

## Thermochemical Properties

Basic thermochemical properties are heat capacities, formation enthalpy, formation Gibbs energy and (absolute) entropy.

### Molar Heat Capacities

Most common is the isobaric heat capacity,  $C_p$ . Its values are often tabulated or correlated as a function of temperature by means of some empirical formula – either polynomial or some more complicated one. The assumption of temperature-independent heat capacity is inappropriate when dealing with a temperature range larger than a few degrees K.

Estimation Methods: Heat capacity of organic compounds in the ideal gas standard state or in the liquid state can be estimated from various QSPRs – Quantitative Structure-Property Relations.

Data Sources: Webbook ( [webbook.nist.gov/chemistry/](http://webbook.nist.gov/chemistry/) )

Wagman D.D. et al.: J. Phys. Chem. Ref. Data, 11, 1982.

TRC Thermodynamic Tables, Thermodynamic Research Center, Texas Engineering Experiment Station, The Texas A&M University System, College Station, 1994.

Chase M.W.: NIST-JANAF Thermochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph 9, 1998, 1-1951.

Bureš M., Holub R., Leitner J., Voňka P.: Termochemické veličiny organických sloučenin, VŠCHT Praha, 1992. (organic compounds in ideal gas standard state)

### Heat Capacity $C_v$

Isochoric heat capacity can be obtained from  $C_p$  using the EOS

$$C_p - C_v = \left( p + \left( \frac{\partial U}{\partial V} \right)_T \right) \left( \frac{\partial V}{\partial T} \right)_p$$

For compound in the ideal gas standard state this heat capacity difference is equal to ( $R = 8,314 \text{ J/K/mol}$ ) – Mayer's relation.

### Formation Enthalpy, Absolute Entropy

#### Formation enthalpy $\Delta H_f^\circ$

Formation enthalpy is the enthalpy of reaction where 1 mole of a compound is formed from its constituent elements at their standard states (most stable phase, gaseous compounds in their most stable forms and in the ideal gas standard state, solids in their most stable crystallographic modifications).

#### Absolute entropy $S^\circ$

Absolute entropy of a system is the entropy change between its actual state and the most stable solid state at 0 K, where the entropy is equal to zero (see Third Law of Thermodynamics).

Both formation enthalpy and absolute entropy are commonly tabulated or presented in the format of some temperature-dependent empirical functions. Minimum information is their values at some reference conditions, usually 298 K. Their change with temperature and pressure can be obtained from thermodynamic relations using as input heat capacity of a compound and its constituent elements.

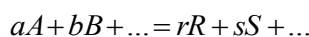
Data Sources: same as for  $C_p$ .

### Formation Gibbs Energy $\Delta G_f^\circ$

The values of  $\Delta G_f^\circ$  are needed e.g. for calculation of the Gibbs energy change in the course of chemical reaction (and subsequently the equilibrium constant of the reaction). If not available explicitly in thermochemical data sources,  $\Delta G_f^\circ$  can be calculated from the values of  $\Delta H_f^\circ$  a  $S^\circ$  for a compound and its constituent elements.

### Thermochemical Calculations

General chemical reaction in algebraic format is



where  $a, b, \dots, r, s, \dots$  are (dimensionless) stoichiometric coefficients and capital letters are for reagents. In a more compact format

$$0 = \sum_{i=1}^k \nu_i R_i$$

where  $\nu_i$  is stoichiometric coefficient of a compound  $R_i$ . Stoichiometric coefficients of reactants are assigned negative sign,  $\nu_i$  values of products are positive.

## Reaction Heat

Reaction heat  $q_r$  is the heat exchanged between the system and its surroundings when  $a$  moles of compound  $A$ ,  $b$  moles of compound  $B$ , ... react to  $r$  moles of compound  $R$ ,  $s$  moles of compound  $S$ , ... at a fixed temperature.

