

# Thermochemistry

## Lecture 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.

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

- Thermochemistry: 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 heat of reaction ( $q$ ):
  - at constant volume:  $q_V = \Delta U$ ,
  - at constant pressure:  $q_p = \Delta H$ .

## 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  $p^\theta = 1 \text{ bar}$  ( $1 \times 10^5 \text{ Pa}$ ) (*definition*).
  - **The standard enthalpy of formation for a compound**  $\Delta_{\text{form}} H^\theta$  is the enthalpy change accompanying its formation from its elements in the standard state.
  - **The standard enthalpy of formation of elements** is zero:  $H_{\text{m}}^\theta = 0 \text{ J/mol}$  *at any temperature!*

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

- **Standard enthalpy change of processes**  $\Delta H^\theta$ : 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).
  - $\Delta H^\theta = H_{m,f}^\theta - H_{m,i}^\theta$
  - $\Delta H^\theta$  values are given for  $n = 1$  mol (*intensive*)
  - The name of the **change** is given as subscript (in abbreviated form):  $\Delta_{\text{name}} H^\theta$
- **Standard enthalpies of formation** and **combustion** are especially important reaction enthalpies, but other may be of significance, too (e.g. enthalpy of neutralization).

Name of the process	Essence of the process	Symbol
Phase transition	$\alpha\text{-phase} \rightarrow \beta\text{-phase}$	$\Delta_{\text{trs}} H$
Melting	$s \rightarrow l$	$\Delta_{\text{fus}} H$
Evaporation	$l \rightarrow g$	$\Delta_{\text{vap}} H$
Sublimation	$s \rightarrow g$	$\Delta_{\text{sub}} H$
Mixing of liquids	pure substances $\rightarrow$ mixture	$\Delta_{\text{mix}} H$
Solution	pure solute $\rightarrow$ solution	$\Delta_{\text{sol}} H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{\text{hyd}} H$
Atomization	$(s, l, g) \rightarrow \text{atoms}(g)$	$\Delta_{\text{at}} H$
Ionization	$X(g) \rightarrow X^{+}(g) + e^{-}(g)$	$\Delta_{\text{i}} H$
Electron gain	$X(g) + e^{-}(g) \rightarrow X^{-}(g)$	$\Delta_{\text{eg}} H$
Reaction	reactants $\rightarrow$ products	$\Delta_{\text{r}} H$
Combustion	$\text{compound}(s, l, g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$	$\Delta_{\text{comb}} H$
Compound formation	elements $\rightarrow$ compound	$\Delta_{\text{form}} H$
Activation	reactants $\rightarrow$ activated complex	$\Delta H^{\#}$

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

physical changes

and

chemical changes

# 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  $\Delta_{\text{trs}}H^\theta$ .
- Some examples:
  - melting  $\rightleftharpoons$  freezing
  - evaporation  $\rightleftharpoons$  condensation
  - sublimation  $\rightleftharpoons$  deposition
  - solid phase transition (orthorhombic  $\rightleftharpoons$  monoclinic S)

# Enthalpies of physical changes

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

	$T_f / \text{K}$	$\Delta_{\text{fus}} H^\theta / (\text{kJ mol}^{-1})$	$T_b / \text{K}$	$\Delta_{\text{vap}} H^\theta / (\text{kJ mol}^{-1})$
He	3.5	0.02	4.2	0.084
Ar	84	1.2	87	6.5
C <sub>6</sub> H <sub>6</sub>	279	10.6	353	31
H <sub>2</sub> O	273	6.0	373	40.7

- All of them are positive as melting and evaporation are *endothermic*!
- Heat is produced at freezing or condensation (*exothermic*), so  $|\Delta_{\text{trs}} H^\theta|$  is the same, but the sign is the opposite.



# 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 reaction 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  $\Delta_r H^\theta$  values of reaction that are experimentally unfeasible. The Born-Haber cycle is such an application.]*

