Thermochemistry

Outline:
I. Thermochemical equations. Thermodynamic definition of the heat of reaction.
II. Standard state. Standard enthalpy of reaction.
III. Hess's law.
IV. Calculation of reaction enthalpies based on enthalpies of formation and combustion enthalpies.
V. Experimental determination of the heat of reaction, calorimetry.
VI. Heat capacity, types of molar heat capacities.
VII. Temperature dependence of reaction enthalpies: Kirchhoff's law.
VIII. The Born–Haber cycle.

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I. Thermochemical equations, thermodynamic definition of the heat of reaction

- Thermochemistry is the "old school" or reaction heat: measurement or calculation of the heat (q) absorbed or produced in chemical reactions.
- **Thermochemistry** is the application of the **first law**.
- **Thermochemical equations**: in addition to the chemical change (reactants, products), it shows the reaction heat (q).
- The sign of q (system-centered):
  - **exothermic** process if heat is produced ($q < 0$).
  - **endothermic** process if heat is absorbed ($q > 0$).
- The old heat of reaction (q) with current terminology:
  - at constant volume: $q_V = \Delta U$,
  - at constant pressure: $q_p = \Delta H$.

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II. Standard state. Standard enthalpy of formation. Standard enthalpy change of processes.

- The absolute values of H and U are unknown and depend on the conditions.
- A reference state (general agreement) needed:
  - **Standard state**: The standard state of a substance *at any temperature* means the pure substance at pressure $p^\theta = 1$ bar (1×10^5 Pa) (*definition*).
  - **The standard enthalpy of formation for a compound** $\Delta_{form}H^\theta$ is the enthalpy change accompanying its formation from its elements in the standard state.
  - **The standard enthalpy of formation of elements** is zero: $H_m^\theta = 0$ J   – *at any temperature!*

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II. Standard state. Standard enthalpy of formation. Standard enthalpy change of processes.

- **Standard enthalpy change of processes** ΔH^θ: the enthalpy change in the process in such a way that initially (i) the reactants are in the standard state (and not mixed) and finally (f) the products are in the standard state (and not mixed).
  - $\Delta H^\theta = H_{m,f}^\theta - H_{m,i}^\theta$
  - ΔH^θ values are given for $n = 1$ mol (*intensive*)
  - The name of the change is given as subscript (in abbreviated form): $\Delta_{name}H^\theta$
- **Standard enthalpies of formation** and **combustion** are especially important reaction enthalpies, but other may be of significance, too (*e.g.* enthalpy of neutralization).

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Name of the process	Essence of the process	Symbol
Phase transition	α-phase $\rightarrow \beta$-phase	$\Delta_{tre}H$
Melting	$s \rightarrow l$	$\Delta_{fus}H$
Evaporation	$l \rightarrow g$	$\Delta_{vap}H$
Sublimation	$s \rightarrow g$	$\Delta_{sub}H$
Mixing of liquids	pure substances $\rightarrow$ mixture	$\Delta_{mix}H$
Solution	pure solute $\rightarrow$ solution	$\Delta_{sol}H$
Hydration (B–H)	$X^\pm(g) \rightarrow X^\pm(aq)$	$\Delta_{hyd}H$
Atomization	$(s,l,g) \rightarrow$ atoms(g)	$\Delta_{at}H$
Ionization (B–H)	$X(g) \rightarrow X^+(g) + e^-(g)$	$\Delta_i H$
Electron gain (B–H)	$X(g) + e^-(g) \rightarrow X^-(g)$	$\Delta_{eg}H$
Reaction	reactants $\rightarrow$ products	$\Delta_r H$
Combustion	compound$(s,l,g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$	$\Delta_{comb}H$
Compound formation	elements $\rightarrow$ compound	$\Delta_{form}H$
Activation	reactants $\rightarrow$ activated complex	$\Delta H^\#$

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physical changes   and   chemical changes

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Enthalpies of physical changes

