Lecture 11 Chemical Thermodynamics of Reaction Systems: Mixtures, Combustion, Thermal Effects

Goal of the lecture: To study the thermodynamic principles governing chemical reaction systems, with emphasis on the behavior of mixtures, combustion processes, and the associated thermal effects.

Brief lecture notes: This lecture discusses the thermodynamic foundations of chemical reaction systems, focusing on how energy and matter interact during chemical transformations.

Main part

Chemical thermodynamics applies the laws of thermodynamics to systems in which chemical composition changes. It provides tools to predict whether a reaction will occur spontaneously and to determine the heat and work involved in the process.

The First Law of Thermodynamics states that energy is conserved during any process, including chemical reactions. For a reacting system:

$$\Delta U = Q - W$$

where $\Delta U$is the change in internal energy, $Q$is the heat added to the system, and $W$is the work done by the system.

In chemical reactions, the most important thermodynamic quantity is enthalpy (H), which represents the heat absorbed or released at constant pressure.

The enthalpy change of reaction is defined as:

$$\Delta H_{rxn} = \sum n_p H_f^\circ(\text{products}) - \sum n_r H_f^\circ(\text{reactants})$$

where $H_f^\circ$are standard enthalpies of formation and $n_p, n_r$are stoichiometric coefficients of products and reactants, respectively.

A negative value of ΔH_{rxn}indicates an exothermic reaction (heat released), while a positive value corresponds to an endothermic reaction (heat absorbed).

Table: Mixtures and Chemical Potential

Concept	Definition / Formula	Description / Physical Meaning	Application / Example
Chemical Potential (μ_i)	$\mu_i = (\frac{\partial G}{\partial n_i})_{T,P,n_j}$	Partial molar Gibbs free energy of component *i*; represents how Gibbs energy changes when one mole of component *i* is added to the system.	Determines the tendency of matter or energy transfer between phases or substances.
Total Gibbs Energy (G)	$G = \sum_i n_i \mu_i$	The total Gibbs energy of a mixture is the sum of the chemical potentials of all components multiplied by their molar amounts.	Used for calculating thermodynamic properties of mixtures.
Equilibrium Condition	$\sum_i \nu_i \mu_i = 0$	Expresses the criterion for chemical equilibrium — the Gibbs energy of the system is minimized.	Defines the equilibrium composition of reacting mixtures.
Stoichiometric Coefficients (ν_i)	—	Represent the number of moles of each substance participating in a chemical reaction.	Positive for products, negative for reactants.

Concept	Definition / Formula	Description / Physical Meaning	Application / Example
Thermodynamic Significance	—	The chemical potential determines how components redistribute during reactions, diffusion, or phase changes.	Helps predict the direction and extent of chemical reactions at given T and P.

Combustion Thermodynamics

Combustion is one of the most important classes of chemical reactions, involving the oxidation of fuels (hydrocarbons, hydrogen, or carbon monoxide) with oxygen to produce heat and combustion products such as CO_2 and H_2O. The released energy can be calculated from standard enthalpies of formation using the reaction enthalpy formula.

For example, for methane combustion:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \Delta H_{rxn} = -890 \text{ kJ/mol}$$

Combustion reactions are typically exothermic, providing the main energy source for thermal power plants, engines, and heating systems.

A key thermodynamic parameter is the adiabatic flame temperature — the maximum temperature achievable when combustion occurs without heat loss. It depends on fuel composition, air-fuel ratio, and the degree of dissociation at high temperatures.

Thermal Effects and Energy Balances

In real systems, combustion and chemical reactions are accompanied by various thermal effects:

- Heat of reaction – energy released or absorbed at standard conditions.
- Heat of formation – energy required to form a compound from its elements.
- Heat of combustion – total energy released during complete oxidation.
- Heat of mixing – energy effect when substances mix at molecular level.

