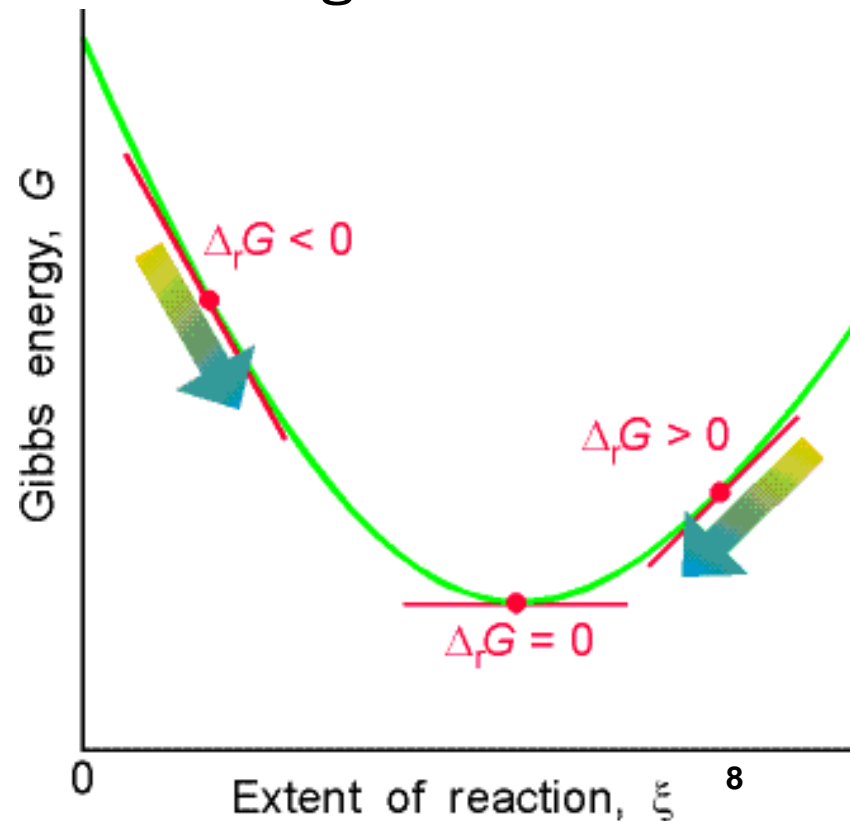
☞ Thermodynamics (universal experience):

- $G$  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:*

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

## ∞ $\Delta_r G^\theta$ : 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**:

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

# 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:

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

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

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

∞  $\Delta_r G = \Delta_r G^\theta + RT \ln Q_p$  equation in equilibrium:

- If  $\Delta_r G = 0$ ,  $Q_p$  is identical to the equilibrium constant  $K_p$ :

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

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

# VI. Other expressions for the equilibrium constant

∞ In gas phase (fugacity or pressure):

$$K = \prod_J \left( \frac{f_J}{p^\ominus} \right)^{\nu_J}$$

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

∞ Based on molality (or mole fractions) :

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

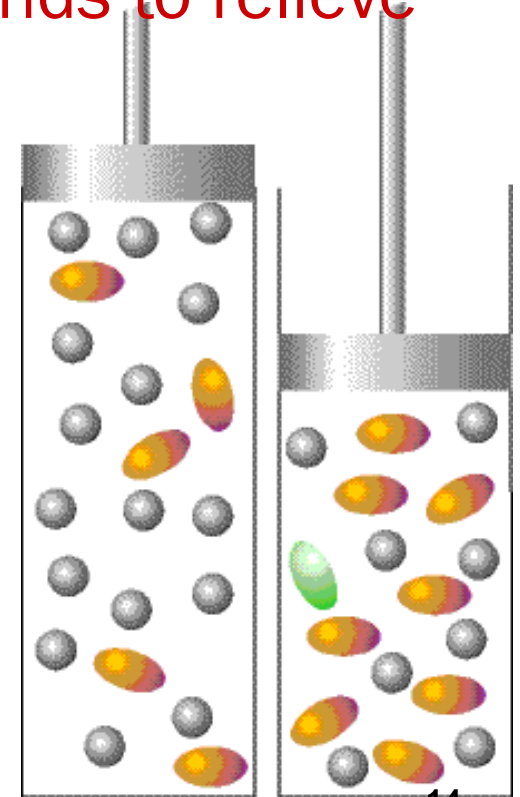
# Influence of external conditions on the chemical equilibrium

- 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.
- VI. Equilibria in biological systems.