- In thermodynamics, **phases** are states of matter that are only different in their physical properties: *g*, *l*, *s*.
- In solid phase, several different modifications (phases) of the same substance are known *[e.g. white and red P; graphite, diamond, fullerene C; orthorhombic and monoclinic S]*
- Changes of state are called **phase transitions**, they are characterized by the standard enthalpy of phase transition $\Delta_{trs}H^{\theta}$.
- Some examples:
  - melting ⇌ freezing
  - evaporation ⇌ condensation
  - sublimation ⇌ deposition
  - solid phase transition (orthorhombic ⇌ monoclinic S)   7

Enthalpies of physical changes

Standard enthalpies of <u>fusion</u> (melting) and <u>evaporation</u> at the temperature of **phase transition**:

	T_f/K	$\Delta_{fus}H^{\theta}$/(kJ mol^{-1})	T_b/K	$\Delta_{vap}H^{\theta}$/(kJ mol^{-1})
He	3.5	0.02	4.2	0.084
Ar	84	1.2	87	6.5
C_6H_6	279	10.6	353	31
H_2O	273	6.0	373	40.7

- All of them are positive as melting and evaporation are *endothermic*!
- Heat is produced at <u>freezing</u> or <u>condensation</u> (*exothermic*), so, $|\Delta_{trs}H^{\theta}|$ is the same, but the sign is the opposite.
- *[The ratio of the values can be interpreted on a molecular level.]*   8

III. Hess's law (different approaches)

- The enthalpy of reaction only depends on the initial and final state, but not on the path or the intermediates. *[Enthalpy is a state function. There are obviously several possible paths.]*
- The standard enthalpy of the reaction is always the sum of the standard enthalpies of the individual reactions steps in the series.
- The net enthalpy change of a cyclic process is zero. *[This is basically a statement of the first law of thermodynamics (conservation of energy) specifically for thermochemistry. It facilitates the calculation of Δ_rH^{θ} values of reaction that are experimentally unfeasible. The Born-Haber cycle is such an application.]*   9

IV. Calculation of reaction enthalpies from enthalpies of formation or combustion.

- A direct way to determine Δ_rH^{θ} is **measurement by calorimetry**. This is typically feasible for fast processes, but often problematic for slow ones.
  - $H_2 + Cl_2 = 2HCl$ *easy* ☺
  - $C_3H_6 + H_2 = C_3H_8$ *do some thinking* ☹
- Δ_rH^{θ} can be calculated from the $\Delta_{form}H^{\theta}$ **formation enthalpies** of reactants and products (if they are known).
  - *[Enthalpy of formation cannot be measured directly neither for C_3H_6, nor for C_3H_8.]*
- $\Delta_{form}H^{\theta}$ enthalpies of formation are not typically measurable directly, but can be calculated from $\Delta_{comb}H^{\theta}$ **combustion enthalpies** by Hess's law.
  - $C_3H_6(g) + 4,5\ O_2(g) \rightarrow 3\ CO_2(g) + 3\ H_2O(l)$ *enthalpy of combustion*
  - $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$ *enthalpy of combustion.*   10

IV. Calculation of reaction enthalpies from enthalpies of <u>formation</u> or combustion.

Calculation of standard reaction enthalpies from standard enthalpies of formation.

- Using the first law: the standard enthalpy of each reaction is the difference between the standard enthalpies of formation of products and reactants:
  - $\Delta_r H^{\theta} = \sum\limits_{products} \nu \left(\Delta_{form}H^{\theta}\right) - \sum\limits_{reactants} \nu \left(\Delta_{form}H^{\theta}\right)$
- In condensed form:
  - $\Delta_r H^{\theta} = \sum \nu_J \left(\Delta_{form}H^{\theta}(J)\right)$
  - The stoichiometric coefficients (ν_J) have signs that should be considered.   11

IV. Calculation of reaction enthalpies from enthalpies of <u>formation</u> or combustion.

An example of calculating a standard enthalpy of reaction from enthalpies of formation:

- $2\ HN_3(l) + 2\ NO(g) \rightarrow H_2O_2(l) + 4\ N_2(g)$ reaction standard enthalpy of reaction:

