DTU

47201 Engineering thermodynamics

Module 10

Recap: Enthalpy, C_v, and C_p

Variation of internal energy:

$$dU = \delta Q + \delta W$$

Boundary work

$$\delta W = -PdV$$

Enthalpy: $H = U + PV$

$$dH = dU + d(PV) = dU + PdV + VdP$$

Heat capacity

$$C = \frac{\delta Q}{\delta T}$$

At constant volume

$$dU = \delta Q \longrightarrow C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

At constant pressure:

$$dH = \delta Q \longrightarrow C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

At a given temperature, which one has more internal energy?

$C + O_2$

or

CO_2

Reaction heat (const. volume)

$$\Delta u = q_V + \cancel{w}$$

$$A \rightarrow B$$

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If the reaction occurs at *constant temperature,* the heat of reaction is exchanged between the system and its surroundings.

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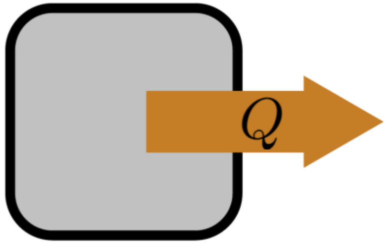
exothermic reaction

$$q_V < 0$$

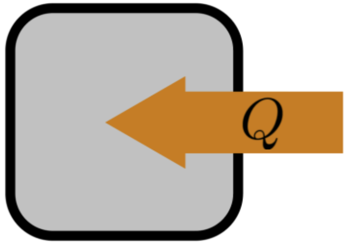


releases heat to the surroundings

produces a temperature increase

endothermic reaction

$$q_V > 0$$



absorbs heat from the surroundings

produces a temperature decrease

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If the reaction occurs in an *isolated system*, it produces a change in the temperature of the system.

exothermic reaction

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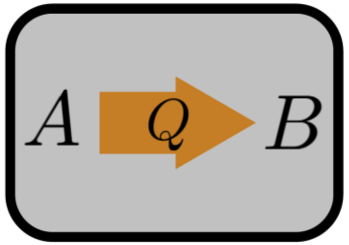

reaction releases heat

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endothermic reaction

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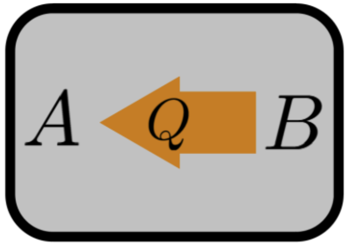

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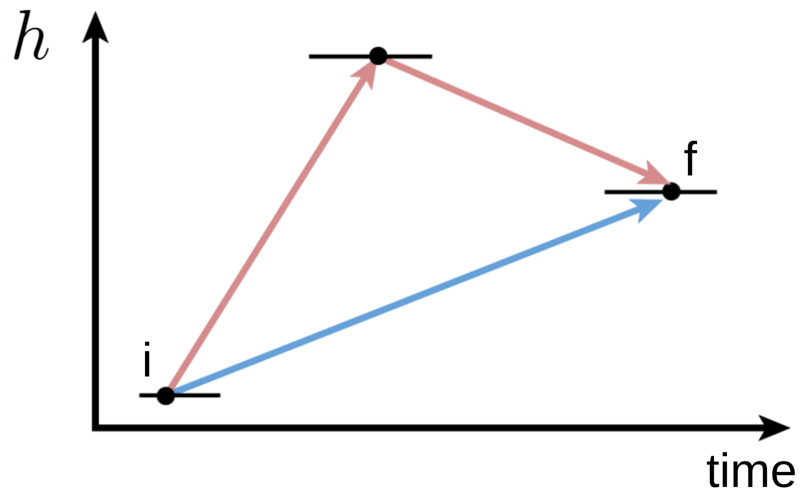
Hess’s law

The enthalpy of a chemical process is independent of the path taken from the initial to the final state



