



INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

THERMOCHEMISTRY

Enthalpy H

= Indication of a total of a substance, it is not possible to be measured but we can measure enthalpy ΔH

Enthalpy change ΔH

= Energy change of a reaction, which occurs at constant, reactants and products, are of the same (energy accepted by the reacting system).

ΔH $0 \text{ kJ}\cdot\text{mol}^{-1} \Rightarrow$ reaction needs energy, heat energy is converted to energy \Rightarrow *ENDOTHERMIC/EXOTHERMIC* reaction

ΔH $0 \text{ kJ}\cdot\text{mol}^{-1} \Rightarrow$ energy is evolved during a reaction, energy is converted to energy \Rightarrow *ENDOTHERMIC/EXOTHERMIC* reaction. Released energy the temperature of the system and then it is transferred to the surroundings as the temperature returns to normal.

Standard enthalpy change ΔH°

= Enthalpy change for a reaction which occurs at a pressure of 101 325 Pa and a temperature of 298 K (25°C).

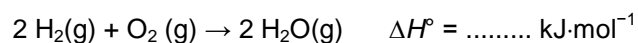
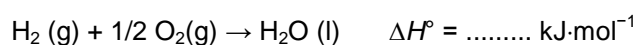
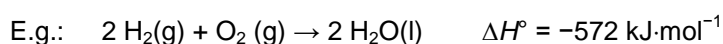
1. Classify the following changes as exothermic or endothermic:

- Water vapour condenses to liquid water in clouds.
- H_2SO_4 dissolves in water and the temperature of the solution rises
- Dry ice (solid CO_2) sublimates spontaneously at room temperature.
- NaCl is mixed with ice in the mass ratio 1:3 and the temperature of the surrounding drops to -20°C .
- Oxygen and hydrogen combine explosively to form water

Thermochemical equations

Equations summarising all the information needed in the study of energetics

- Amounts of reactants and products (moles)
- Phases of reactants and products: s =
l =
g =
aq =
- Quantity of energy involved





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2. Use the equations above to calculate the enthalpy change when:
 - a. 4 moles of liquid water are formed from its elements
 - b. 5 moles of hydrogen burn with oxygen to form liquid water
 - c. 64 grams of oxygen react with hydrogen to form water vapour

3. $2 \text{ Al (s)} + 3 \text{ Cl}_2(\text{l}) \rightarrow 2 \text{ AlCl}_3(\text{s}) \quad \Delta H^\circ = -705.63 \text{ kJ}\cdot\text{mol}^{-1}$
 Calculate the enthalpy change when 270 g of aluminium react with chlorine to form solid aluminium chloride according to the equation above.

4. Write a thermochemical equation showing that when 1 mole of carbon burns completely in oxygen, 394 kJ of heat are liberated.

5. Calculate the enthalpy change on complete combustion of:
 - a. 3 mol of carbon
 - b. 0.1 mol of carbon
 - c. 6 g of carbon
 - d. 50 g of carbon

6. What mass of carbon would have to be burnt to produce:
 - a. 788 kJ
 - b. 1000 kJ

Labelling enthalpy changes:

Certain types of reactions and their enthalpy changes are tabulated (they may be found in a book of data)

Standard enthalpy change of formation ΔH_f° (teplo)

The heat absorbed when one mole of a substance is formed from its elements under standard conditions, e.g. enthalpy change of formation of toluene: $\Delta H_f^\circ [\text{C}_6\text{H}_5\text{CH}_3 (\text{l})] = 12 \text{ kJ}\cdot\text{mol}^{-1}$ response to a reaction described by the equation: $7 \text{ C (s)} + 4 \text{ H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_5\text{CH}_3 (\text{l})$

$\Delta H_f^\circ[\text{element(its standard state)}] = \dots\dots \text{ kJ}\cdot\text{mol}^{-1}$

7. The value of the enthalpy change of formation of barium hydrogen carbonate is $-1922 \text{ kJ}\cdot\text{mol}^{-1}$.
Write down the complete thermochemical equation for this enthalpy change.
8. Write down thermochemical equations for the following enthalpy changes of formation, find their values in the books of data.
 - a. $\Delta H_f^\circ[\text{CuSO}_4\cdot 5\text{H}_2\text{O}(\text{s})]$
 - b. $\Delta H_f^\circ[\text{C}_6\text{H}_6(\text{l})]$
 - c. $\Delta H_f^\circ[\text{KClO}_3(\text{s})]$



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Standard enthalpy change of combustion ΔH_c° (teplo

= The enthalpy change when 1 mole of the substance is completely burnt in oxygen under standard conditions

Mainly for organic substances (substances containing carbon, hydrogen (and oxygen) burn to produce carbon dioxide and water (liquid).