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

- A direct way to determine  $\Delta_r H^\theta$ : **measurement by calorimetry**. This is typically feasible for fast processes, but often problematic.
  - $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$  fast, easy ☺
  - $\text{C}_3\text{H}_6 + \text{H}_2 = \text{C}_3\text{H}_8$  do some thinking ☹
- $\Delta_r H^\theta$  can be **calculated from** the  $\Delta_{\text{form}} H^\theta$  **formation enthalpies** of reactants and products (if they are known).
  - *[Enthalpy of formation cannot be measured directly neither for  $\text{C}_3\text{H}_6$ , nor for  $\text{C}_3\text{H}_8$ !]*
- $\Delta_{\text{form}} H^\theta$  enthalpies of formation are not typically measurable directly but can be calculated from  $\Delta_{\text{comb}} H^\theta$  **combustion enthalpies** by Hess's law.
  - $\text{C}_3\text{H}_6(\text{g}) + 4,5 \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 3 \text{ H}_2\text{O}(\text{l})$  *enthalpy of combustion*
  - $\text{C}_3\text{H}_8(\text{g}) + 5 \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{l})$  *enthalpy of combustion.*

## IV. Calculation of reaction enthalpies from enthalpies of formation 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:

$$\blacksquare \Delta_r H^\theta = \sum_{\text{products}} \nu (\Delta_{\text{form}} H^\theta) - \sum_{\text{reactants}} \nu (\Delta_{\text{form}} H^\theta)$$

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

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

- $2 \text{HN}_3(l) + 2 \text{NO}(g) \rightarrow \text{H}_2\text{O}_2(l) + 4 \text{N}_2(g)$  reaction standard enthalpy of reaction:

$$\begin{aligned}\Delta_r H^\theta &= \\&= \left\{ \Delta_{\text{form}} H^\theta(\text{H}_2\text{O}_2, l) + 4 \cdot \Delta_{\text{form}} H^\theta(\text{N}_2, g) \right\} - \left\{ 2 \cdot \Delta_{\text{form}} H^\theta(\text{HN}_3, l) + 2 \cdot \Delta_{\text{form}} H^\theta(\text{NO}, g) \right\} = \\&= \left\{ 1 \cdot 188 \text{ kJ mol}^{-1} + 4 \cdot 0 \text{ kJ mol}^{-1} \right\} - \left\{ 2 \cdot 264 \text{ kJ mol}^{-1} + 2 \cdot 90 \text{ kJ mol}^{-1} \right\} = \\&= -892 \text{ kJ mol}^{-1}\end{aligned}$$

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

Calculation of the standard reaction enthalpy from enthalpies of combustion:

- The previous calculation can be based on combustions.

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

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

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

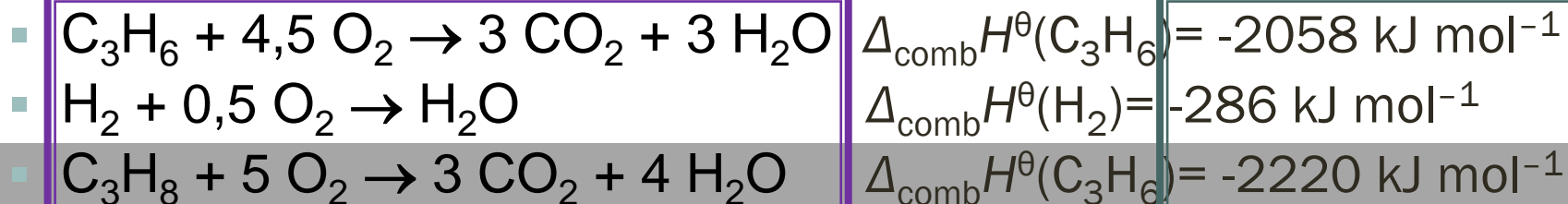
- Calculate  $\Delta_r H^\theta$  for the  $\text{C}_3\text{H}_6 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8$  reaction.
- All three substances can be burnt in a calorimeter
  - $\text{C}_3\text{H}_6 + 4,5 \text{ O}_2 \rightarrow 3 \text{ CO}_2 + 3 \text{ H}_2\text{O}$   $\Delta_{\text{comb}} H^\theta(\text{C}_3\text{H}_6) = -2058 \text{ kJ mol}^{-1}$
  - $\text{H}_2 + 0,5 \text{ O}_2 \rightarrow \text{H}_2\text{O}$   $\Delta_{\text{comb}} H^\theta(\text{H}_2) = -286 \text{ kJ mol}^{-1}$
  - $\text{C}_3\text{H}_8 + 5 \text{ O}_2 \rightarrow 3 \text{ CO}_2 + 4 \text{ H}_2\text{O}$   $\Delta_{\text{comb}} H^\theta(\text{C}_3\text{H}_8) = -2220 \text{ kJ mol}^{-1}$
- Standard enthalpy of the hydrogenation reaction:

$$\begin{aligned}\Delta_r H^\theta &= \left\{ \Delta_{\text{comb}} H^\theta(\text{C}_3\text{H}_6, \text{g}) + \Delta_{\text{comb}} H^\theta(\text{H}_2, \text{g}) \right\} - \left\{ \Delta_{\text{comb}} H^\theta(\text{C}_3\text{H}_8, \text{g}) \right\} = \\ &= \left\{ -2058 \text{ kJ mol}^{-1} + (-286 \text{ kJ mol}^{-1}) \right\} - \left\{ -2220 \text{ kJ mol}^{-1} \right\} = \\ &= -124 \text{ kJ mol}^{-1}\end{aligned}$$