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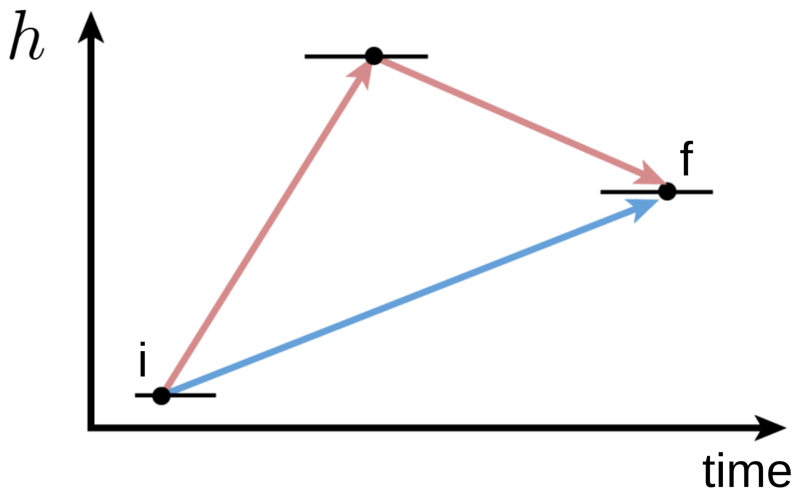

$$\frac{1}{2}\mathrm{N_2(g)} + \mathrm{O_2(g)} \rightarrow \mathrm{NO_2(g)} \qquad \Delta H^\circ = ?$$

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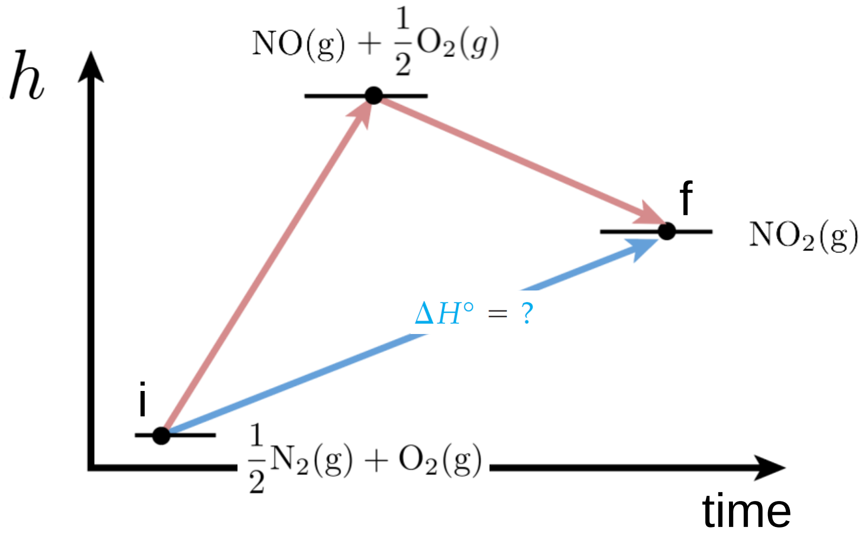

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g) \qquad \Delta H° = +90.25\,\text{kJ}$$

$$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad \Delta H° = -57.07\,\text{kJ}$$

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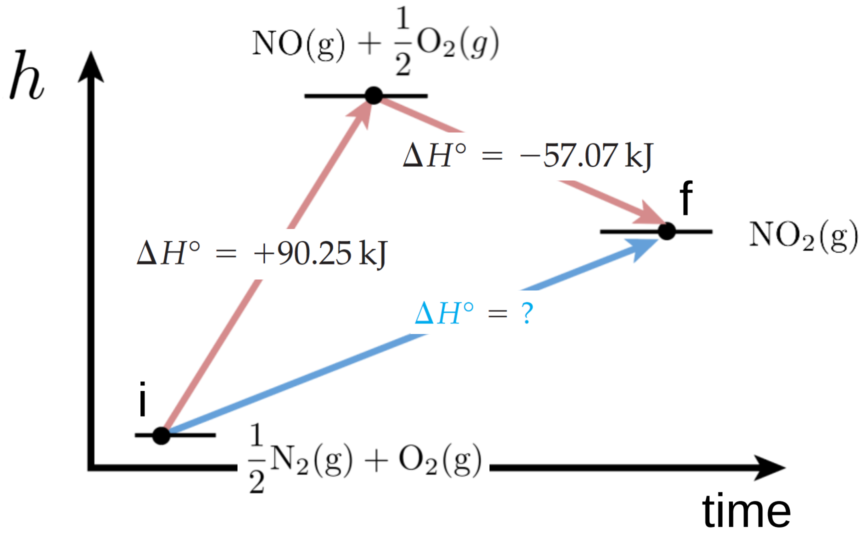