# 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.



(a)

(b)

# 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...

# 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.**



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

∞ The van't Hoff equation:

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

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

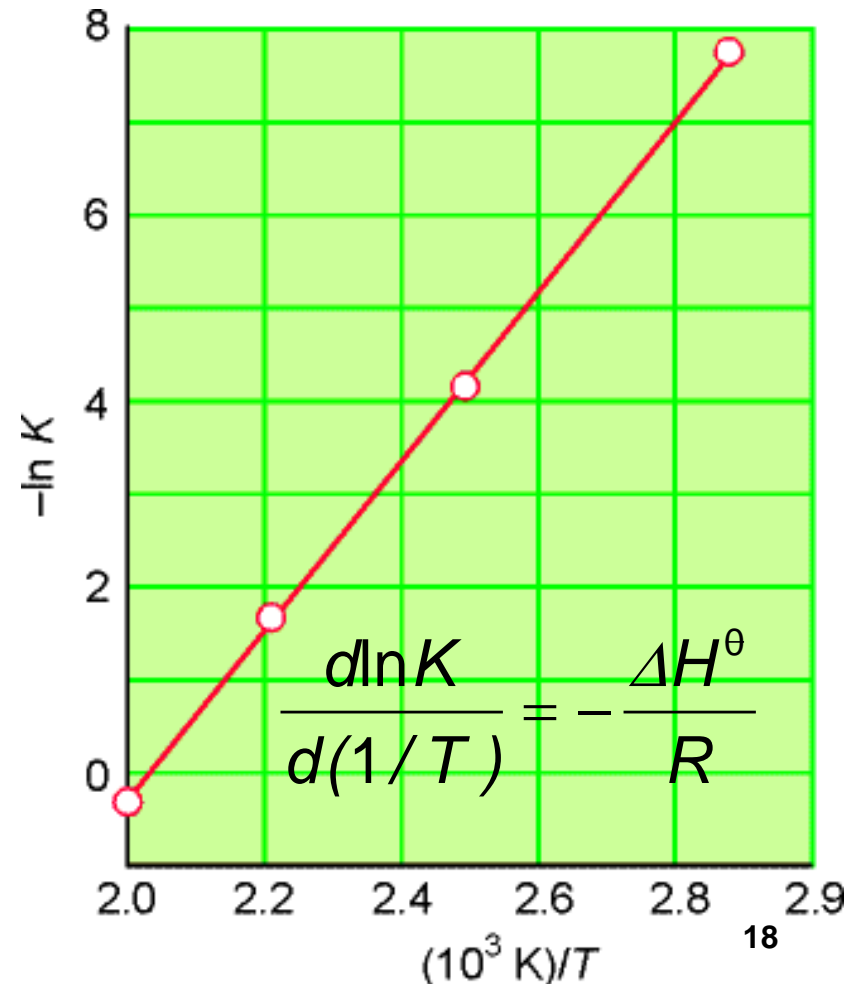
# III. Influence of temperature on the equilibrium constant and the equilibrium composition

∞ Determination  $\Delta H^\theta$  by integration:

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

- Condition:  $\Delta H^\theta$  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:



# IV. Influence of substance addition or removal on the equilibrium

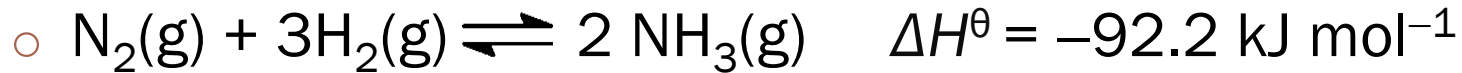
- ∞ A change in the  $x_j$  concentration of reactants or products only influences the equilibrium composition, but not the value of  $K$ .
- ∞ **Le Chatelier's principle** ( $K$  remains unchanged):
  - addition of more reactants will result in the formation of more product and vice versa,
  - removal of the product will result in the formation of more product from the reactant and vice versa.