9. The value of the enthalpy change of combustion of toluene is $-3910 \text{ kJ}\cdot\text{mol}^{-1}$. Write down the complete thermochemical equation for this process.
10. Write down thermochemical equations for the following enthalpy changes of combustion; find their values in the books of data.
- $\Delta H_c^\circ[\text{HCOOH}(l)]$ (formic acid)
 - $\Delta H_c^\circ[\text{C}_6\text{H}_6(l)]$ (benzene)
 - $\Delta H_c^\circ[\text{CH}_3\text{OH}(l)]$ (methanol)
 - $\Delta H_c^\circ[\text{Ca}(s)]$
 - $\Delta H_c^\circ[\text{C}_6\text{H}_5\text{NO}_2(l)]$ (nitrobenzene)
11. Select the specific terms which describe the enthalpy changes of the following reactions:
- $\text{C}_2\text{H}_5\text{OH}(l) + 3 \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 3 \text{H}_2\text{O}(l)$
 - $\text{H}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$
 - $\text{P}(\text{red}) + 5/4 \text{O}_2(g) \rightarrow 1/4 \text{P}_4\text{O}_{10}(s)$
- Using your book of data, list the numerical value of the enthalpy change in each of these reactions.
12. Write complete thermochemical equations showing:
- the standard heat of combustion of ethane, C_2H_4
 - the standard heat of formation of magnesium chloride, MgCl_2
 - the standard heat of formation of ethanoic acid, CH_3COOH
13. Write thermochemical equations (including the values of ΔH°) to represent the following reactions at standard conditions:
- the combustion of 2 moles of sulphur
 - the formation of 1 mole of $\text{AlCl}_3(s)$ from its elements
 - the combustion of 1 mol of pentane, $\text{C}_5\text{H}_{12}(g)$

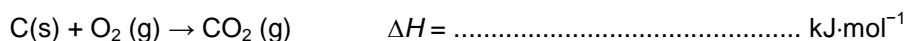
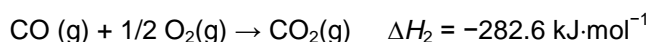
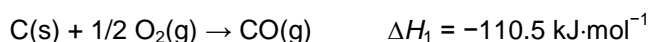
First law of thermochemistry

14. Use the book of data to write down the thermochemical equation for:
- the formation of $\text{HI}(g)$
 - the decomposition of $\text{HI}(g)$ to hydrogen and solid iodine.

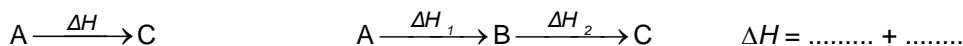
- c. the enthalpy change of combustion of glucose.
d. the photosynthesis.

The values of an enthalpy change of a reaction and a reaction which takes place at the same conditions in the opposite direction, are and they differ in the

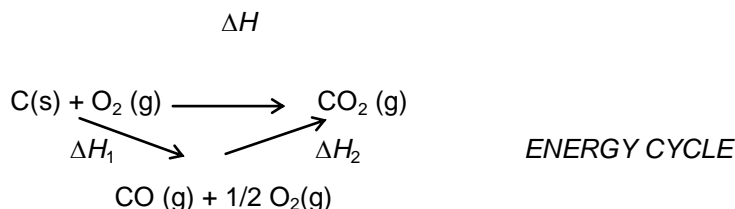
Second law of thermochemistry



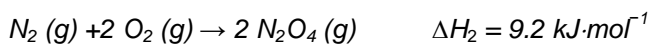
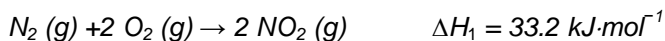
Hess' law: The standard reaction enthalpy is the sum of the standard reaction enthalpies of each step into which the reaction can be formally divided.



The heat of reaction doesn't depend on the way the reaction occurs but only on the initial and final states of reactants and products.

