Thermochemistry

- part of thermodynamics (study of heat)
- the study of energy transfer during reactions
- defined through “system” and “surroundings”

Energy Flow in Thermochemistry

\[ \Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}} \]

- system loses energy \( \Delta E < 0 \)
- system gains energy \( \Delta E > 0 \)
Heat and Work: Two Forms of Energy

Heat \((q)\) as thermal energy
Work \((w)\) as all other (mechanical, electrical etc)

\[ \Delta E = q + w \]

Heat

no work, \(w = 0\)

\[ \Delta E = q \]

In this case, \(q\) and \(\Delta E\) are negative
Work
no heat, $q = 0$

$\Delta E = w$

In this case, $w$ and $\Delta E$ are positive
Units of Energy

The SI unit

1 Joule = 1 kg\( \cdot \)m\(^2\)/s\(^2\)

calorie: energy to heat 1 g of H\(_2\)O by 1 °C

1 cal = 4.184 J

1 kJ = 1000 J \quad 1 \text{kcal} = 1000 \text{cal}

The First Law of Thermodynamics

\[ \Delta E_{\text{universe}} = 0 \]

energy is exchanged, not created or destroyed
Energy is a State Function

$\Delta E$ is independent of how the change takes place

1. $C + O_2 \rightarrow CO + O_2 \rightarrow CO_2$

2. $C + O_2 \rightarrow CO_2$

Overall $\Delta E$ is the same!

Enthalpy ($H$): Heat at Constant $P$

Pressure is equal in the initial and final states

$w = -P\Delta V$

Enthalpy: $H = E + PV$
Enthalpy \((H)\): Heat at Constant \(P\)

\[
\begin{align*}
\Delta E &= q_P + w = q_P - P\Delta V \\
\Delta H &= \Delta E + P\Delta V \\
q_P &= \Delta E + P\Delta V = \Delta H
\end{align*}
\]

the change in enthalpy equals heat lost or gained at constant pressure!

Enthalpy is a State Function

\(\Delta H\) is independent of how the change takes place

1. \(\text{C} + \text{O}_2 \rightarrow \text{CO} + \text{O}_2 \rightarrow \text{CO}_2\)
2. \(\text{C} + \text{O}_2 \rightarrow \text{CO}_2\)

overall \(\Delta H\) is the same!
\[ \Delta H \text{ and } \Delta E \]
\[ \Delta H = \Delta E + P\Delta V \]

1. Reactions that do not involve gases:
\[ \text{KOH} + \text{HCl} \rightarrow \text{KCl} + \text{H}_2\text{O}; \text{P} \Delta V \approx 0; \Delta H \approx \Delta E \]

2. Reactions where the amount (mol) of gases does not change.
\[ \text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}; \text{P} \Delta V = 0; \Delta H = \Delta E \]

3. Reactions in which the amount of gases does change:
\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}; \Delta H \gg P\Delta V; \Delta H \approx \Delta E \]

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Exothermic and Endothermic Processes

*new definitions for processes -*

**exothermic:** heat is released

**endothermic:** heat is consumed
Exothermic and Endothermic Processes

new definitions for processes -

**exothermic**: heat is released

**endothermic**: heat is consumed

“energy diagram”

for exothermic process:

\[ A \rightarrow B \]

\[ \Delta H < 0 \]

\[ \text{Time} \]

\[ H \]

\[ \text{for exothermic process:} \]

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H = -891 \text{ kJ/mol} \]

exothermic reaction

\[ \text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)} \quad \Delta H = 6.02 \text{ kJ/mol} \]

endothermic process

\[ \text{negative} \]

\[ \text{positive} \]
Practice Problem

Assuming complete heat transfer, combustion of how many L of methane (at STP) is required to melt 2.2 lb (1 kg) of ice?

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H = -891 \text{ kJ/mol}
\]

\[
\text{H}_2\text{O} (s) \rightarrow \text{H}_2\text{O} (l) \quad \Delta H = 6.02 \text{ kJ/mol}
\]

Types of Enthalpy

• Heat of combustion (\(\Delta H_{\text{comb}}\))
  \[
  \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_{\text{comb}} = -891 \text{ kJ/mol}
  \]

• Heat of formation (\(\Delta H_{f}\))
  \[
  2\text{K} + \text{Br}_2 \rightarrow 2\text{KBr} \quad \Delta H = \Delta H_{f} < 0
  \]

• Heat of fusion (\(\Delta H_{\text{fus}}\))
  \[
  \text{NaCl}(s) \rightarrow \text{NaCl}(l) \quad \Delta H = \Delta H_{\text{fus}}
  \]