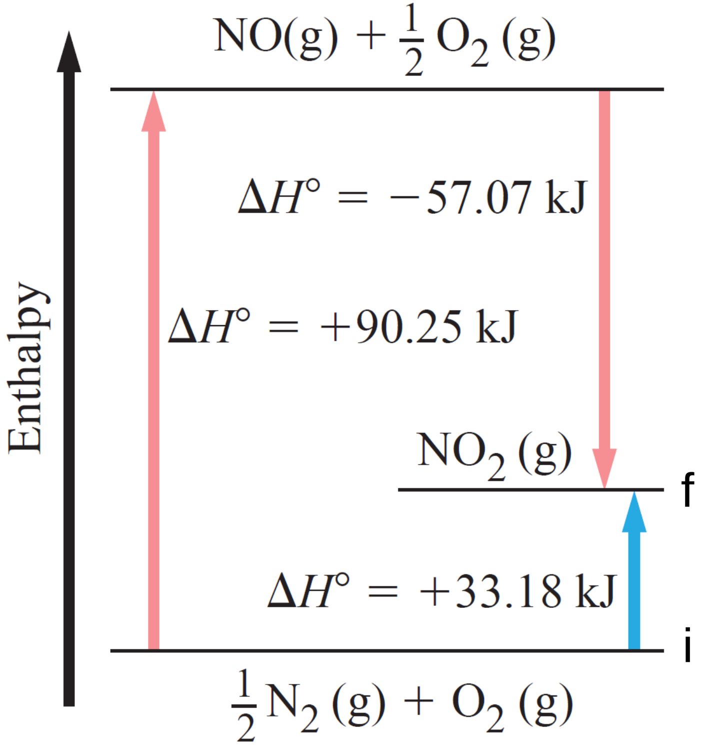

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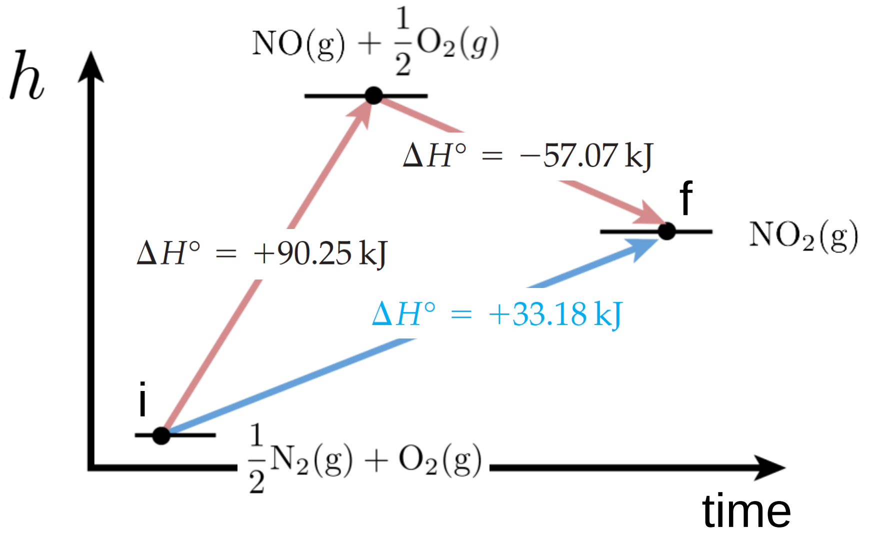