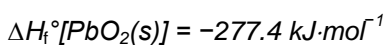


15. Use the second law of thermochemistry and the energy cycle to calculate the standard enthalpy change for the reaction $2 \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ given the thermochemical equations:



(-24 kJ·mol⁻¹)

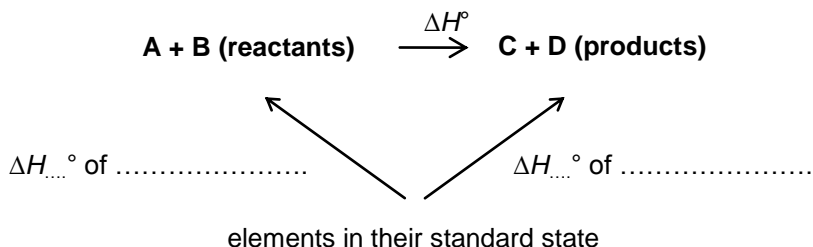
16. Use the second law of thermochemistry and the energy cycle to calculate the standard enthalpy change for the reaction $\text{PbO(s)} + 1/2 \text{O}_2(\text{g}) \rightarrow \text{PbO}_2(\text{s})$ given $\Delta H_f^\circ[\text{PbO(s)}] = -219 \text{ kJ}\cdot\text{mol}^{-1}$



(-58.4 kJ·mol⁻¹)

Calculating the standard enthalpy changes

1. from standard heats of formation, ΔH_f°



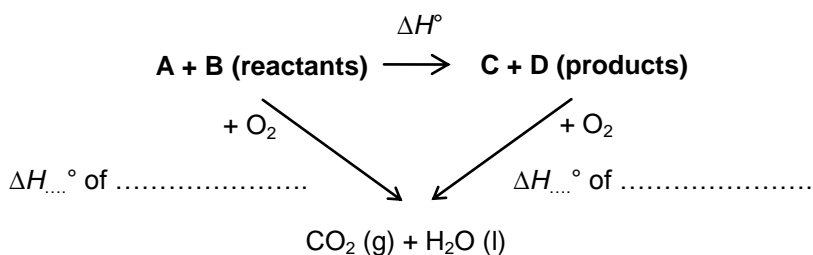
$$\Delta H^\circ = \sum \Delta H_f^\circ (\dots\dots\dots) - \sum \Delta H_f^\circ (\dots\dots\dots)$$

17. Calculate the standard enthalpy change of the following reactions using ΔH_f° .

- $2 \text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) \rightarrow 3 \text{S}(\text{rombic}) + 2 \text{H}_2\text{O}(\text{l})$ ($\Delta H_f^\circ(\text{H}_2\text{S}(\text{g})) = -20.63 \text{ kJ}\cdot\text{mol}^{-1}$) $(-233 \text{ kJ}\cdot\text{mol}^{-1})$
- $\text{CH}_3\text{OH}(\text{l}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$ $(-726.5 \text{ kJ}\cdot\text{mol}^{-1})$
- $\text{ZnCO}_3(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{CO}_2(\text{g})$ $(-71 \text{ kJ}\cdot\text{mol}^{-1})$
- $2 \text{Al}(\text{s}) + \text{Fe}_2\text{O}_3(\text{s}) \rightarrow 2 \text{Fe}(\text{s}) + \text{Al}_2\text{O}_3(\text{s})$ $(-851 \text{ kJ}\cdot\text{mol}^{-1})$
- $\text{MgO}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{MgCO}_3(\text{s})$ ($\Delta H_f^\circ(\text{MgO}(\text{s})) = -601.24 \text{ kJ}\cdot\text{mol}^{-1}$,
 $\Delta H_f^\circ(\text{MgCO}_3(\text{s})) = -20.63 \text{ kJ}\cdot\text{mol}^{-1}$) $(974 \text{ kJ}\cdot\text{mol}^{-1})$
- $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CO}(\text{g}) + 3 \text{H}_2(\text{g})$ $(250.5 \text{ kJ}\cdot\text{mol}^{-1})$
- $1/2 \text{N}_2(\text{g}) + 3/2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_3(\text{g}) + 3/4 \text{O}_2(\text{g})$ $(383 \text{ kJ}\cdot\text{mol}^{-1})$
- $\text{HCl}(\text{g}) + \text{C}_2\text{H}_4(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{Cl}(\text{g})$ ($\Delta H_f^\circ[\text{CH}_3\text{CH}_2\text{Cl}(\text{g})] = -106.7 \text{ kJ}\cdot\text{mol}^{-1}$) $(-66.7 \text{ kJ}\cdot\text{mol}^{-1})$
- $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$ $(-176 \text{ kJ}\cdot\text{mol}^{-1})$

