Bomb Calorimetry

- constant volume
- often used for combustion reactions
- heat released by reaction is absorbed by calorimeter contents
- need heat capacity of calorimeter
- \( q_{\text{cal}} = -q_{\text{rxn}} = q_{\text{bomb}} + q_{\text{water}} \)

Example 4

When 0.187 g of benzene, \( \text{C}_6\text{H}_6 \), is burned in a bomb calorimeter, the surrounding water bath rises in temperature by 7.48\(^\circ\text{C}\). Assuming that the bath contains 250.0 g of water and that the calorimeter has a heat capacity of 4.90 kJ/\(^\circ\text{C}\), calculate the energy change for the combustion of benzene in kJ/g.

\[
\text{C}_6\text{H}_6(\ell) + \frac{15}{2}\text{O}_2(g) \rightarrow 6 \text{CO}_2(g) + 3 \text{H}_2\text{O}(\ell)
\]

\( q_{\text{cal}} = (4.90 \text{ kJ/}^\circ\text{C})(7.48^\circ\text{C}) = 36.7 \text{ kJ} \)

\( q_{\text{cal}} = -q_{\text{rxn}} = -36.7 \text{ kJ} / 0.187 \text{ g C}_6\text{H}_6 = -196 \text{ kJ/g} \)

\( q_p = \Delta E = -196 \text{ kJ/g} \)

Energy and Enthalpy

Most physical and chemical changes take place at constant pressure

- Heat transferred at constant \( P \) - enthalpy (H)
  - Can only measure \( \Delta H \)
  - \( \Delta H = H_{\text{final}} - H_{\text{initial}} = q_p \)
  - sign of \( \Delta H \) indicates direction of heat transfer
Energy and Enthalpy

- Melting and freezing
  - Quantity of thermal energy that must be transferred to a solid to cause melting - heat of fusion \( (q_{\text{fusion}}) \)
  - Quantity of thermal energy that must be transferred from a solid to cause freezing - heat of freezing \( (q_{\text{freezing}}) \)
  - \( q_{\text{fusion}} = -q_{\text{freezing}} \)
  - heat of fusion of ice = 333 J/g at 0°C
Enthalpy and Phase Changes

• Vaporization and condensation
  – Similarly: $q_{\text{vaporization}} = -q_{\text{condensation}}$
  – heat of vaporization of water = 2260 J/g at 100°C
  – 333 J of heat can melt 1.00 g ice at 0°C but it will boil only:

$$333 \text{ J} \times \left(\frac{1.00 \text{ g}}{2260 \text{ J}}\right) = 0.147 \text{ g water}$$

Enthalpy and Phase Changes

$$\begin{align*}
\text{H}_2\text{O} (l) & \rightarrow \text{H}_2\text{O} (g) \quad \text{endothermic} \\
\text{H}_2\text{O} (s) & \rightarrow \text{H}_2\text{O} (l) \\
\text{H}_2\text{O} (g) & \rightarrow \text{H}_2\text{O} (l) \\
\text{H}_2\text{O} (l) & \rightarrow \text{H}_2\text{O} (s) \quad \text{exothermic}
\end{align*}$$

State Functions

• Value of a state function is independent of path taken to get to state - depends only on present state of system
• Internal energy is state function
State Functions

- $q$ and $w$ not state functions

Enthalpy and PV Work

$H$ - state function
$q$ - not a state function

$\Delta E = q + w$
$\Delta H = q$

How do internal energy and enthalpy differ?

Answer: work

Enthalpy and PV Work

$P \rightarrow E / A$
$P \rightarrow E / A$

Cross-sectional area $= A$

Initial state
Final state
Example 5

A gas is confined to a cylinder under constant atmospheric pressure. When the gas undergoes a particular chemical reaction, it releases 89 kJ of heat to its surroundings and does 36 kJ of PV work on its surroundings. What are the values of $\Delta H$ and $\Delta E$ for this process?