$\Delta_r H^{\theta} =$
$= \left\{\Delta_{form}H^{\theta}(H_2O_2,l) + 4\cdot\Delta_{form}H^{\theta}(N_2,g)\right\} - \left\{2\cdot\Delta_{form}H^{\theta}(HN_3,l) + 2\cdot\Delta_{form}H^{\theta}(NO,g)\right\} =$
$= \left\{1\cdot188\,kJ\,mol^{-1} + 4\cdot0\,kJ\,mol^{-1}\right\} - \left\{2\cdot264\,kJ\,mol^{-1} + 2\cdot90\,kJ\,mol^{-1}\right\} =$
$= -892\,kJ\,mol^{-1}$ 12

IV. Calculation of reaction enthalpies from enthalpies of formation or <u>combustion</u>.

Calculation of the standard reaction enthalpy from enthalpies of combustion:

- The previous calculation can be based on combustions.

$$\Delta_r H^\ominus = \sum_{\text{reactants}} \nu \left(\Delta_{\text{comb}} H^\ominus \right) - \sum_{\text{products}} \nu \left(\Delta_{\text{comb}} H^\ominus \right)$$

$$\Delta_r H^\ominus = -\sum \nu_J \left(\Delta_{\text{comb}} H^\ominus (J) \right)$$

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IV. Calculation of reaction enthalpies from enthalpies of formation or <u>combustion</u>.

An example of calculating standard reaction enthalpy for enthalpies of combustion:

- Calculate $\Delta_r H^\ominus$ for the $C_3H_6 + H_2 \rightarrow C_3H_8$ reaction.
- All three substances can be burnt in a calorimeter
  - $C_3H_6 + 4.5\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O$ $\Delta_{\text{comb}}H^\ominus(C_3H_6)$= -2058 kJ mol^{-1}
  - $H_2 + 0.5\ O_2 \rightarrow H_2O$ $\Delta_{\text{comb}}H^\ominus(H_2)$= -286 kJ mol^{-1}
  - $C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$ $\Delta_{\text{comb}}H^\ominus(C_3H_6)$= -2220 kJ mol^{-1}
- Standard enthalpy of the hydrogenation reaction:

$$\Delta_r H^\ominus = \left\{ \Delta_{\text{comb}}H^\ominus(C_3H_6,g) + \Delta_{\text{comb}}H^\ominus(H_2,g) \right\} - \left\{ \Delta_{\text{comb}}H^\ominus(C_3H_8,g) \right\} =$$
$$= \left\{ -2058\ \text{kJ mol}^{-1} + \left(-286\ \text{kJ mol}^{-1} \right) \right\} - \left\{ -2220\ \text{kJ mol}^{-1} \right\} =$$
$$= -124\ \text{kJ mol}^{-1}$$

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IV. Calculation of reaction enthalpies from enthalpies of formation or <u>combustion</u>.

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  - $3\ CO_2 + 4\ H_2O \rightarrow C_3H_8 + 5\ O_2$ $-\Delta_{\text{comb}}H^\ominus(C_3H_8)$= 2220 kJ mol^{-1}
- Standard enthalpy of the hydrogenation reaction:

$$\Delta_r H^\ominus = \left\{ \Delta_{\text{comb}}H^\ominus(C_3H_6,g) + \Delta_{\text{comb}}H^\ominus(H_2,g) \right\} - \left\{ \Delta_{\text{comb}}H^\ominus(C_3H_8,g) \right\} =$$
$$= \left\{ -2058\ \text{kJ mol}^{-1} + \left(-286\ \text{kJ mol}^{-1} \right) \right\} - \left\{ -2220\ \text{kJ mol}^{-1} \right\} =$$
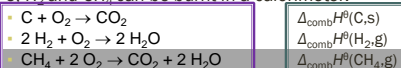$$= -124\ \text{kJ mol}^{-1}$$

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IV. Calculation of <u>enthalpies of formation from enthalpies of combustion</u>.