# 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.

# V. Practical applications

∞ Ammonia synthesis:



∞ Ammonia formation is favored by:

- high pressure  $\equiv$  high initial concentrations of  $\text{N}_2$  and  $\text{H}_2$ ,
- low temperature.

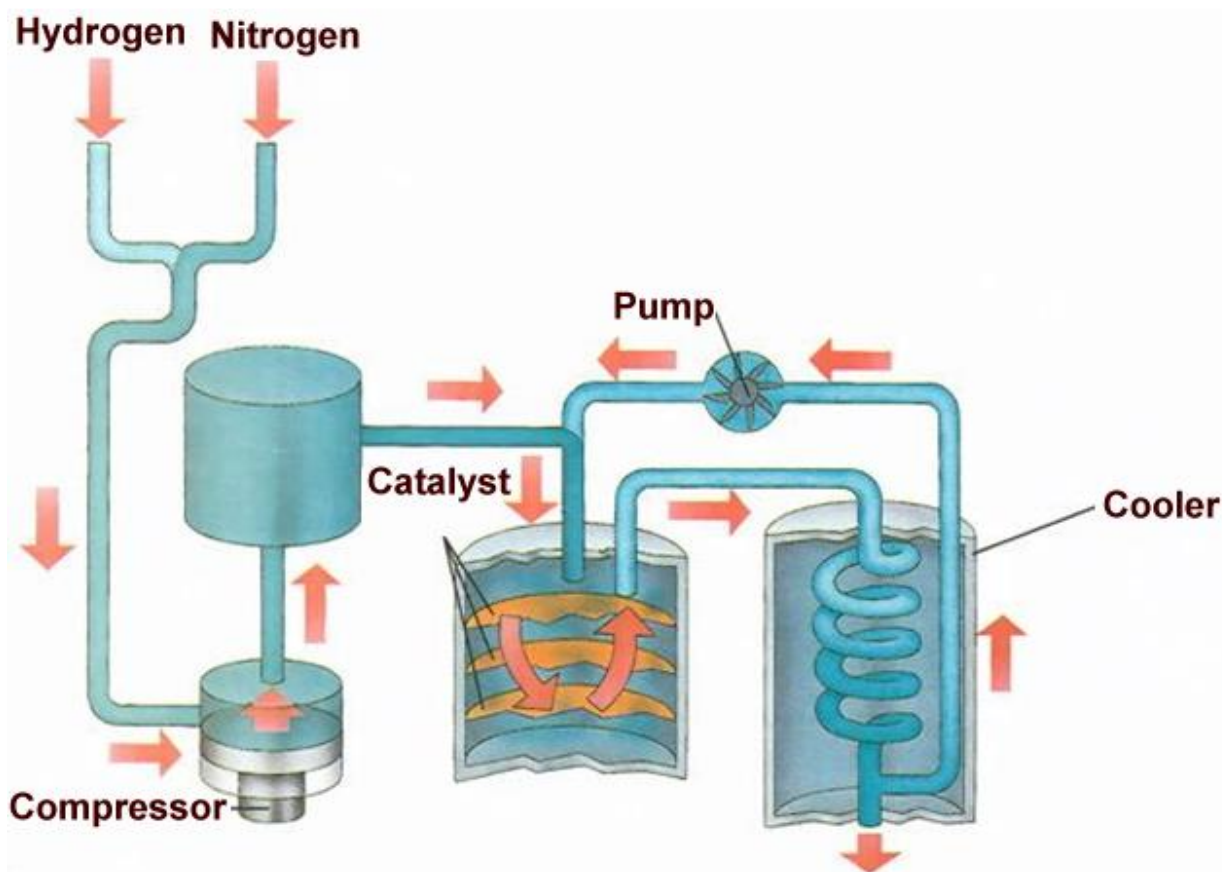
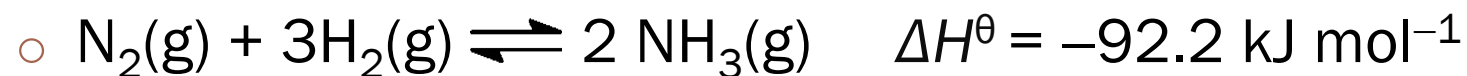
∞ **Problem:** at low temperature, the rate of the reaction is also low (kinetics!), so the reaction takes too long.

