Inovace bakalářského studijního oboru Aplikovaná chemie

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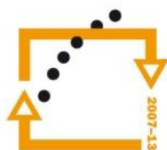
Lecture vocabulary:

reaction heat	reakční teplo		
specifies reactant	daný reaktant		
ambient temperature	okolní teplota		
circumstance	okolnost		
initial / final conditions	počáteční / koncové podmínky		
heat supplied to the systém	teplo dodané (do) systému		
differential	diferenciál		
expansion work	objemová práce (expansion = rozpínání)		
only possible	jediná možná		
accompanying	doprovázející		
reverse process	opačný děj		
collaborate	spolupracovat		
discovery	objev		
latent heat	latentní (skryté) teplo, tj. skupenské teplo		
independent	nezávislý		
pathway	cesta, dráha		
provided that	za předpokladu, že …		
condition	podmínka		
combustion	spalování, tepelný rozklad		
heat of combustion	spalné teplo		
given standard state	daný standardní stav		
element	prvek		
undergo	podléhat		
variation with temperature	teplotní změna		
difference	rozdíl		
permit	dovolit, umožnit		
evaluation	odhad, vyhodnocení		
phase transition	fázová přeměna		
igniting	vznícení, zapálení, zažehnutí		
insulated	izolovaný		
fine wire	jemný drát		
heat flow	tepelný tok		
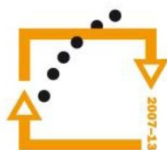
Introduction to Physical Chemistry

Lecture 4

- **Thermochemistry**
  - The reaction heat
  - Laplace-Lavoisier's law
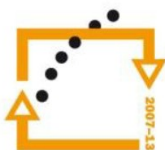 - Hess's law
  - Kirchhoff equation
  - calorimetry

The heat of reaction

Heat of reaction is the amount of heat that must be added or removed during a chemical reaction in order to keep all of the substances present at the same temperature

The units of heat of reaction are kJ·mol^{-1} for a specified reactant or product
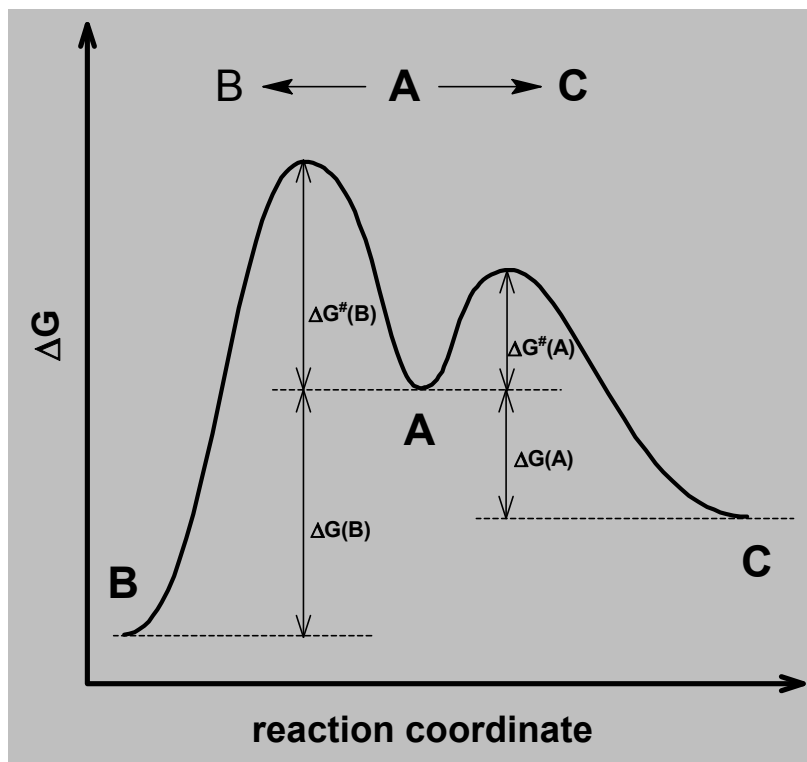
The reaction can be

exergonic / endergonic
exothermic / endothermic
ΔH=negative/ ΔH=positive

Reaction enthalpy

Often, instead of looking at things at constant volume, we often look at things at constant pressure (i.e. we work under ambient atmosphere in an open vessel). Under such circumstances, introducing *enthalpy* is useful:

$$H = U + pV$$

Like the energy, the enthalpy is a state function. The variables involved only depend on initial and final conditions. The change in enthalpy at constant pressure is the heat supplied to the system.