**Exothermic Reaction** is releasing heat out of the system,  $q_r < 0$ .

**Endothermic Reaction** is accepting heat to the system,  $q_r > 0$ .

If pressure remains fixed during the reaction, reaction heat is equal to reaction enthalpy, i.e. the change of enthalpy of products and reactants.

## Hess Law

If chemical reaction  $R$  is a linear combination of reactions  $R_1, R_2, \dots$ , its reaction enthalpy is obtained as the same linear combination of  $R_1, R_2, \dots$  reaction enthalpies. Hess Law is a consequence of enthalpy being the state variable.

## Standard Reaction Enthalpy $\Delta H_r^\circ$

Standard reaction enthalpy is stated at a standard pressure ( $p = 101,325 \text{ kPa}$ ) and temperature  $T$  (must be specified). Usually it is calculated from tabulated standard formation enthalpies:

$$\Delta H_r^\circ = r(\Delta H_{\text{sl}}^\circ)_R + s(\Delta H_{\text{sl}}^\circ)_S + \dots - a(\Delta H_{\text{sl}}^\circ)_A - b(\Delta H_{\text{sl}}^\circ)_B - \dots$$

## Reaction Heat Change with Temperature – Kirchhoff Law

$$\left( \frac{\partial \Delta H_r}{\partial T} \right)_p = \Delta C_p$$

$$\Delta C_p = r(C_{p,m})_R + s(C_{p,m})_S + \dots - a(C_{p,m})_A - b(C_{p,m})_B - \dots$$

This equation follows from the definition of heat capacity. By integrating from temperature  $T_1$  to  $T_2$  we get

$$\Delta H_r(T_2) = \Delta H_r(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

commonly known as Kirchhoff law. This equation allows re-calculation of reaction enthalpy from one temperature to another, using the heat capacity functions of reacting species. E.g. the (tabulated) value of formation enthalpy at 298 K can be re-calculated to temperature  $T$  as

$$\Delta H_r^\circ(T) = \Delta H_r^\circ(298) + \int_{298}^T \Delta C_p dT$$

where  $\Delta C_p$  is the difference of molar heat capacity of a compound and its constituent elements.

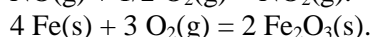
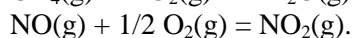
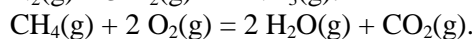
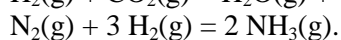
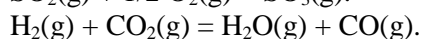
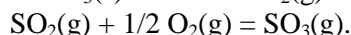
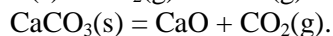
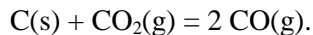
## Enthalpy Balance

Enthalpy balance of a chemical reaction is understood as the enthalpy change of a reaction where reactant  $A$  enters the reaction at temperature  $T_A$ , reactant  $B$  at temperature  $T_B$ , ... and products exit the reaction at temperature  $T_{\text{prod}}$ ; reaction itself proceeds at temperature  $T_1$ .  $\Delta H_r$  of this process is

$$\Delta H_r = \int_{T_A}^{T_1} a(C_{p,m})_A dT + \int_{T_B}^{T_1} b(C_{p,m})_B dT + \Delta H_r(T_1) + \int_{T_1}^{T_{\text{prod}}} r(C_{p,m})_R dT + \int_{T_1}^{T_{\text{prod}}} s(C_{p,m})_S dT + \dots$$

where  $T_1$  is the temperature (usually 298,15 K) at which we know the reaction enthalpy for a given reaction.

**Homework 4:** Calculate the heat that has to be added/retrieved from a batch reactor, operating at 798,15 K.



Reactants enter the reactor pre-heated to 798,15 K and products leave the reactor at the same temperature. Assume ideal behavior of gaseous components and neglect the pressure dependence of reaction enthalpy.