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

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

# V. Practical applications

## ∞ Ammonia synthesis:



# VI. Equilibria in biological systems – the thermodynamics of ATP

- Living systems are powered by energy in food. Part of this energy is used as it is produced, but some of them is stored for later use.
- A complicated mechanism works in which there are energy storing and energy utilizing steps.
- Important: energy stored in exergonic reaction my drive other, endergonic processes.
- It is practicable to use a **biological standard state**.

# VI. Equilibria in biological systems – the thermodynamics of ATP

∞ **Biological standard state:** pH = 7

- $a_{\text{H}^+} = 1$  (pH = 0) would be too acidic.
- Designation:  $^0$

∞ Example:  $A + v \text{H}^+(\text{aq}) \rightarrow P$

$$\Delta_r G = \mu_P - \mu_A - v \mu_{\text{H}^+}$$

∞ After some derivations:

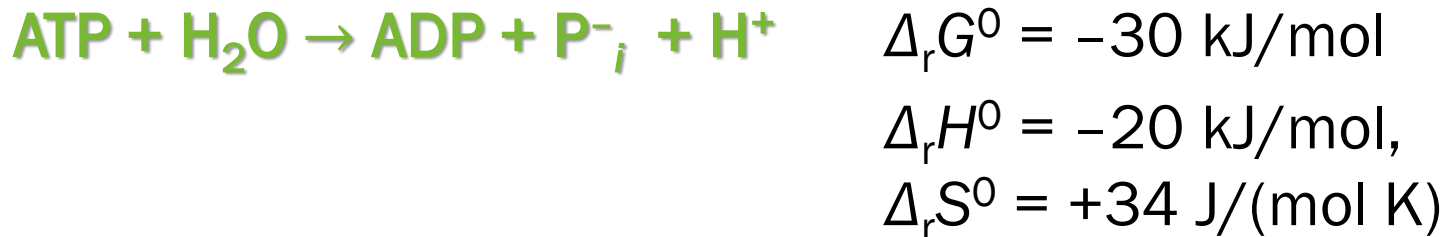
$$\Delta_r G^0 = \Delta_r G^\theta + 7 \cdot v R T \ln 10$$

- (The two standard  $\Delta_r G$  values are only different if  $\text{H}^+$  participates in the process.)