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

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

- Calculate  $\Delta_r H^\theta$  for the  $\text{C}_3\text{H}_6 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8$  reaction.
- All three substances can be burnt in a calorimeter

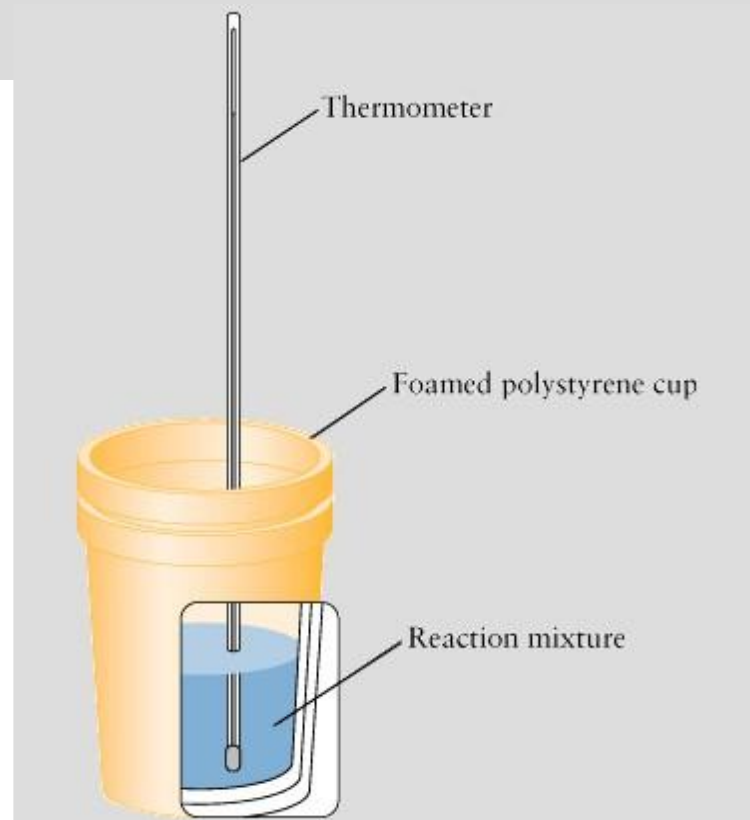
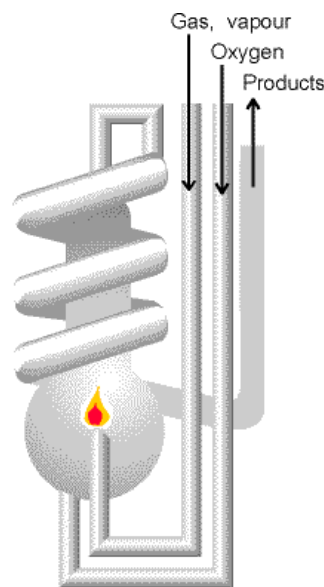
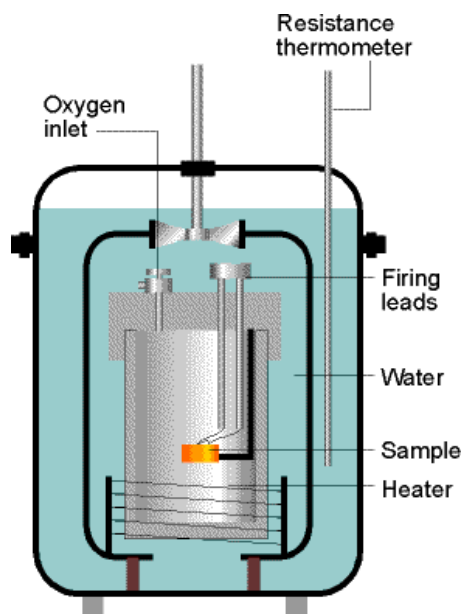