Proof:
The differential of enthalpy is: $dH = dU + pdV - Vdp$
According to the first thermodynamic law $dU = \delta q + \delta w = \delta q - pdV$ (if expansion work is the only possible). Combining the expression we get $dH = \delta q - pdV + pdV - Vdp$, at constant presure $dH = \delta q$.
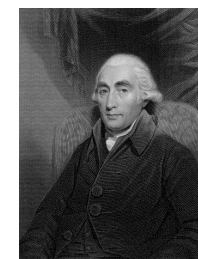
Laplace – Lavoisier's law

The energy change accompanying any transformation is equal and opposite to energy change accompanying the reverse process.

$$\Delta H_{A \to B} = -\Delta H_{B \to A}$$

Laplace collaborated with Lavoisier and constructed the so-called ice calorimeter. They were inspired by Joseph Black's discovery of latent heat in 1761.
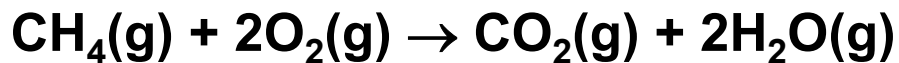
Hess's law

The energy change for any chemical or physical process is independent of the pathway or number of steps required to complete the process provided that the final and initial reaction conditions are the same.

$$\Delta H_{A \to B} = \Delta H_{A \to I_1} + \Delta H_{I_1 \to I_2} + \ldots + \Delta H_{I_{n-1} \to I_n} + \Delta H_{I_n \to B}$$
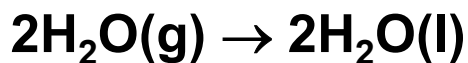
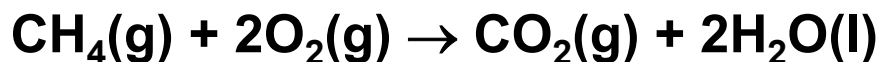German Ivanovich Gess, August 7, 1802–November 30, 1850, was a Swiss-born Russian chemist

