Lecture 2 Application of the First Law of Thermodynamics to the Analysis of Closed Physicochemical Systems

Goal of the lecture: To study how the First Law of Thermodynamics is applied to closed physicochemical systems, focusing on the relationships between heat, work, and internal energy during physical and chemical processes.

Brief lecture notes: This lecture focuses on the application of the First Law of Thermodynamics — the principle of conservation of energy — to closed physicochemical systems. We will analyze how energy is transferred in the form of heat and work, and how internal energy changes during physical transformations and chemical reactions. The lecture discusses the mathematical formulation of the First Law, introduces concepts of enthalpy and specific heat, and explains how energy balance is used to interpret experimental data. Examples include heating and expansion of gases, chemical reactions in closed reactors, and phase transitions. Understanding these principles allows for predicting system behavior and calculating energy changes in practical thermodynamic and chemical processes.

Main part

1. Introduction to the First Law of Thermodynamics

The First Law of Thermodynamics is the principle of energy conservation applied to thermodynamic systems. It states that energy can neither be created nor destroyed, only transformed from one form to another. This equation shows that when heat is added to a system, part of it increases the internal energy, and the rest is used to perform work on the surroundings. If no work is done ($W = 0$), all the heat goes into increasing internal energy.

2. Internal Energy and Closed Systems

Internal energy (U) represents the total microscopic energy (kinetic and potential) of the particles within the system. For a closed system, the change in internal energy depends only on the initial and final states, not on the process path.

When a gas is heated in a sealed container, molecules move faster, and internal energy increases. For an ideal gas, this can be written as:

$$\Delta U = nC_v\Delta T$$

where

n— number of moles,

C_v— molar heat capacity at constant volume,

ΔT— temperature change.

If the process occurs at constant volume, no expansion work is done, so all heat added increases the internal energy directly ($Q_v = \Delta U$).

3. Work and Heat Transfer

In thermodynamics, work is energy transfer caused by a force acting through a distance, and heat is energy transfer due to a temperature difference.

For a reversible expansion or compression, work is calculated as:

$$W = \int_{V_1}^{V_2} P\,dV$$

If the pressure is constant (isobaric process):

$$W = P(V_2 - V_1)$$

Thus, when a gas expands, it performs positive work; when it is compressed, work is done on the gas.

At constant pressure, the total heat supplied includes both internal energy change and the expansion work. Therefore, it is convenient to introduce a new thermodynamic function — enthalpy (H):

$$H = U + PV$$

For processes at constant pressure:

$$\Delta H = Q_p$$

That is, the heat exchanged at constant pressure equals the enthalpy change of the system.

4. Application to Physicochemical Systems

The First Law is widely applied to physical and chemical processes occurring in **closed** systems.

In chemical reactions, energy changes can be represented as the difference between the enthalpies of products and reactants:

$$\Delta H_{\text{reaction}} = \sum H_{\text{products}} - \sum H_{\text{reactants}}$$

If $\Delta H < 0$, the reaction is exothermic (heat is released). If $\Delta H > 0$, the reaction is endothermic (heat is absorbed).

For example, in a bomb calorimeter (a constant-volume closed system), the heat measured equals the change in internal energy ($Q_v = \Delta U$). In contrast, for reactions in open vessels at constant pressure, the heat corresponds to enthalpy change ($Q_p = \Delta H$).

Physical transformations such as melting, evaporation, and condensation are also governed by the First Law. In these processes, heat supplied or released (latent heat) changes the phase of a substance without changing its temperature.

5. Enthalpy and Energy Balance

Concept	Definition	Key Equation	Applications / Notes
Enthalpy (H)	A thermodynamic quantity defined as the sum of internal energy and the product of pressure and volume.	H=U+PV	Useful for processes at constant pressure (e.g., chemical reactions, heating, or cooling under open conditions).
Change in Enthalpy (ΔH)	Represents the heat absorbed or released during a process at constant pressure.	ΔH=Qp	- ΔH > 0: Endothermic process (heat absorbed). - ΔH < 0: Exothermic process (heat released).
Energy Balance for Closed Systems	Expresses conservation of energy within a system where no mass crosses the boundary.	Q=ΔU+W	Used to calculate how energy is stored, transferred, or converted in physical and chemical systems.

Concept	Definition	Key Equation	Applications / Notes
Practical Importance	Helps analyze the efficiency of real systems such as heat exchangers, engines, and combustion processes.	—	Provides basis for evaluating energy conservation and conversion efficiency.

Questions for Self-Control

1. What does the First Law of Thermodynamics state?
2. How does energy transfer occur in closed systems?
3. What is the difference between internal energy (U) and enthalpy (H)?
4. How is the First Law applied to chemical reactions at constant volume and constant pressure?
5. What forms of work can occur in closed physicochemical systems?

Literature

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