- *Oxidation* – burning (most of the organic) in a large excess (pressure) oxygen in a bomb calorimeter – is usually complete and fast so the calculation of $\Delta_f H^\ominus$ formation enthalpy if often feasible based on easily measurable $\Delta_{\text{comb}}H^\ominus$ combustion enthalpies.
- Calculate the enthalpy of combustion of methane.
  - The process $C + 2\ H_2 \rightarrow CH_4$ is totally unfeasible!
  - C, H_2 and CH_4 can be burnt in a calorimeter:
    - $C + O_2 \rightarrow CO_2$ $\Delta_{\text{comb}}H^\ominus(C,s)$
    - $2\ H_2 + O_2 \rightarrow 2\ H_2O$ $\Delta_{\text{comb}}H^\ominus(H_2,g)$
   - $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ $\Delta_{\text{comb}}H^\ominus(CH_4,g)$

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    - $2\ H_2 + O_2 \rightarrow 2\ H_2O$ $\Delta_{\text{comb}}H^\ominus(H_2,g)$
    - $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ $\Delta_{\text{comb}}H^\ominus(CH_4,g)$

V. Experimental determination of the heat of reaction, calorimetry

- simple calorimeter (for measuring e.g. enthalpy of dilution or neutralization)
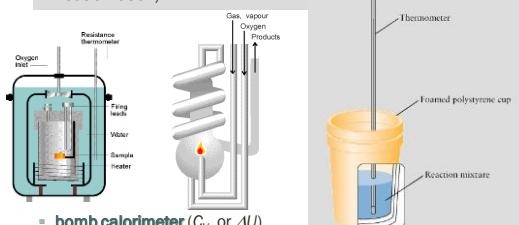
  - **bomb calorimeter** (C_V, or ΔU)
  - **flame calorimeter** (C_p, or ΔH)
- Technical and biological importance of combustion.

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VI. Heat capacity, types of molar heat capacity.

- Heat capacities were already discussed in detail (last week):
- Types of heat capacity at constant volume or at constant pressure:
  - C_V, C_p: heat capacity (arbitrary n); *extensive*; **J K^{-1}**
  - $C_{V,m}$, $C_{p,m}$: molar heat capacity (for 1 mol); *intensive*; **J mol^{-1} K^{-1}**
  - c_V, c_p: specific heat (1 kg); *intensive*; **J kg^{-1} K^{-1}**

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

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VI. Heat capacity, types of molar heat capacity.

- Heat capacities were already discussed in detail (last week):
- Molecular interpretation of heat capacity:
  - monatomic gases:
    $C_{V,m} = 3/2\ R$ = [12.47 J K^{-1} mol^{-1}]
  - diatomic molecules:
    $C_{V,m} = 5/2\ R$ = [20.785 J K^{-1} mol^{-1}]
  - nonlinear polyatomic molecules:
    $C_{V,m} = 3R$ = [24.94 J K^{-1} mol^{-1}]

- https://www.youtube.com/watch?v=0xhtszEjNN0

VII. Temperature dependence of reaction enthalpies: Kirchhoff's law.

Use of molar heat capacities in calculating reaction enthalpies
- Values of $\Delta_r H^\theta$ depend on T, and this is important.
- Possibilities of determination:
  - measurement of $\Delta_r H^\theta$ directly at several values of T,
  - from the T dependence of the H_m of substances ($C_{p,m}$):
    - $C_p = (\partial H/\partial T)_p$. So $dH = \int C_p dT$. (last week)
    - $C_{p,m} = (\partial H_m/\partial T)_p$. so $dH_m = \int C_{p,m} dT$.
- If the enthalpy change is known at temperature T_1, integration yields $H(T_2)$ *[provided that no phase transition occurs between T_1 and T_2]*.

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VII. Temperature dependence of reaction enthalpies: Kirchhoff's law.

- As it was shown earlier (last week):
- From the C_p heat capacity, the H enthalpy of a given system can be calculated for different temperatures:

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

- In practice, the temperature-dependence of the enthalpy of a (chemical) reaction is more important. This can be calculated from the appropriate weighted sum of the heat capacities of the substances participating in the reactions:

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_{p,m} dT$$

- In thermochemistry, this is called **Kirchhoff's law**. 22

VII. Temperature dependence of reaction enthalpies: Kirchhoff's law.

- for n = 1 mol:
- From the $C_{p,m}$ heat capacity, the H_m molar enthalpy of a given system can be calculated for different temperatures :

$$H_m(T_2) = H_m(T_1) + \int_{T_1}^{T_2} C_{p,m} dT$$

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VII. Temperature dependence of reaction enthalpies: Kirchhoff's law.

