



**MEDICAL UNIVERSITY – PLEVEN
FACULTY OF PHARMACY**

**DIVISION OF PHYSICS AND BIOPHYSICS, HIGHER
MATHEMATICS AND INFORMATION TECHNOLOGIES**

LECTURE No5

THERMODYNAMIC POTENTIALS

*Internal energy . Entalpy. Helmholtz free energy.
Gibbs free energy. Chemical and electrochemical
potentials*

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Thermodynamic potentials

$-TS$



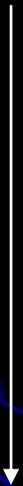
U

Internal energy

F

Helmholz free energy

$+PV$



H

Enthalpy

G

Gibbs free energy

$$U=f(S, V)$$

$$H=f(S, P)$$

$$F=f(T, V)$$

$$G=f(T, P)$$



When considering different types of processes, we will be interested in two main issues:

- What determines the **stability** of a system and how the system evolves towards an equilibrium?
- How much **work** can be extracted from a system?

There exist energetic quantities, called thermodynamic potentials - the quantitative measure of the stored energy in the system.

Potentials are used to measure energy changes in systems as they evolve from an initial state to a final state.

- The potential used depends on the constraints of the system, such as constant temperature or pressure.

E.g. Helmholtz free energy is the energy available for doing useful work at fixed temperature.

- Thermodynamics is the study of the energy, principally heat energy, that accompanies chemical or physical changes.
- Some chemical reactions release heat energy; they are called **exothermic reactions**, and they have a negative enthalpy change. Others absorb heat energy and are called **endothermic reactions**, and they have a positive enthalpy change.
- But thermodynamics is concerned with more than just heat energy. The change in level of organization or disorganization of reactants and products as changes take place is described by the **entropy change of the process**. E.g., the conversion of 1 g of water to gas is in the direction of increasing disorder, which is described as an increase in entropy, $dS > 0$.

- **Experimental discovery** - almost all chemical reactions either absorb or release heat. Consequently, the *heat of a reaction* is the difference in the heat contents of the products and reactants:
- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
- The equation states that the change in enthalpy during a reaction equals the enthalpy of the products minus the enthalpy of the reactants. **You can consider enthalpy to be chemical energy that is commonly manifested as heat.**
- Use the decomposition of ammonium nitrate as an example of an enthalpy calculation.
- $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$

Table 1. Enthalpies of Compounds	
Compound	H [kJ/mol]
NH ₄ NO ₃ (s)	-366
N ₂ O (g)	82
H ₂ O (g)	-242

- The overall enthalpy of the reaction is $\Delta H = -36$ kJ, which means that the decomposition of 1 mole of ammonium nitrate releases 36 kJ of heat.

Table 2. Enthalpy and Heat Flow		
Sign of ΔH	Type of Reaction	Heat
Negative	Exothermic	Released
Positive	Endothermic	Absorbed

- If you reverse the previous reaction, the sign of the enthalpy of the reaction is reversed: $\Delta H = +36 \text{ kJ}$
- The reversed reaction is, therefore, endothermic. It would require the addition of 36 kcal of energy in order to cause the nitrous oxide and water vapor to react to form 1 mole of ammonium nitrate.
- The values at 25°C and 1 atm are called *standard enthalpies*.

● For elements, the standard enthalpy is defined as 0.

- For compounds, the values are called standard enthalpies of formation because the compounds are considered to be formed from elements in their standard state.

Table 3. Standard Enthalpies of Formation [kJ/mol]

Compound	ΔH_f°	Compound	ΔH_f°
Al (s)	0	MgCl ₂ (s)	-642
AlCl ₃ (s)	-704	MgO (s)	-602
Al ₂ O ₃ (s)	-1676	Mg(OH) ₂ (s)	-925
CCl ₄ (g)	-103	N ₂ (g)	0
CCl ₄ (l)	-140	NH ₃ (g)	-46
CO (g)	-111	NO (g)	90
CO ₂ (g)	-394	N ₂ O (g)	82
CaF ₂ (s)	-1220	O ₂ (g)	0
CaO (s)	-635	O ₃ (g)	143
Ca(OH) ₂ (s)	-987	S (s)	0
HCl (g)	-92	SO ₂ (g)	-297
H ₂ O (g)	-242	SO ₃ (g)	-396
H ₂ O (l)	-286	ZnCl ₂ (s)	-415
H ₂ S (g)	-21	ZnO (s)	-348