18. Classify each of the reactions as endothermic or exothermic.

2. from standard heats of combustion, ΔH_c°



$$\Delta H^\circ = \sum \Delta H_c^\circ (\dots\dots\dots) - \sum \Delta H_c^\circ (\dots\dots\dots)$$

19. Calculate the standard enthalpy change of the following reactions using ΔH_c°

- $\text{C}_2\text{H}_2(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$ $\Delta H_c^\circ[\text{H}_2(\text{g})] = \Delta H_f^\circ[\text{H}_2\text{O}(\text{l})]$ $(-311 \text{ kJ}\cdot\text{mol}^{-1})$
- $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$ $(-137 \text{ kJ}\cdot\text{mol}^{-1})$

- c. $C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$ $\Delta H_c^\circ[H_2O(l)] = 0 \text{ kJ}\cdot\text{mol}^{-1}$ water doesn't burn $(-44 \text{ kJ}\cdot\text{mol}^{-1})$
- d. $C_2H_5OH(l) \rightarrow CH_3CHO(l) + H_2(g)$ $(99 \text{ kJ}\cdot\text{mol}^{-1})$
- e. $C_2H_5OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(l)$ $(-492 \text{ kJ}\cdot\text{mol}^{-1})$
- f. $2 \text{ CH}_3\text{OH}(l) \rightarrow \text{H}_2\text{O}(l) + \text{CH}_3\text{OCH}_3(g)$ ($\Delta H_c^\circ[\text{CH}_3\text{OCH}_3(g)] = -1460 \text{ kJ}\cdot\text{mol}^{-1}$) $(-18 \text{ kJ}\cdot\text{mol}^{-1})$

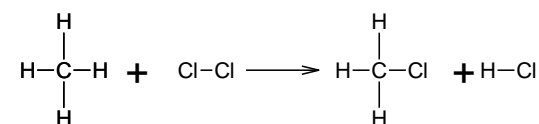
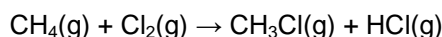
3. from bond enthalpies, H_D

Bond enthalpy = the energy needed to break a particular bond in a particular compound

A chemical reaction = breaking the bonds of reactants (energy needed) + forming new bonds in products (energy liberated)

Worked example:

Calculate the standard enthalpy change of the following reaction using bond enthalpies



Bonds broken:

(energy

Bonds made:

(energy

$$\Delta H_r = \sum H_D(\text{bonds in}) - \sum H_D(\text{bonds in})$$

20. Calculate the standard enthalpy change of the following reactions using H_D . Use the values from the books of data and the following: $H_D(\text{C}=\text{C})_{\text{in } C_3H_8} = 598 \text{ kJ}\cdot\text{mol}^{-1}$, $H_D(\text{C}-\text{C})_{\text{in } C_3H_8} = 356 \text{ kJ}\cdot\text{mol}^{-1}$, $H_D(\text{C}-\text{Br}) = 284 \text{ kJ}\cdot\text{mol}^{-1}$, $H_D(\text{C}-\text{Cl})_{\text{in } C_2H_5Cl} = 340 \text{ kJ}\cdot\text{mol}^{-1}$ (it is about the same in all halogenoalkanes), $H_D(\text{C}-\text{OH}) = 427 \text{ kJ}\cdot\text{mol}^{-1}$, $H_D(\text{C}-\text{I}) = 238 \text{ kJ}\cdot\text{mol}^{-1}$, $H_D(\text{C}=\text{C})_{\text{in } C_2H_4} = 682 \text{ kJ}\cdot\text{mol}^{-1}$. For $H_D(\text{C}-\text{H})$ and $H_D(\text{C}-\text{C})$ in ethanol (C_2H_5OH) and iodoethane (C_2H_5I) use the values for corresponding $H_D(\text{C}-\text{H})$ and $H_D(\text{C}-\text{C})$ in ethane (C_2H_6) (in books of data).