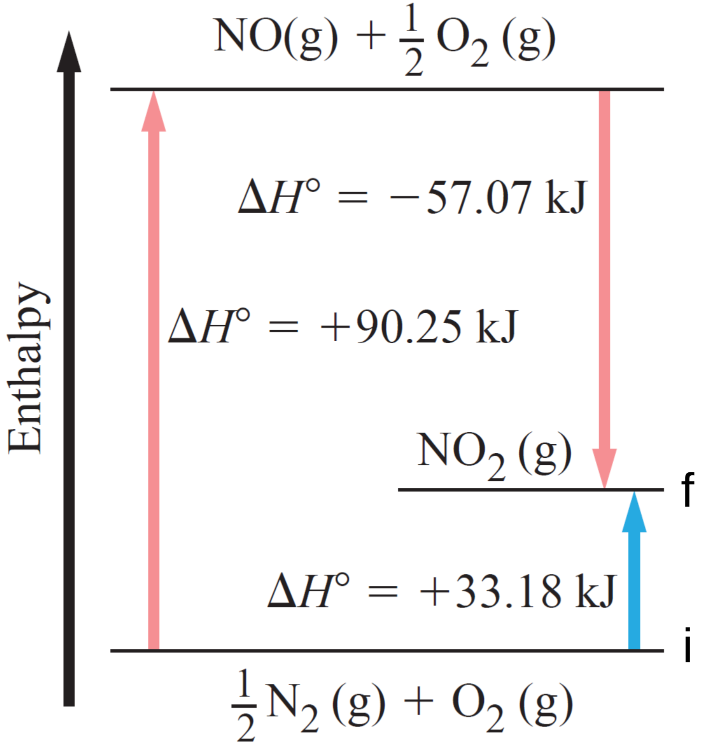

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Enthalpy of formation

Change of enthalpy during the formation of 1 mole of the substance from its constituent elements in their reference form.

The standard enthalpy of formation of a pure element in its reference form is 0.

Reference form means the molecules spontaneously formed by elements, e.g. H_2

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Why is this useful?

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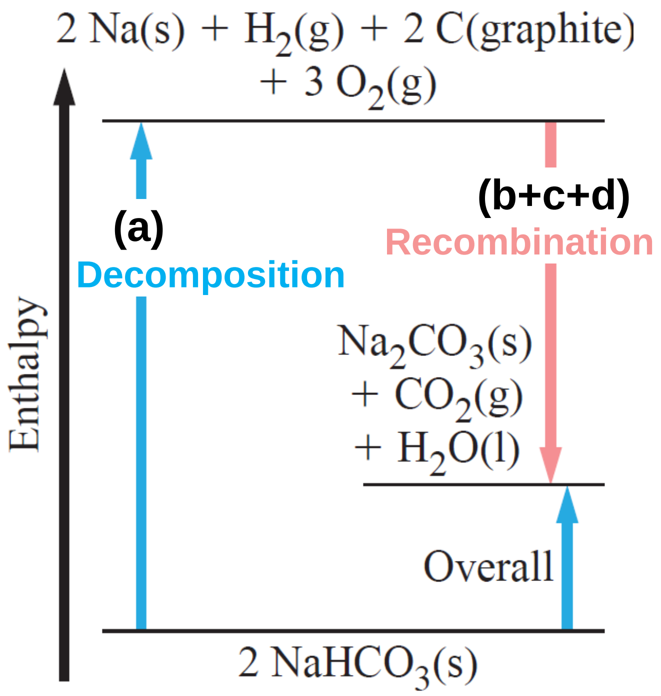

$$2\,NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g) \qquad \Delta H^\circ = ?$$

Enthalpy of formation

Decomposition

(a) $2\,NaHCO_3(s) \longrightarrow 2\,Na(s) + H_2(g) + 2\,C\,(graphite) + 3\,O_2(g)$

$$\Delta H^\circ = -2 \times \Delta H_f^\circ[NaHCO_3(s)]$$

Recombination

(b) $2\,Na(s) + C(graphite) + \frac{3}{2}O_2(g) \longrightarrow Na_2CO_3(s)$

$$\Delta H^\circ = \Delta H_f^\circ[Na_2CO_3(s)]$$

(c) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\quad \Delta H^\circ = \Delta H_f^\circ[H_2O(l)]$

(d) $C(graphite) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H^\circ = \Delta H_f^\circ[CO_2(g)]$