Energy balance for a steady-flow reacting system can be written as:

$$\dot{Q} - \dot{W} = \sum \dot{m}_{out} h_{out} - \sum \dot{m}_{in} h_{in}$$

This allows evaluation of the performance of combustion chambers, reactors, and furnaces.

Comparative Summary (Table in Text Form)

Different reaction types show characteristic thermal effects:

- Combustion reactions release large amounts of energy (exothermic, $\Delta H < 0$).
- Dissociation reactions require energy input (endothermic, $\Delta H > 0$).
- Neutralization reactions between acids and bases typically release moderate heat.
- Mixing reactions can be slightly exothermic or endothermic depending on intermolecular interactions.
- Formation reactions provide fundamental reference data for all others, defining standard enthalpies of compounds.

This classification helps engineers and chemists estimate energy requirements and efficiency in chemical process design.

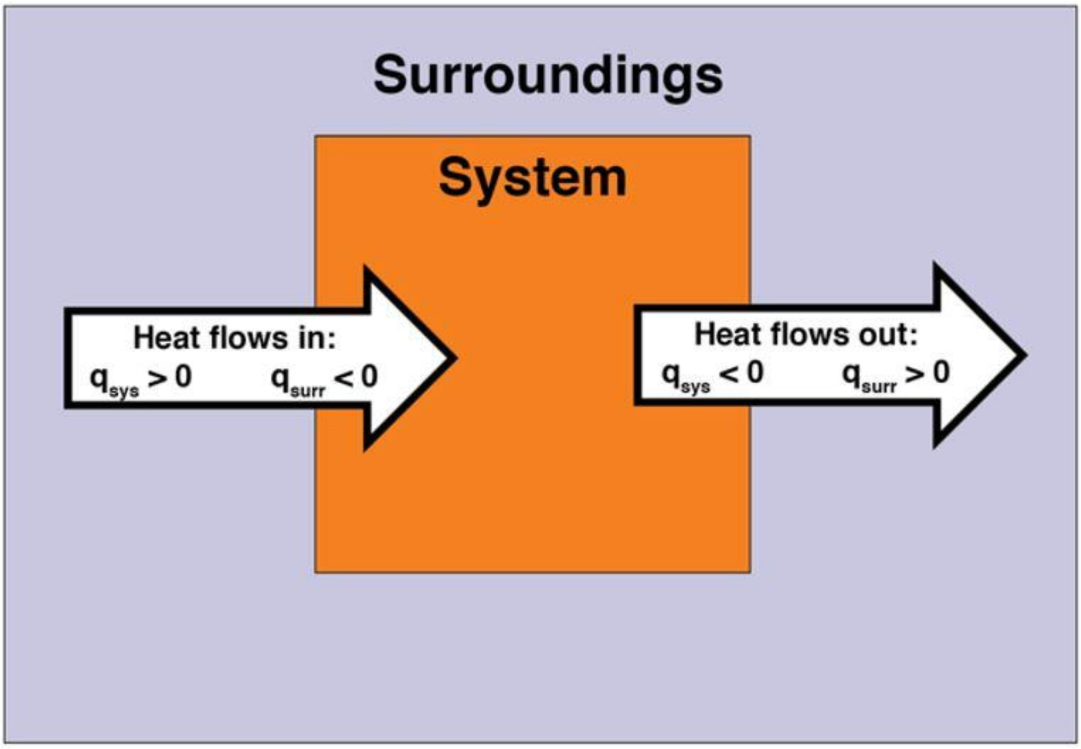

Figure 1 : Energy profile diagram of an exothermic chemical reaction, showing reactants at a higher energy level, a transition state, and products at a lower energy level with heat release $\Delta H < 0$.

Questions for Self-Control

1. What thermodynamic quantities are used to describe chemical reactions?
2. How is the enthalpy change of a reaction calculated from standard enthalpies of formation?
3. What role does chemical potential play in reaction equilibrium?
4. How does the adiabatic flame temperature depend on fuel composition and operating conditions?
5. What are the main differences between exothermic and endothermic reactions?

Literature

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