- Integration gives:

$$H_m(T_2) = H_m(T_1) + \int_{T_1}^{T_2} C_{p,m} dT$$

- This is summed for all substances. This is **Kirchhoff' law** (in a thermodynamic approach): the standard enthalpy of reaction at T_2 can be calculated from $\Delta_r H^\theta(T_1)$ and the molar heat capacities of reactants and products:

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_{p,m} dT$$
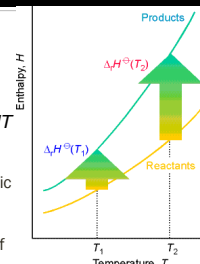
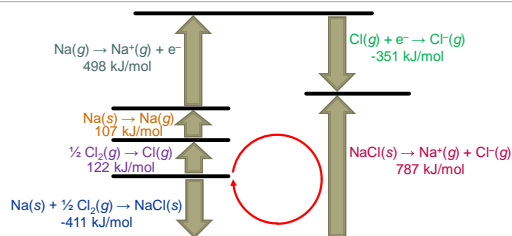$$\Delta_r C_{p,m} = \sum_{products} \nu(C_{p,m}) - \sum_{reactants} \nu(C_{p,m})$$

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VIII. The Born–Haber cycle.

- **A common application of the first law** is to calculate the $\Delta_{lat}H^{\theta}$ lattice enthalpies of crystals or the $\Delta_{hyd}H^{\theta}$ hydration enthalpies of ions, sometimes the $\Delta_{ea}H^{\theta}$ electron affinity of ions – based on the thermodynamic data directly obtained for the rest of the processes in a cycle.
- In a cycle, the net enthalpy change is zero!

- ½ $\Delta_{diss}H^{\theta}(Cl_2)$ + $\Delta_{sub}H^{\theta}(Na)$ + $\Delta_i H^{\theta}(Na)$ + $\Delta_{ea}H^{\theta}(Cl)$ + $\Delta_{hyd}H^{\theta}(NaCl)$ − $\Delta_f H^{\theta}(NaCl,aq)$ = 0

- ½ $\Delta_{diss}H^{\theta}(Cl_2)$ + $\Delta_{sub}H^{\theta}(Na)$ + $\Delta_i H^{\theta}(Na)$ + $\Delta_{ea}H^{\theta}(Cl)$ − $\Delta_{lat}H^{\theta}(NaCl)$ − $\Delta_f H^{\theta}(NaCl,s)$ = 0

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VIII. The Born–Haber cycle.
Determination of lattice enthalpy

$Na(g) \rightarrow Na^+(g) + e^-$
498 kJ/mol

$Cl(g) + e^- \rightarrow Cl^-(g)$
-351 kJ/mol

$Na(s) \rightarrow Na(g)$
107 kJ/mol

½ $Cl_2(g) \rightarrow Cl(g)$
122 kJ/mol

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$
787 kJ/mol

$Na(s) + ½ Cl_2(g) \rightarrow NaCl(s)$
-411 kJ/mol

- ½ $\Delta_{diss}H^{\theta}(Cl_2)$ + $\Delta_{sub}H^{\theta}(Na)$ + $\Delta_i H^{\theta}(Na)$ + $\Delta_{ea}H^{\theta}(Cl)$ − $\Delta_{lat}H^{\theta}(NaCl)$ − $\Delta_f H^{\theta}(NaCl,s)$ = 0

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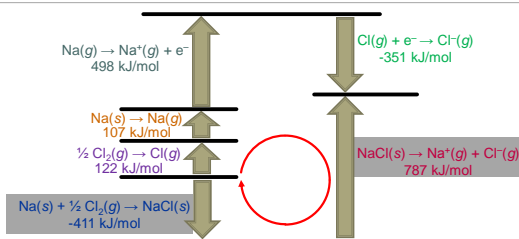
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VIII. The Born–Haber cycle.
Determination of the enthalpy of hydration