- Standard enthalpy of the hydrogenation reaction:

$$\begin{aligned}\Delta_r H^\theta &= \left\{ \Delta_{\text{comb}} H^\theta(\text{C}_3\text{H}_6, \text{g}) + \Delta_{\text{comb}} H^\theta(\text{H}_2, \text{g}) \right\} - \left\{ \Delta_{\text{comb}} H^\theta(\text{C}_3\text{H}_8, \text{g}) \right\} = \\ &= \left\{ -2058 \text{ kJ mol}^{-1} + (-286 \text{ kJ mol}^{-1}) \right\} - \left\{ -2220 \text{ kJ mol}^{-1} \right\} = \\ &= -124 \text{ kJ mol}^{-1}\end{aligned}$$

# V. Experimental determination of the heat of reaction, calorimetry

- simple calorimeter (for measuring e.g. enthalpy of dilution or neutralization)



- **bomb calorimeter** ( $C_V$ , ill.  $\Delta U$ )
- **flame calorimeter** ( $C_p$ , ill.  $\Delta H$ )
- Technical and biological importance of combustion.



# VI. Heat capacity, types of molar heat capacity.

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

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

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

- As it was shown earlier:
- 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:

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

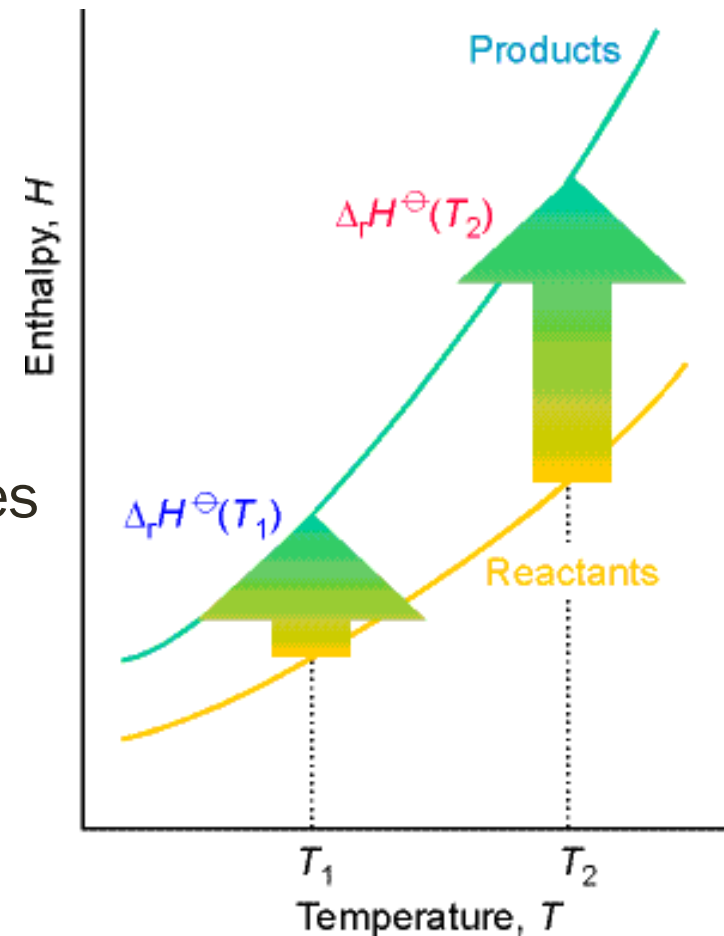
- In thermochemistry, this is called **Kirchhoff's law**.

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

- **Kirchhoff' law** (in a thermodynamic approach): the standard enthalpy of reaction at  $T_2$  can be calculated from  $\Delta_r H^\ominus(T_1)$  and the molar heat capacities of reactants and products:

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

$$\Delta_r C_{p,m} = \sum_{\text{products}} \nu(C_{p,m}) - \sum_{\text{reactants}} \nu(C_{p,m})$$

