III. Thermochemistry

Thermodynamics, of which thermochemistry is one area, is the study of the heat change in a system and work done on the system by the surroundings.

A) Heat

When a hot block is placed next to a cold block, the temperature of the cold block rises and the temperature of the hot block drops. At thermal equilibrium the temperatures of the two block are the same value. The change in temperature of each block is related by the equation

\[ m_h c_h (T_h - T_f) = m_c c_c (T_f - T_c) \]

where \( T_i \) is the temperature of each block at thermal equilibrium and \( c \) is the specific heat. The specific heat is the amount of heat required to raise the temperature of 1.00 g of a substance one degree. The right side of the equation is the change in heat of the hot block and the left side is the change in heat of the cold block.

\[ \text{heat gained by cold block:} \quad q_c = m_c c_c (T_f - T_c) \]

\[ \text{heat lost by hot block:} \quad q_h = m_h c_h (T_f - T_h) \]

Since \( q_c \) is a positive number (heat absorbed) and \( q_h \) is a negative number (heat evolved), then

\[ q_h + q_c = 0 \]

\( q \) is defined as the heat absorbed by a substance and

\[ q = mc \Delta T \quad \text{where} \quad \Delta T = (T_{\text{final}} - T_{\text{initial}}) \]

\[ \text{or} \]

\[ q = nC \Delta T \]

where \( n \) is the number of moles of the substance and \( C \) is the molar heat capacity of the substance. The molar heat capacity is the amount of heat required to raise the temperature of one mole of substance one degree.
B) Work

Work is the result of an action against an opposing force over some distance.

\[ \text{work} = \text{force} \times \text{distance} \]

Although there are many kinds of work, we are interested primarily in the work done by a frictionless piston on an ideal gas.

When \( P_{\text{ext}} < P_{\text{int}} \), then the gas expands and work is done against \( P_{\text{ext}} \); when \( P_{\text{ext}} > P_{\text{int}} \), then the gas is compressed and work is done against \( P_{\text{int}} \); and when \( P_{\text{ext}} = P_{\text{int}} \), then the gas is in equilibrium with the piston.

Thermodynamic terms:

- **System** - any piece of matter under consideration
  - **Examples:** ideal gas, chemical reaction

- **Surroundings** - any matter that can interact with the system
  - **Examples:** cylinder, piston, reaction flask

\( w \) is defined as the work done on the system by the surroundings.

For pressure-volume work (\( PV \) work), \( w \) is defined by the equation

\[ w = - \int_{V_1}^{V_2} P \, dV = - (\text{area under } PV \text{ curve}) \]

Consider the expansion of an ideal gas from \( P_1 V_1 \) to \( P_2 V_2 \).
A plot of the pressures and volumes of the ideal gas during the reversible expansion.

Since $V_2 > V_1$, the (area under the PV curve) > 0 and $w = - (\text{area under the PV curve}) < 0$.

Note: number > 0 is a positive number and number < 0 is a negative number.

The reverse of the definition of $w$ occurred i.e. the gas (the system) did work on the piston (the surroundings).

Consider the compression of an ideal gas from $P_1V_1$ to $P_2V_2$. 
A plot of the pressures and volumes of the ideal gas during the reversible compression.

Since $V_2 < V_1$, the (area under the PV curve) < 0 and $w = -\text{(area under the PV curve)} > 0$. The piston (the surroundings) did work on the ideal gas (the system).

The magnitude of $w$ is dependent on the path taken from the initial state (State #1) to the final state (State #2). The magnitude of $w$ is path dependent.

**Example:** Consider the expansion of an ideal gas by two different pathways in which the initial state ($P_1 V_1$) and the final state ($P_2 V_2$) are the same in both pathways.

1) Expansion into a vacuum: $P_{\text{ext}} = 0$

$$w = -\int_{V_1}^{V_2} P_{\text{ext}} \, dV = -\int_{V_1}^{V_2} 0 \, dV = 0$$
2) Expansion against a constant external pressure: \( P_{\text{ext}} = \text{constant} \)

\[
W = - \int_{V_1}^{V_2} P_{\text{ext}} \, dV = - P_{\text{ext}} \int_{V_1}^{V_2} dV = P_{\text{ext}} (V_2 - V_1)
\]

\[ W = - P_{\text{ext}} \Delta V \]

Note: **Under the condition of constant pressure** \( w = - P \Delta V \) for an ideal gas.

C) First Law of Thermodynamics

Consider a *cyclic* process for an ideal gas in a cylinder with a frictionless piston.

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**Cyclic Process**

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The net work, $w_{net}$, done in one cyclic is the sum of the work associated each step.

$$w_{net} = w_a + w_b + w_c + w_d = -P_1 (V_2 - V_1) - P_2 (V_1 - V_2)$$

Payment for the net work, $w_{net}$, is in the form of heat, $q_{net}$. In Step a heat must be added in order to increase the volume of the gas at constant $P$ and $n$. To lower the pressure of the gas under the condition of constant $V$ and $n$, in Step b, heat must be removed. In Step c the gas must lose heat and in Step d the gas must gain heat.

$$q_{net} = q_a + q_b + q_c + q_d$$

For a cyclic process

$$w_{net} = -q_{net}$$

$$q_{net} + w_{net} = 0$$

In those cases where $q > w$, the excess heat is absorbed by the system and the internal energy of the system will increase. When $q < w$, some of the internal energy of the system will used to do the work and there will be a reduction in the internal energy of the system.