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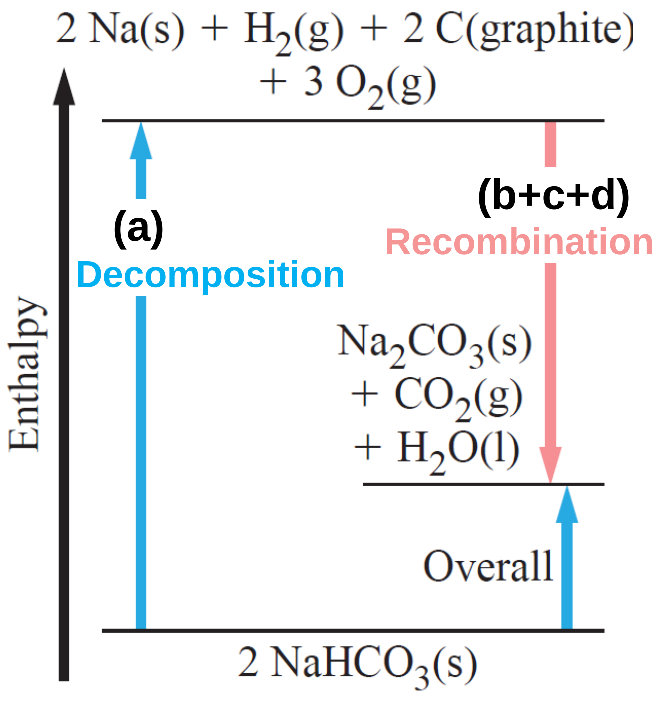

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Enthalpy of formation

[See wikipedia page](#)

Thermochemical properties of selected substances at 298.15 K and 1 atm

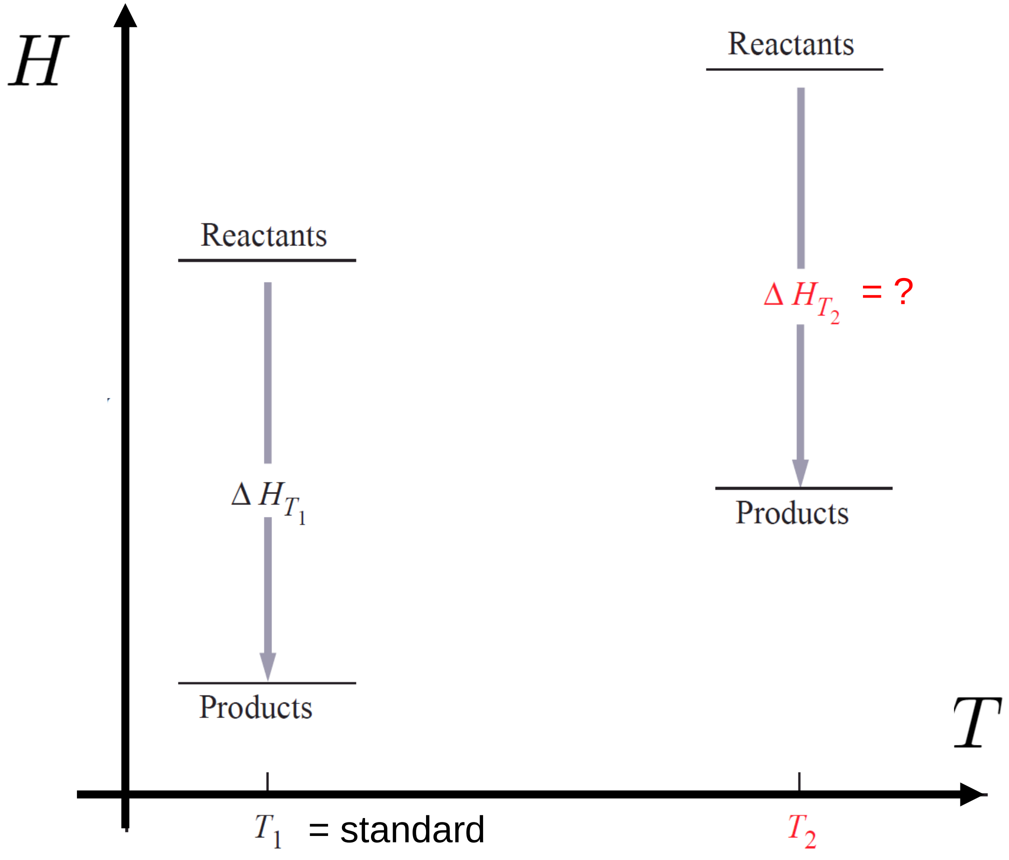
Inorganic substances [edit]