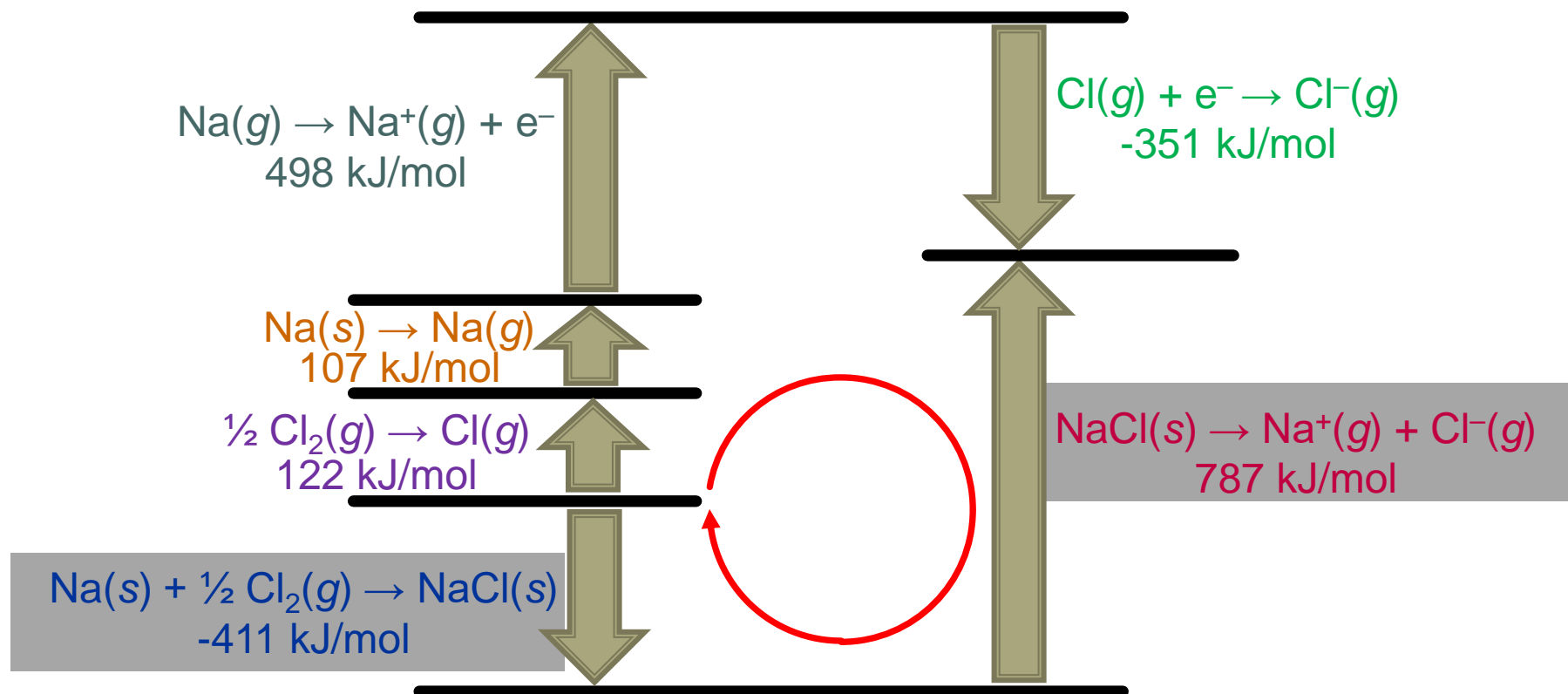


# VIII. The Born–Haber cycle.

- **A common application of the first law** is to calculate the  $\Delta_{\text{lat}}H^\theta$  lattice enthalpies of crystals or the  $\Delta_{\text{hyd}}H^\theta$  hydration enthalpies of ions, sometimes the  $\Delta_{\text{ea}}H^\theta$  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!
- $\frac{1}{2} \Delta_{\text{diss}}H^\theta(\text{Cl}_2) + \Delta_{\text{sub}}H^\theta(\text{Na}) + \Delta_{\text{i}}H^\theta(\text{Na}) + \Delta_{\text{ea}}H^\theta(\text{Cl}) + \Delta_{\text{hyd}}H^\theta(\text{NaCl}) - \Delta_{\text{f}}H^\theta(\text{NaCl},aq) = 0$
- $\frac{1}{2} \Delta_{\text{diss}}H^\theta(\text{Cl}_2) + \Delta_{\text{sub}}H^\theta(\text{Na}) + \Delta_{\text{i}}H^\theta(\text{Na}) + \Delta_{\text{ea}}H^\theta(\text{Cl}) - \Delta_{\text{lat}}H^\theta(\text{NaCl}) - \Delta_{\text{f}}H^\theta(\text{NaCl},s) = 0$