- **For example:**

$CH_4(g) + 2O_2(g) \to CO_2(g) + 2H_2O(g)$ $\Delta H = -802$ kJ

$2H_2O(g) \to 2H_2O(l)$ $\Delta H = -88$ kJ

$CH_4(g) + 2O_2(g) \to CO_2(g) + 2H_2O(l)$ $\Delta H = -890$ kJ

Heats of formation and heats of combustion

Standard Heat (Enthalpy) of formation of a given compound is the enthalpy change of the reaction by which it is formed from its elements.
- The reactants and products are all in a given standard state.
- By definition, the standard enthalpy (heat) of formation of an element in its standard state is zero.
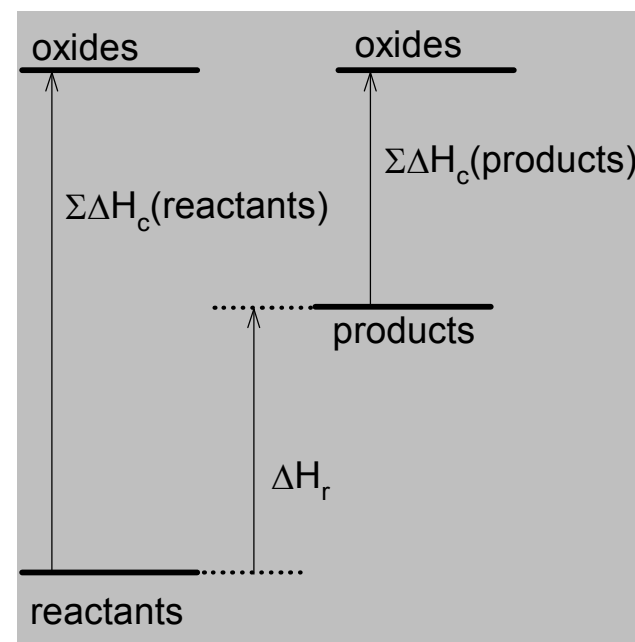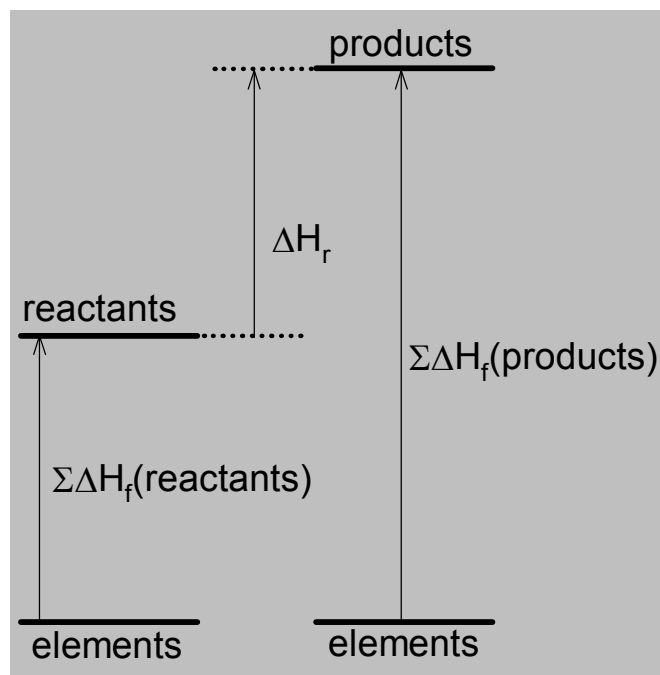
The heat of combustion is the energy released as heat when a compound undergoes complete combustion with oxygen under standard conditions. The chemical reaction is typically a hydrocarbon reacting with oxygen to form carbon dioxide, water and heat.
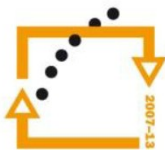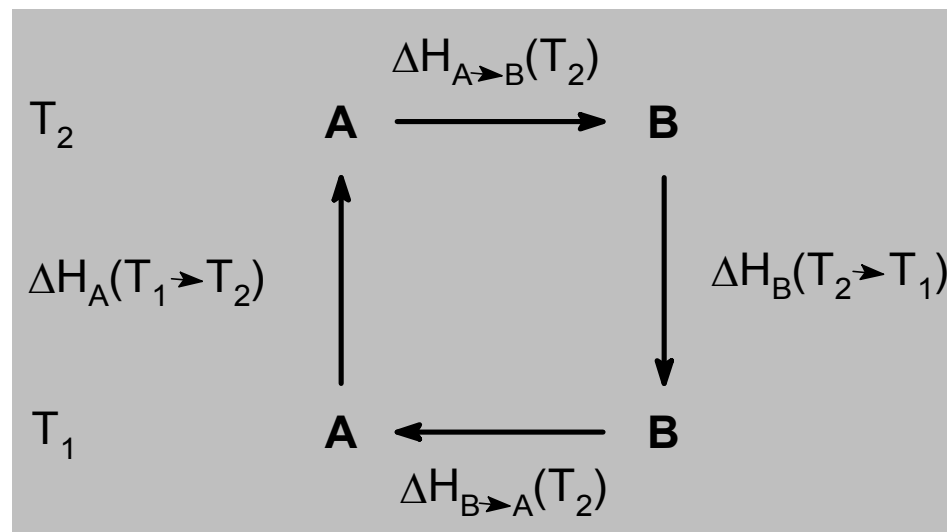
Kirchoff equation

$$\Delta H_{A \to B}(T_2)$$

$$T_2 \qquad A \xrightarrow{\hspace{3cm}} B$$

$$\Delta H_A(T_1 \to T_2) \qquad\qquad \Delta H_B(T_2 \to T_1)$$

$$T_1 \qquad A \xleftarrow{\hspace{3cm}} B$$

$$\Delta H_{B \to A}(T_2)$$

$$\Delta H_{A \to B}(T_2) = -\int_{T_2}^{T_1} C_p^B(T)\,dt + \Delta H_{A \to B}(T_1) - \int_{T_1}^{T_2} C_p^A(T)\,dT =$$

$$= \Delta H_{A \to B}(T_1) + \int_{T_1}^{T_2} \left(C_p^B(T) - C_p^A(T) \right) dT$$