Species	Phase	Chemical formula	$\Delta_f H^{\ominus}$ /(kJ/mol)
Aluminium	Solid	Al	0
Aluminium chloride	Solid	$AlCl_3$	−705.63
Aluminium oxide	Solid	Al_2O_3	−1675.5
Aluminium hydroxide	Solid	$Al(OH)_3$	−1277
Aluminium sulphate	Solid	$Al_2(SO_4)_3$	−3440
Barium chloride	Solid	$BaCl_2$	−858.6
Barium carbonate	Solid	$BaCO_3$	−1216
Barium hydroxide	Solid	$Ba(OH)_2$	−944.7
Barium oxide	Solid	BaO	−548.1
Barium sulfate	Solid	$BaSO_4$	−1473.3
Beryllium	Solid	Be	0
Beryllium hydroxide	Solid	$Be(OH)_2$	−903
Beryllium oxide	Solid	BeO	−609.4
Boron trichloride	Solid	BCl_3	−402.96
Bromine	Liquid	Br_2	0
Bromide ion	Aqueous	Br^-	−121

Temperature dependence

Standard enthalpies of formation refer to standard pressure (10^5 Pa) and specified temperature T_1 (which may vary, but often is 25 °C = 298.15 K).

How do we calculate the reaction enthalpy if the reaction happens at a different temperature T_2?



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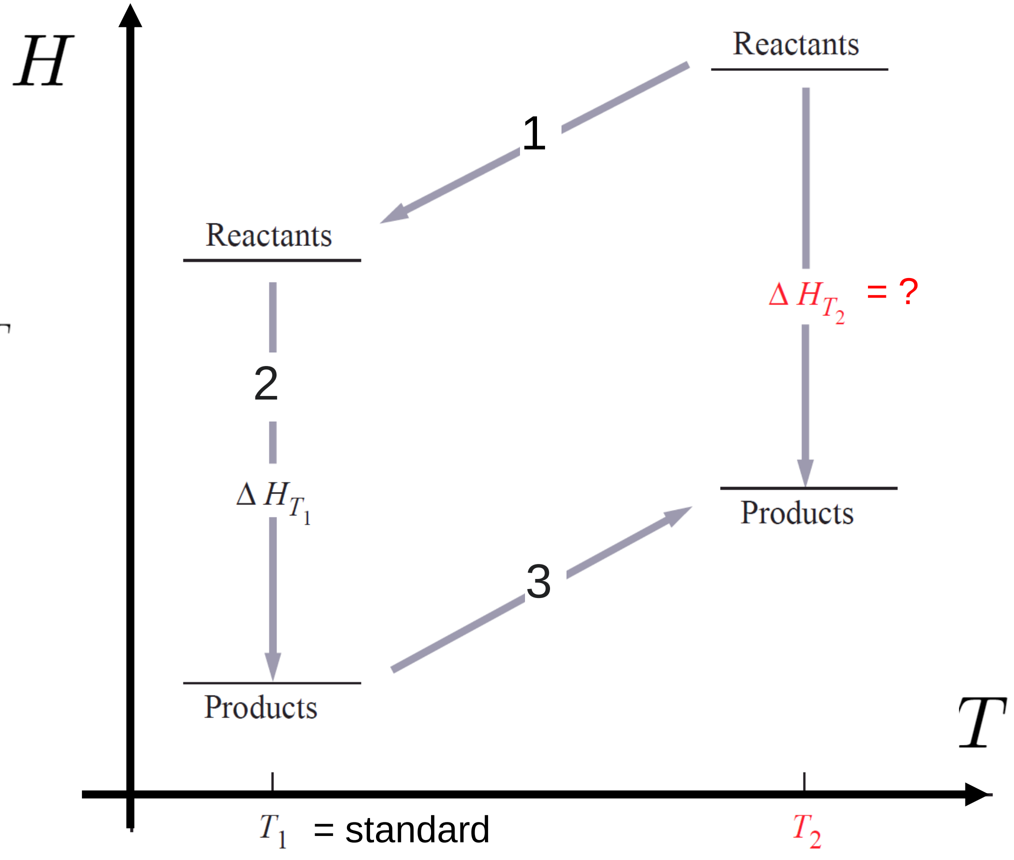
We split it in steps and apply conservation of energy:

1. We bring the reactants from T_2 to T_1: $$\Delta H = \sum_{\text{Reactants}} \int_{T_2}^{T_1} C_p(T)dT$$
2. We perform the reaction at standard temperature T_1
3. We bring the products back to T_2: $$\Delta H = \sum_{\text{Products}} \int_{T_1}^{T_2} C_p(T)dT$$

We add the enthalpy variations for the three steps.