# VIII. The Born–Haber cycle.

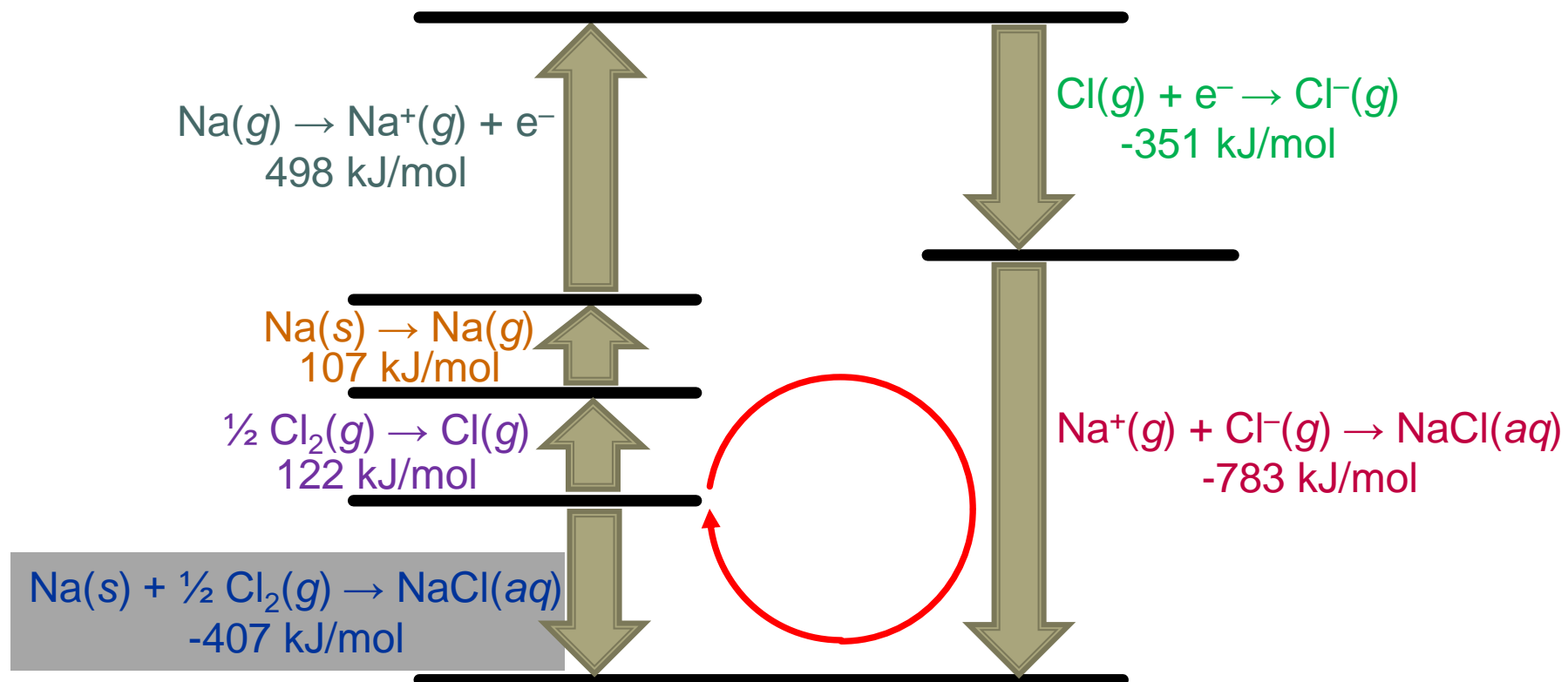
## Determination of lattice enthalpy



$$\frac{1}{2} \Delta_{\text{diss}} H^{\ominus}(\text{Cl}_2) + \Delta_{\text{sub}} H^{\ominus}(\text{Na}) + \Delta_{\text{i}} H^{\ominus}(\text{Na}) + \Delta_{\text{ea}} H^{\ominus}(\text{Cl}) - \Delta_{\text{lat}} H^{\ominus}(\text{NaCl}) - \Delta_{\text{f}} H^{\ominus}(\text{NaCl, s}) = 0$$

# VIII. The Born–Haber cycle.

## Determination of the enthalpy of hydration



$$\frac{1}{2} \Delta_{\text{diss}} H^\theta(\text{Cl}_2) + \Delta_{\text{sub}} H^\theta(\text{Na}) + \Delta_i H^\theta(\text{Na}) + \Delta_{\text{ea}} H^\theta(\text{Cl}) + \Delta_{\text{hyd}} H^\theta(\text{NaCl}) - \Delta_f H^\theta(\text{NaCl, aq}) = 0$$