• Heat of vaporization (\(\Delta H_{\text{vap}}\))
  \[
  \text{C}_6\text{H}_6(l) \rightarrow \text{C}_6\text{H}_6(g) \quad \Delta H = \Delta H_{\text{vap}}
  \]
Types of Enthalpy

- Heat of combustion ($\Delta H_{\text{comb}}$)
  \[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_{\text{comb}} = -891 \text{ kJ/mol} \]

- Heat of formation ($\Delta H_f$)
  \[ 2\text{K} + \text{Br}_2 \rightarrow 2\text{KBr} \quad \Delta H = \Delta H_f \quad < 0 \]

- Heat of fusion ($\Delta H_{\text{fus}}$)
  \[ \text{NaCl}(s) \rightarrow \text{NaCl}(l) \quad \Delta H = \Delta H_{\text{fus}} \quad > 0 \]

- Heat of vaporization ($\Delta H_{\text{vap}}$)
  \[ \text{C}_6\text{H}_6(l) \rightarrow \text{C}_6\text{H}_6(g) \quad \Delta H = \Delta H_{\text{vap}} \quad > 0 \]
Key Use of $\Delta H$: Bond Strength

$$2H_2 + O_2 \xrightarrow{\Delta H_f=-285.8 \text{ kJ/mol}} 2H_2O$$ $\Delta H \approx \Delta E$
Key Use of $\Delta H$: Bond Strength

$$2H_2 + O_2 \overset{\Delta H_f = -285.8 \text{ kJ/mol}}{\longrightarrow} 2H_2O$$

$\Delta E$ (and $\Delta H$) is mostly due to differences in “bond strength” in reactants and products.

Rabbit Eating Butter

$\Delta H = -30.0 \text{ kJ/g}$

$1 \text{ g}$ butter $\rightarrow$ burn $\rightarrow$ CO$_2 + H_2O$

$\Delta H_{\text{comb}}$ and nutritional value
Rabbit Eating Butter

\[ \text{butter} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

\[ \Delta H = -30.0 \text{ kJ/g} \]

\( \Delta H \) of \( \text{CH}_4 \) and \( \text{CH}_3\text{OH} \)

**Methane (natural gas)**

\[ \text{H} \equiv \text{C} \equiv \text{H} + \text{O}_2 \xrightarrow{\Delta H_{\text{comb}} = 890 \text{ kJ/mol}} \text{CO} \equiv \text{O} + \text{O}^\cdot \text{H} \]

\[ \Delta H_{\text{comb}} = 890 \text{ kJ/mol} \]

\[ \Delta H_{\text{comb}} = 55.5 \text{ kJ/g} \]

**Methanol**

\[ \text{H} \equiv \text{C} \equiv \text{O} \equiv \text{H} + \text{O}_2 \xrightarrow{\Delta H_{\text{comb}} = 727 \text{ kJ/mol}} \text{CO} \equiv \text{O} + \text{O}^\cdot \text{H} \]

\[ \Delta H_{\text{comb}} = 727 \text{ kJ/mol} \]

\[ \Delta H_{\text{comb}} = 22.7 \text{ kJ/g} \]
Calorimetry

• measures $\Delta H_{\text{rxn}}$, which is $q_p$, by measuring heat transfer
Specific Heat Capacity, $c$

$$c \ (J/g\cdot K) = \frac{q}{\text{mass} \times \Delta T}$$

- **specific heat capacity**: the quantity of heat required to change the temperature of 1 gram of substance by 1 K

Calorimetry: Constant-Pressure

$$q_P = \Delta H$$

*common use:* to determine specific heat capacity of a solid
Calorimetry: Constant-Pressure

\[ q_P = \Delta H \]

*common use:*

to determine specific heat capacity of a solid

HEAT EXCHANGE

\[ q_A + q_B = 0 \]
\[ q_A = -q_B \]

Calorimetry: Constant-Pressure

**Sample Problem 6.4 (follow-up).**

As a purity check for industrial diamonds, a 10.25-carat (1 carat = 0.2000 g) diamond is heated to 74.21 °C and immersed in 26.05 g of water at 27.20 °C in a constant pressure calorimeter. After equilibration, the final recorded temperature is 27.65 °C. What is the specific heat capacity of the diamond? (\( c_{\text{water}} = 4.184 \text{ J/g\cdotK} \))

\[ c = 0.519 \text{ J/g\cdotK} \]
Calorimetry: Constant-Volume

\[ \Delta E = q + w \]

\[ \Delta E = q_V + P\Delta V \]

\[ q_V = \Delta E \approx \Delta H \]

the difference is < 1%

Stoichiometry of Thermochemical Equations

- sign
- magnitude

2H\(_2\)O \rightarrow 2H\(_2\) + O\(_2\) \quad \Delta H = 572 \text{ kJ}

2 moles \quad 2 moles \quad 1 mole

2H\(_2\) + O\(_2\) \rightarrow 2H\(_2\)O \quad \Delta H = -572 \text{ kJ}

2 moles \quad 1 mole \quad 2 moles

H\(_2\) + \frac{1}{2}O\(_2\) \rightarrow H\(_2\)O \quad \Delta H = -286 \text{ kJ}