Gustav Kirchhoff showed in 1858 that the variation of the heat of reaction with temperature is given by the difference in heat capacity between products and reactants: dΔH / dT = ΔCp.
Integration of this equation permits the evaluation of the heat of reaction at one temperature from measurements at another temperature.
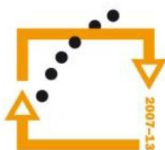
Calorimetry

Technique to determine reaction heats and heat capacities

Heat capacities: dQ = CdT

- Usually not constant, but changing with temperature $C = a + bT + cT^2$…
- Not defined at phase transition

- **Specific**
- **Molar**
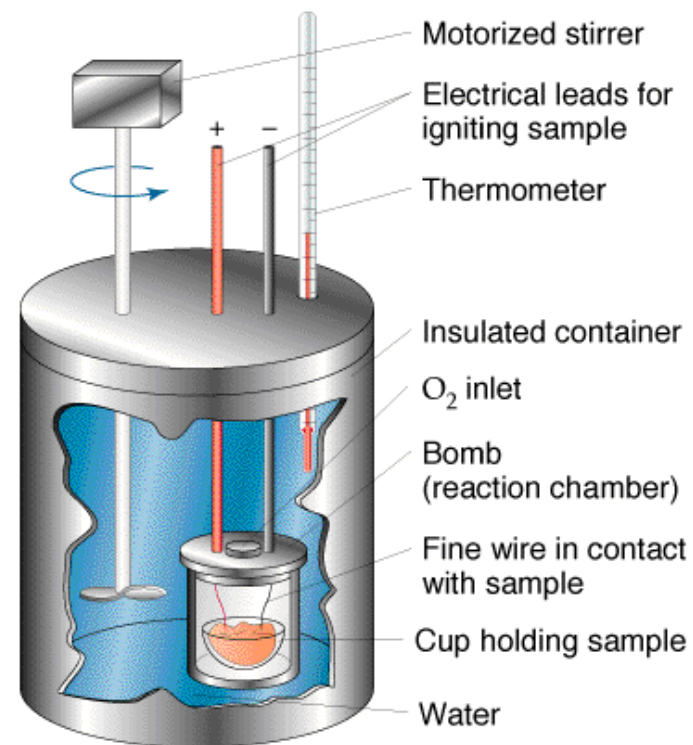
- **At constant volume** $C_p = \dfrac{dU}{dT}$

- **At constant pressure** $C_p = \dfrac{dH}{dT}$

For ideal gas: $C_p = C_v + R$

Calorimetric equation:

$$c_1 m_1(t_1 - t) = c_2 m_2(t - t_2)$$

Motorized stirrer

Electrical leads for igniting sample

Thermometer

Insulated container

O_2 inlet

Bomb (reaction chamber)

Fine wire in contact with sample

Cup holding sample

Water

Bomb calorimeter

Thermoanalytical techniques

Differential scanning calorimetry **or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature.**

Differential thermal analysis **(DTA). In this technique it is the heat flow to the sample and reference that remains the same rather than the temperature. When the sample and reference are heated identically phase changes and other thermal processes cause a difference in temperature between the sample and reference.**

Isothermal titration calorimetry **(ITC) is a technique used to determine the thermodynamic parameters of interactions in solution. As chemical reactions occur in the sample cell, heat is generated or absorbed. The temperature difference between the sample and reference cells due to chemical reactions occuring in the sample cell is kept at a constant value (i.e. base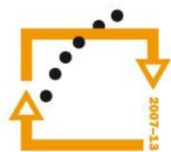line) by the addition or removal of heat to the sample cell.**