# VI. Equilibria in biological systems – the thermodynamics of ATP

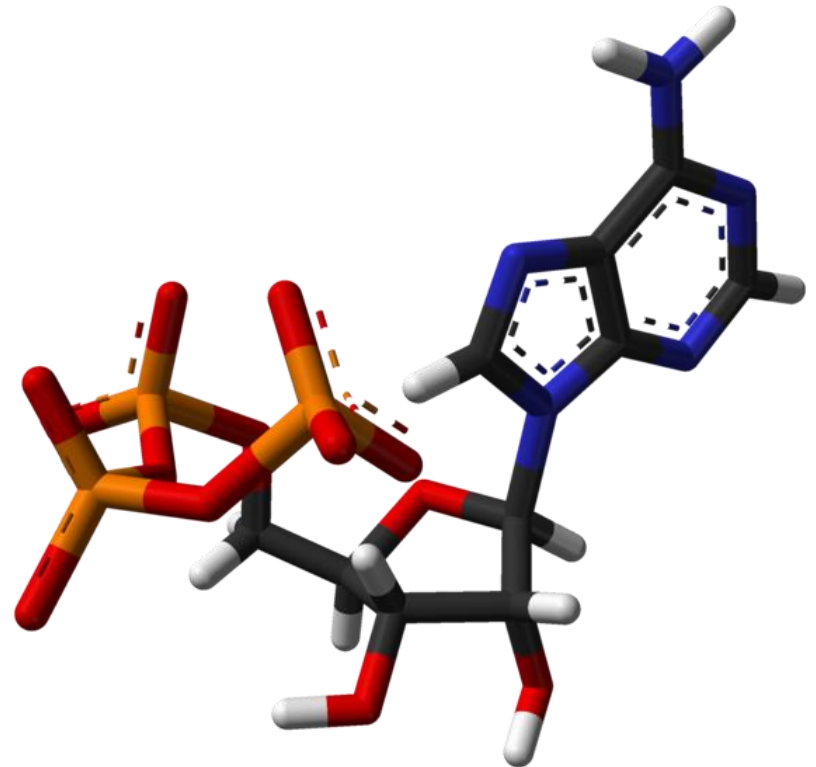
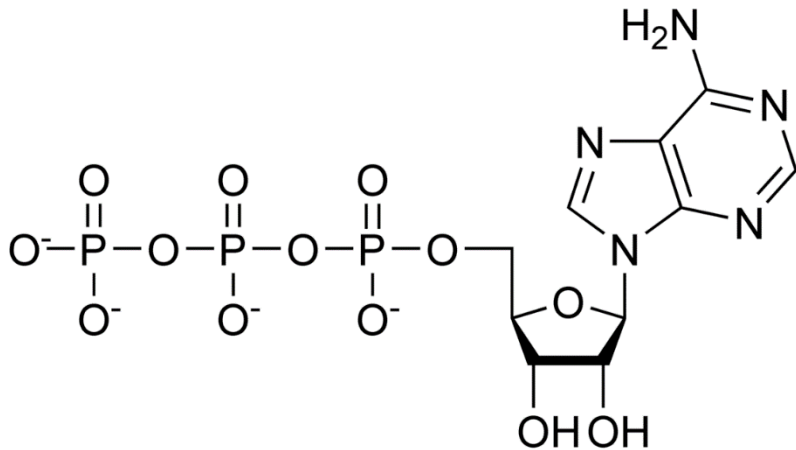
- ∞ **Endergonic reactions:** do not proceed spontaneously (protein biosynthesis, muscle contractions, vision etc.)
- ∞ **Exergonic reactions:** energy is stored in adenosine triphosphate (ATP) molecules. Its hydrolysis is exergonic and can drive other, endergonic reactions.



- Where does the energy of ATP (hydrolyzable phosphate ester bonds) come from? Its origin is the oxidation (burning) of food (carbohydrate, fat) in complicated, coupled processes.

# VI. Equilibria in biological systems – the thermodynamics of ATP

- ATP (adenosine-5'-triphosphate): the common unit of energy transfer in biological systems



# VI. Equilibria in biological systems – the thermodynamics of ATP

## Anaerobic cell metabolism (in the absence of oxygen).

∞ Insufficient O<sub>2</sub> (at birth; long-distance running):



∞ Source of energy: partial oxidation of glucose to lactate.

∞ Exergonic process:  $\Delta_r G^0 = -218$  kJ/mol.

∞ Two molecules of ADP converted to ATP:  $2 \times (+30)$ .

∞  $\Delta_r G^0 = -218 + 2 \times 30 = -158$  kJ/mol is available.

- Food is both a source of direct energy and energy stored for later use by ADP → ATP transformation.
- Poor efficiency. [*Aerobic respiration is better, the burning of glucose in total oxidation yields -2880 kJ/mol.*]

# VI. Equilibria in biological systems – the thermodynamics of ATP

## Aerobic cell metabolism (with oxygen).

∞ Energy source: the total oxidation of glucose to carbon dioxide and water:  $\Delta_r G^0 = -2880$  kJ/mol ( $\text{CO}_2$  is exhaled)

∞ Schematically (as the mechanism is very complicated):



∞ For 38 ATP,  $38 \times 30 = 1140$  kJ needed. Available 1740 kJ!

- To produce sucrose from glucose and fructose ( $\Delta_r G^0 = 23$  kJ/mol), one molecule of ATP ( $-30$  kJ) is sufficient.
- For protein synthesis, a lot of ATP is needed: a single peptide bond is  $\Delta_r G^0 = 17$  kJ/mol endergonic, but its indirect biosynthesis needs 3 molecules of ATP. In myoglobin (relatively small protein)  $\sim 150$  peptide bonds require 450 molecules of ATP, i.e. 12 molecules of glucose in aerobic oxidation.