1 mole \quad 0.5 moles \quad 1 mole
Stoichiometry of Thermochemical Equations

• **sign**
• **magnitude**

\[
2H_2O \rightarrow 2H_2 + O_2 \quad \Delta H = 572 \text{ kJ}
\]

\[
2 \text{ moles} \quad 2 \text{ moles} \quad 1 \text{ mole}
\]

\[
2H_2 + O_2 \rightarrow 2H_2O \quad \Delta H = -572 \text{ kJ}
\]

\[
2 \text{ moles} \quad 1 \text{ mole} \quad 2 \text{ moles}
\]

\[
2H_2 + O_2 \rightarrow 2H_2O \quad \Delta H_f = -286 \text{ kJ/mol}
\]

**Fundamental Strategy**

\[
\text{moles (starting)} \leftrightarrow \text{moles (final)} \rightarrow \text{kJ}
\]

\[
2H_2 + O_2 \rightarrow 2H_2O \quad \Delta H_f = -286 \text{ kJ/mol}
\]

Input (g, ml, kg, etc) $\rightarrow$ moles (starting) $\leftrightarrow$ moles (final) $\rightarrow$ Output (g, ml, kg, etc) $\rightarrow$ kJ
Stoichiometry of Thermochemical Equations

Sample Problem 6.57(b)

A mercury mirror forms inside a test tube by the thermal decomposition of mercury (II) oxide:

$$2\text{HgO} \rightarrow 2\text{Hg} + \text{O}_2 \quad \Delta H_{\text{rxn}} = 181.6 \text{ kJ}$$

If 275 kJ of heat is absorbed, how many grams of mercury form?

Hess’s Law

**Hess’s law of heat summation:** *the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps*

$$\Delta H = a$$

$$\Delta H = b$$

$$\Delta H_{\text{overall}} = a+b$$
Hess’s Law

Hess’s law of heat summation: the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps

\[ 4\text{NO}_2 + \text{O}_2 \rightarrow 2\text{N}_2\text{O}_5 \quad \Delta H = ? \]
\[ 2\text{N}_2\text{O}_5 \rightarrow 4\text{NO} + 3\text{O}_2 \quad \Delta H = 223.7 \text{ kJ/mol (N}_2\text{O}_5) \]
\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad \Delta H = -57.1 \text{ kJ/mol (NO)} \]

(sample problem 6.7)

Standard Heats of Reaction (\(\Delta H_{rxn}^o\))

\(\Delta H\) at standard states is \(\Delta H^o\)

standard states:

• **gases:** 1 atm and the gas behaving ideally

• **aqueous solution:** 1 M concentration

• **pure substance:** most stable form at 1 atm, 25°C usually
Standard Heats of Formation ($\Delta H_f^o$)

$\text{C(graphite)} + 2\text{H}_2 \rightarrow \text{CH}_4 \quad \Delta H_f^o = -74.9 \text{ kJ/mol}$

$2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl} \quad \Delta H_f^o = -411.1 \text{ kJ/mol}$

$4\text{C(graphite)} + 6\text{H}_2 + \text{O}_2 \rightarrow 2\text{C}_2\text{H}_5\text{OH} \quad \Delta H_f^o = -277.6 \text{ kJ/mol}$

➢ for elements at standard state $\Delta H_f^o = 0$

$\Delta H_{\text{rxn}}^o$ and $\Delta H_f^o$

$$\Delta H_{\text{rxn}}^o = \sum m \Delta H_f^o(\text{products}) - \sum n \Delta H_f^o(\text{reactants})$$

$m,n$ - stoichiometric coefficients
$\Delta H^o_{\text{rxn}}$ and $\Delta H^o_f$

Use the following information to find $\Delta H^o_f$ of methanol

CH$_3$OH + 3/2O$_2$ → CO$_2$ + 2H$_2$O  $\Delta H^o_{\text{comb}} = -638.5$ kJ/mol
$\Delta H^o_f$ of CO$_2$ = -393.5 kJ/mol  $\Delta H^o_f$ of H$_2$O = -241.8 kJ/mol