$Na(g) \rightarrow Na^+(g) + e^-$
498 kJ/mol

$Cl(g) + e^- \rightarrow Cl^-(g)$
-351 kJ/mol

$Na(s) \rightarrow Na(g)$
107 kJ/mol

½ $Cl_2(g) \rightarrow Cl(g)$
122 kJ/mol

$Na^+(g) + Cl^-(g) \rightarrow NaCl(aq)$
-783 kJ/mol

$Na(s) + ½ Cl_2(g) \rightarrow NaCl(aq)$
-407 kJ/mol
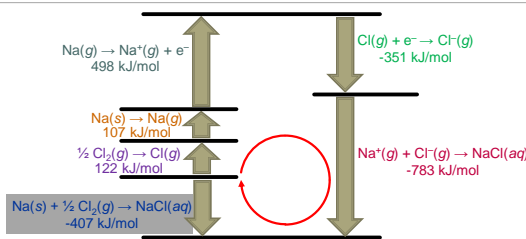
- ½ $\Delta_{diss}H^{\theta}(Cl_2)$ + $\Delta_{sub}H^{\theta}(Na)$ + $\Delta_i H^{\theta}(Na)$ + $\Delta_{ea}H^{\theta}(Cl)$ + $\Delta_{hyd}H^{\theta}(NaCl)$ − $\Delta_f H^{\theta}(NaCl,aq)$ = 0

Short summary:

- Thermochemistry focuses on the heat absorbed or produced in chemical reactions.
- Hess's law is a specific form of the first law of thermodynamics stated for the enthalpy changes of processes at constant pressure.
- Each substance has an H enthalpy (which is a state function and its absolute value is unknown).
- Agreement needed for calculations:
  - concept of standard state: 1 bar and specified T;
  - standard enthalpy of formation for elements: $H_m^{\theta} = 0$;
  - H_m^{θ} of compounds: reaction enthalpy of the formation from their elements = $\Delta_{form}H^{\theta}$.

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Enthalpies and enthalpy changes:

- If a compound cannot be prepared directly from tis elements, the enthalpy of formation $\Delta_{form}H$ can be calculated using Hess's law based on the easily measurable enthalpies of combustion $\Delta_{comb}H$.
- Enthalpy changes $\Delta_r H$ of physical processes or chemical reactions can be determined by either
  - direct measurements on the reaction or
  - calculation from the standard molar enthalpies H_m^{θ} or formation $\Delta_{form}H^{\theta}$ or combustion $\Delta_{comb}H^{\theta}$ enthalpies:

$$\Delta_r H^{\theta} = \sum_{products} \nu H_m^{\theta} - \sum_{reactants} \nu H_m^{\theta}$$

$$\Delta_r H^{\theta} = \sum_{products} \nu \left(\Delta_{form}H^{\theta}\right) - \sum_{reactants} \nu \left(\Delta_{form}H^{\theta}\right) = \sum_{reactants} \nu \left(\Delta_{comb}H^{\theta}\right) - \sum_{products} \nu \left(\Delta_{comb}H^{\theta}\right)$$

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Temperature dependence of enthalpies and enthalpy changes:

- Both the enthalpy of a substance and the enthalpy change of a reaction is dependent on temperature.
- The temperature dependence of the enthalpy of a substance is the molar heat capacity: $(\partial H_m / \partial T)_p = C_{p,m}$.
- For a range of temperature:

$$H_m(T_2) = H_m(T_1) + \int_{T_1}^{T_2} C_{p,m} dT$$

- „Unfortunately" C_p also depends on T: $C_{p,m} = a + bT + c/T^2$
  - This dependence must be measured, but $C_{p,m}$ is easily measurable.
- The T-dependence of reaction enthalpies can also be characterized by C_p values:

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_{p,m} dT$$

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Most important experimental methods of obtaining thermodynamic data:

- Measurement of c_p and c_V specific heats, $C_{p,m}$, $C_{V,m}$ molar heat capacities and other thermodynamic properties (π_T (internal pressure), γ (heat capacity ratio), μ (adiabatic Joule–Thomson coefficient)),*
- measurements of combustion enthalpies in a bomb or flame calorimeter,
- equilibria, equilibrium constants (various concentration measurements)* [later],
- electromotive force of galvanic cells* [later].

*The methods marked by * are suitable for precise measurements of temperature dependence as well.*

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