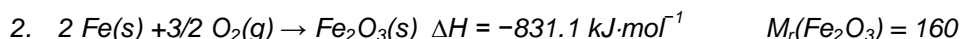
- a. $H_2(g) + Cl_2(g) \rightarrow 2 \text{ HCl}(g)$ $(-184 \text{ kJ}\cdot\text{mol}^{-1})$
- b. $\text{CH}_2=\text{CH}-\text{CH}_3(g) + \text{Br}_2(g) \rightarrow \text{CH}_2\text{BrCHBrCH}_3(g)$ $(-132 \text{ kJ}\cdot\text{mol}^{-1})$
- c. $C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + \text{HCl}(g)$ $(-118.5 \text{ kJ}\cdot\text{mol}^{-1})$
- d. $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$ $(-24 \text{ kJ}\cdot\text{mol}^{-1})$
- e. $C_2H_4(g) + \text{HI}(g) \rightarrow C_2H_5I(g)$ $(-35.6 \text{ kJ}\cdot\text{mol}^{-1})$

Further questions:

1. $C_3H_8(g) + 5 \text{ O}_2(g) \rightarrow 3 \text{ CO}_2(g) + 4 \text{ H}_2\text{O}(l)$ $\Delta H = -2.19 \text{ MJ}\cdot\text{mol}^{-1}$, calculate:
- a. heat liberated by burning 1g of propane (49.77 kJ)
- b. ΔH for making 5 moles of CO_2 by burning propane (-3.65 MJ)

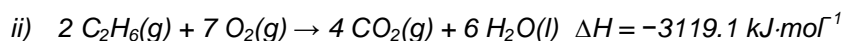
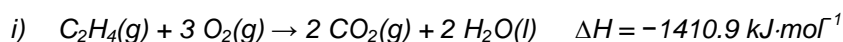
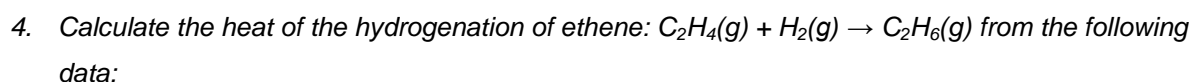
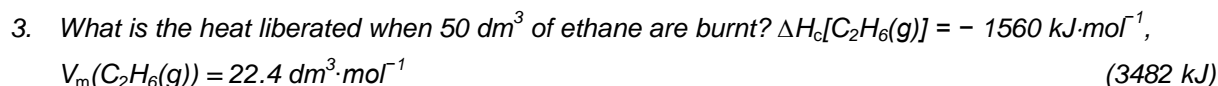


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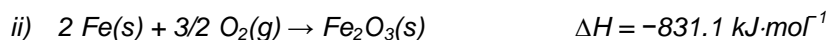
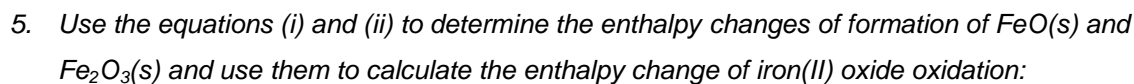


Calculate the heat liberated when:

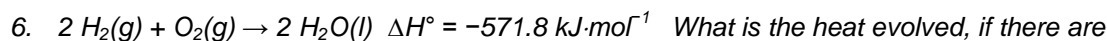
- 0.1 mol of iron reacts (41.555 kJ)
- 0.5 mol of iron reacts (207.775 kJ)
- 320 g of the product is made (1662.2 kJ)
- 400 g of the product is made (2077.75 kJ)



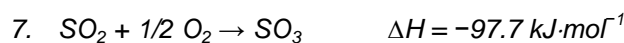
(-637.25 kJ·mol⁻¹)



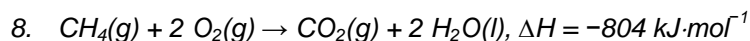
(-292.7 kJ·mol⁻¹)



- 7 moles of hydrogen and 3 moles of oxygen in the reacting mixture at the beginning of the reaction? (17154 kJ)
- 1 moles of H₂ and 0.5 moles of O₂? (285.9 kJ)
- 5 moles of water are made? (1429.5 kJ)



- What is ΔH of a decomposition of 2 moles of sulphur trioxide to oxygen and sulphur dioxide? (195.4 kJ)
- What is ΔH of a reaction of 2 moles of sulphur dioxide with oxygen? (-195.4 kJ)



What is the heat liberated when:

- 0.5 mol of methane is burnt? (402 kJ)
- 2.5 mol of methane is burnt? (2010 kJ)
- 11 g of carbon dioxide is made this way? (201 kJ)