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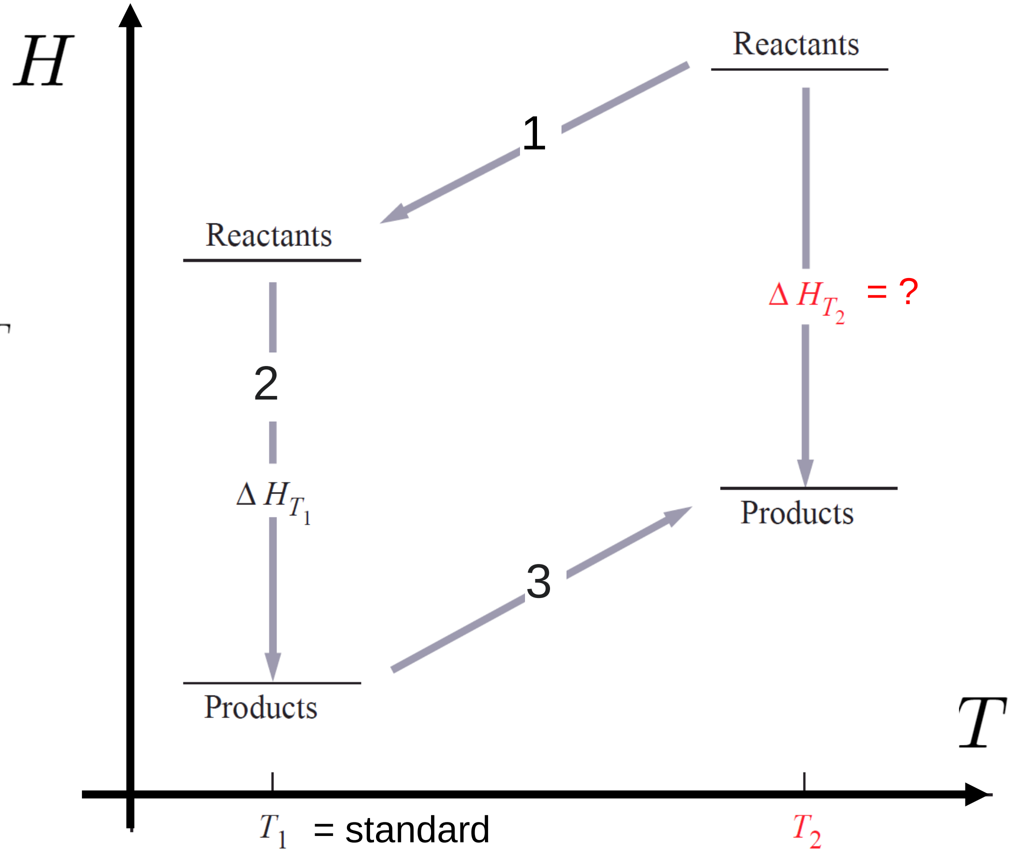
The result might be different due to the different heat capacities between reactants and products.



Constant volume reactions

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For obtaining the heat of reaction at constant pressure, we need to consider the work done against the external pressure.

$$q_V = q_P + w$$

Is it clear why do we have a plus sign?

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While at constant pressure some energy is used for boundary work, at constant volume all the energy is entirely converted into heat.

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$$w = -P\Delta v$$ work that would be done in const. P

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Sometimes, we just need to consider the gases (using the ideal gas law) since the volumes of solids and liquids are very small in comparison.

Reactions happening at a different pressure

Standard enthalpies of formation refer to standard pressure (P_1 =10^5 Pa) and specified temperature T.

How do we calculate the reaction enthalpy (heat of reaction) if the reaction happens at a different pressure P_2?

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We need to consider again the work done against the external pressure.

$$q_V = q_{P_1} + w_1 = q_{P_2} + w_2$$

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To calculate the work, we need to know the pressure and specific volumes of all the reactants and products (at the right pressure!).

$$w_1 = -P_1 \Delta v_1$$

$$w_2 = -P_2 \Delta v_2$$

Conclusions

There is some book-keeping to be done, but ultimately it always boils down to conservation of energy.

One always has to remember that specific enthalpy and specific internal energy are state functions: for each substance they only depend on the temperature.

Since they are extensive properties, they are proportional to the amount of each substance, and we have to sum the contributions for each chemical compound.