$q = -89 \text{ kJ} \quad w = -36 \text{ kJ}$

@ constant pressure:

$\Delta H = q_p = -89 \text{ kJ}$

$\Delta E = \Delta H + w = -89 \text{ kJ} - 36 \text{ kJ} = -125 \text{ kJ}$

Thermochemical Equations

$\Delta H = H_{\text{final}} - H_{\text{initial}} = H_{\text{(products)}} - H_{\text{(reactants)}}$

$\Delta H_{\text{rxn}}$ = enthalpy or heat of reaction

$2 \text{ H}_2 (g) + \text{ O}_2 (g) \rightarrow 2 \text{ H}_2\text{O} (l) \quad \Delta H^\circ = -571.66 \text{ kJ}$

coefficients of equation represent # of moles of reactants and products producing this energy change

Thermochemical Equations

$\Delta H^\circ$

- standard enthalpy change
- defined as enthalpy change at 1 bar pressure and 25°C
“Rules” of Enthalpy

- Enthalpy is an extensive property. The magnitude of ∆H depends on amounts of reactants consumed.
- Enthalpy change of a reaction is equal in magnitude but opposite in sign to ∆H for the reverse reaction.
- Enthalpy change for a reaction depends on the states of the reactants and products.

Example 6

Hydrogen peroxide can decompose to water and oxygen by the reaction:

\[ 2 \text{H}_2\text{O}_2(\ell) \rightarrow \text{2H}_2\text{O}(\ell) + \text{O}_2(g) \]

Calculate the value of q when 5.00 g of \( \text{H}_2\text{O}_2(\ell) \) decomposes.

Example 7

Consider the following reaction, which occurs at room temperature and pressure:

\[ 2 \text{Cl}(\ell) \rightarrow \text{Cl}_2(\ell) \]

\( \Delta H = -243.4 \text{ kJ} \)

Which has the higher enthalpy under these conditions, \( \text{Cl}_2 \) or \( \text{Cl} \)?

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Example 8

When solutions containing silver ions and chloride ions are mixed, silver chloride precipitates:

\[ \text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \rightarrow \text{AgCl} (s) \quad \Delta H = -65.5 \text{ kJ} \]

(a) Calculate \( \Delta H \) for the formation of 0.200 mol of AgCl by this reaction.

\[ \Delta H = \left( 0.200 \text{ mol AgCl} \right) \left( \frac{-65.5 \text{ kJ}}{1 \text{ mol AgCl}} \right) = -13.1 \text{ kJ} \]

Example 8 (cont’d)

\[ \text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \rightarrow \text{AgCl} (s) \quad \Delta H = -65.5 \text{ kJ} \]

(b) Calculate \( \Delta H \) when 0.350 mmol AgCl dissolves in water.

\[ \text{AgCl} (s) \rightarrow \text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \quad \Delta H = +65.5 \text{ kJ} \]

\[ \Delta H = \left( 0.350 \times 10^{-3} \text{ mol AgCl} \right) \left( \frac{+65.5 \text{ kJ}}{1 \text{ mol AgCl}} \right) = 0.0229 \text{ kJ} = 22.9 \text{ J} \]

Bond Enthalpies

- during chemical reaction bonds are broken and made
- breaking bonds requires energy input (endothermic)
- formation of bonds releases energy (exothermic)
- weaker bonds broken and stronger bonds formed
Hess’s Law

- we can calculate $\Delta H$ for a reaction using $\Delta H$s for other known reactions
- $\Delta H$ is a state function - result is same no matter how we arrive at the final state
- Hess’s Law - if a reaction is carried out in a series of steps, $\Delta H$ for overall reaction is equal to sum of $\Delta H$s for steps

\[
\begin{align*}
C(s) + O_2(g) & \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ} \\
CO(g) + 1/2 O_2(g) & \rightarrow CO_2(g) \quad \Delta H = -283.0 \text{ kJ} \\
\text{What is } \Delta H \text{ for } C(s) + 1/2 O_2(g) & \rightarrow CO(g) \text{ ???} \\
C(s) + O_2(g) & \rightarrow CO(g) \quad \Delta H = -393.5 \text{ kJ} \\
CO(g) + 1/2 O_2(g) & \rightarrow CO_2(g) \quad \Delta H = +283.0 \text{ kJ} \\
C(s) + 1/2 O_2(g) & \rightarrow CO(g) \quad \Delta H = -110.5 \text{ kJ}
\end{align*}
\]