- Whether a chemical reaction or physical change will occur depends on both the **enthalpy** and **entropy** of the process.
- Both terms are combined in the **Gibbs free energy** - the third and most important thermodynamic term.
- If the change in free energy is negative, the reaction will proceed to the right; this reaction is called a **spontaneous reaction**. If the sign is positive, the reaction will not proceed as written; this reaction is **nonspontaneous**.
- A powerful prediction as to whether a reaction will or will not take place can be made using tabulated data to calculate the change in Gibbs free energy.

Living cells and organisms **must perform work** to stay alive, to grow, and to reproduce themselves.

The ability to harness energy from a variety of metabolic pathways so to channel it into biological work is a fundamental property of all living organisms.

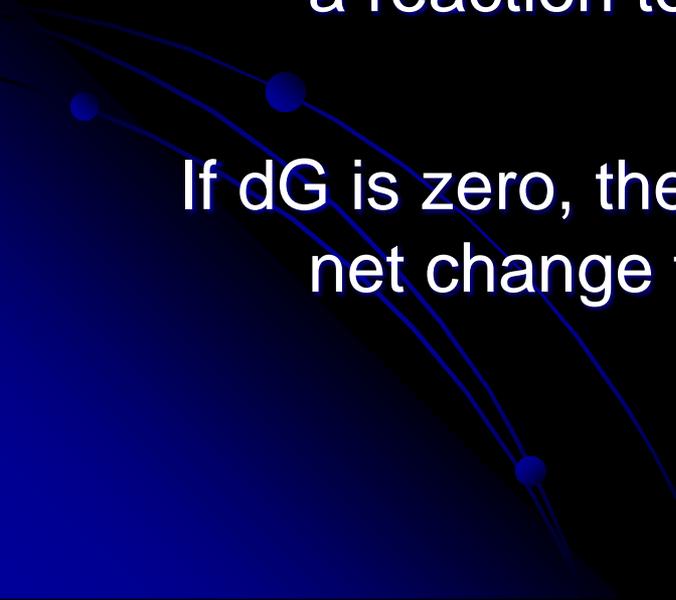
Thermodynamically, the amount of energy capable of doing work during a chemical reaction is measured quantitatively by the change in the Gibbs free energy.

If dG is negative in sign, the reaction proceeds **spontaneously** with loss of free energy, i.e. it is **exergonic**. If, in addition, dG is of a great magnitude, the reaction goes virtually to completion and is essentially irreversible.

If dG is positive, the reaction cannot occur spontaneously and proceeds only if free energy can be gained, i.e. it is endergonic.

If, in addition, the magnitude of dG is great, the system is stable with little or no tendency for a reaction to occur.

If dG is zero, the system is at equilibrium and no net change takes place.



The general term describing the change in free energy G (meaning that energy available for useful work) due to the change in the number of molecules of particular species that enter or leave the system under consideration is known as the **chemical potential**.

$$dU = TdS - pdV + \mu dn$$

The change in U is due not only to heat exchange ($dQ = TdS$) and work done ($dW = pdV$), but also to the change in the number of the particles of the system.

$$d\mu^* = d\mu_0 + RT \ln \frac{c_2}{c_1} + zF(\varphi_2 - \varphi_1)$$

Its change is equal to the work done to:

1. Synthesize one mol of a substance (state 2) from reactants (state 1) and to put it in a solution (term $\Delta\mu_0$)
2. To concentrate a solution from C_1 to C_2 .
3. To overcome the repulsive electrostatic forces due to the potential difference between solutions ($\varphi_2 - \varphi_1$).

In physico-chemical systems the change in free energy is given by the change in the electrochemical potential.

$$dG = nd\mu^*$$