Example 9

Calculate $\Delta H$ for the conversion of $S$ to $SO_3$ given the following equations:

\[
\begin{align*}
S(s) + O_2(g) & \rightarrow SO_2(g) \quad \Delta H = -296.8 \text{ kJ} \\
SO_2(g) + 1/2 O_2(g) & \rightarrow SO_3(g) \quad \Delta H = +98.9 \text{ kJ} \\
\text{want } S(s) & \rightarrow SO_3(g) \\
S(s) + O_2(g) & \rightarrow SO_2(g) \quad \Delta H = -296.8 \text{ kJ} \\
SO_2(g) + 1/2 O_2(g) & \rightarrow SO_3(g) \quad \Delta H = +98.9 \text{ kJ} \\
S(s) + 3/2 O_2(g) & \rightarrow SO_3(g) \quad \Delta H = -395.7 \text{ kJ}
\end{align*}
\]
Enthalpies of Formation

- tables of enthalpies ($\Delta H_{\text{vap}}$, $\Delta H_{\text{fus}}$, etc.)
- $\Delta H_f$ - enthalpy of formation of a compound from its constituent elements.
- magnitude of $\Delta H$ - condition dependent
- standard state - state of substance in pure form at 1 bar and 25°C
- $\Delta H_f^\circ$ - change in enthalpy for reaction that forms 1 mol of compound from its elements (all in standard state)
- $\Delta H_f^\circ$ of most stable form of any element is 0

$\text{CO}_2$: $\text{C (graphite)} + \text{O}_2 (g) \rightarrow \text{CO}_2 (g) \quad \Delta H_f^\circ = -393.5 \text{ kJ/mol}$

Calculating $\Delta H_{\text{rxn}}^\circ$ from $\Delta H_f^\circ$

- we can use $\Delta H_f^\circ$ values to calculate $\Delta H_{\text{rxn}}^\circ$ for any reaction
- $\Delta H_{\text{rxn}}^\circ = \sum [n \Delta H_f^\circ \text{(products)}] - \sum [n \Delta H_f^\circ \text{(reactants)}]$  
  
  $\text{C}_6\text{H}_6 (l) + 15/2 \text{O}_2 (g) \rightarrow 6 \text{CO}_2 (g) + 3 \text{H}_2\text{O} (l)$  
  
  $\Delta H_{\text{rxn}}^\circ = [(6 \text{ mol})(-393.5 \text{ kJ/mol}) + (3 \text{ mol})(-285.83 \text{ kJ/mol})]  
  - [(1 \text{ mol})(49.0 \text{ kJ/mol}) + (15/2 \text{ mol})(0 \text{ kJ/mol})]$  
  
  $\Delta H_{\text{rxn}}^\circ = -3267 \text{ kJ/mol}$

Example 10

Styrene ($\text{C}_8\text{H}_8$), the precursor of polystyrene polymers, has a standard heat of combustion of $-4395.2$ kJ/mol. Write a balanced equation for the combustion reaction and calculate $\Delta H_f^\circ$ for styrene (in kJ/mol).

$\Delta H_f^\circ \text{(CO}_2) = -393.5 \text{ kJ/mol}$

$\Delta H_f^\circ \text{(H}_2\text{O}) = -285.8 \text{ kJ/mol}$  

$\text{C}_8\text{H}_8 (l) + 10 \text{ O}_2 (g) \rightarrow 8 \text{ CO}_2 (g) + 4 \text{ H}_2\text{O} (l)$  

$\Delta H_{\text{rxn}}^\circ = -4395.2 \text{ kJ/mol} = [(8 \text{ mol})(-393.5 \text{ kJ/mol}) + (4 \text{ mol})(-285.8)]  
  - [(1 \text{ mol})(49.0 \text{ kJ/mol}) + (10/2 \text{ mol})(0 \text{ kJ/mol})]$  

$\Delta H_f^\circ \text{(C}_8\text{H}_8) = 104.0 \text{ kJ/mol}$