$E$ is the symbol for internal energy.

**Example of Internal Energy:** When an ideal monatomic gas is the thermodynamic system, then $E$, internal energy, is the kinetic energy of translation, $E_T = 3RT/2$.

The change in the internal energy of the system is

$$\Delta E = q + w$$

where $q$ is the heat absorbed by the system and $w$ is the work done on the system by the surroundings.

The First Law of Thermodynamics states

i) $\Delta E = q + w$

ii) $E$ is a state function.

A state function is any function in which the change in going from the initial state (state #1) to the final state (state #2) depends only on the “conditions” of the initial and final states but not on the path taken between the two states. State functions are path independent.

**Example:** Consider the expansion of one mole of an ideal monatomic gas from the same initial state, State #1, to the same final state, State #2, by two different paths. As can be seen from the PV curves below, the amount of work done in the process associated with Path #1 is different from the work associated with Path #2. However, since the initial and final states are the same in both paths, $\Delta E$ for both paths must have the same value.

**Path #1:**

$$\Delta E = q + w = 6481J - 6481J = 0$$

**Path #2:**

$$\Delta E = q + w = 2906J - 2960J = 0$$
D) Enthalpy, \( H \)

\( q_v \) is the heat absorbed by the system in a constant volume process.
\( q_p \) is the heat absorbed by the system in a constant pressure process.

1) A Constant Volume Process

\[
\Delta E = q_v + w
\]

at constant volume \( w = 0 \) and \( \Delta E = q_v + 0 \)

\[
\Delta E = q_v
\]

Thus \( q_v \) is a state function.

2) A Constant Pressure Process

\[
\Delta E = q_p + w
\]

at constant pressure \( w = -P \Delta V \) and \( \Delta E = q_p - P \Delta V \)

Rearranging

\[
\Delta E + P \Delta V = q_p
\]
\[ q_p = \Delta E + P\Delta V = (E_2 - E_1) + P(V_2 - V_1) \]

\[ q_p = (E_2 + PV_2) - (E_1 + PV_1) = H_2 - H_1 = \Delta H \]

\[ q_p = \Delta H \]

Since the magnitude of \( q_p \) depends only on the “conditions” of the initial and final states, \( q_p \) is a state function.

\( H \) is called enthalpy and is defined as \( H = E + PV \). Enthalpy, \( H \), is a state function.

**At Constant Pressure:** \( \Delta H = q_p \)

3) When a Chemical Reaction is the Thermodynamic System - the Relationship between \( \Delta E \) and \( \Delta H \)

a) Reactants and/or Products are Gases

Consider the reaction at constant \( T \) and \( P \)

\[ \text{N}_2 (g) + 3 \text{H}_2 (g) \rightarrow 2 \text{NH}_3 (g) \quad \Delta H = -93.38 \text{kJ} \]

Since \( T \) and \( P \) are the same in the initial and final states, then a change in volume, \( \Delta V \), will result from a change in the total moles of the gases, \( \Delta n \). Assuming ideal gas behavior

**State #1:** \( P_1 V_1 = (n_{N_2} + n_{H_2})RT \) and **State #2:** \( P_2 V_2 = n_{NH_3}RT \)

\[ P_1 = P_2 = P \]

\[ P\Delta V = P(V_2 - V_1) = [n_{NH_3} - (n_{N_2} + n_{H_2})]RT = \Delta n RT \]

Substituting eq 2 into eq 1

\[ \Delta H = \Delta E + \Delta n RT \]
For solids and liquids \( \Delta V = 0 \) and \( P \Delta V = 0 \)

and thus \( \Delta H = \Delta E + 0 = \Delta E \)

**Note:** Physical states: \( g = \text{gas}, l = \text{liquid}, s = \text{solid}, aq = \text{aqueous solution} \)

**Example:** Calculate \( \Delta H \) at 25°C for the reaction below.

\[
\text{C}_6\text{H}_6 (l) + \frac{15}{2} \text{O}_2 (g) \rightarrow 6 \text{CO}_2 (g) + 3 \text{H}_2\text{O} (l) \quad \Delta E = -3264 \text{kJ}
\]

\[
\Delta H = \Delta E + \Delta nRT
\]

\[
\Delta n = n_{\text{CO}_2} - n_{\text{O}_2} = 6 - \frac{15}{2} = -\frac{3}{2} \text{ mole}
\]

\[
\Delta H = -3264 \text{kJ} + \left[ -\frac{3}{2} \text{mole} \right] \left[ \frac{8.314 \text{ J}}{\text{mol-K}} \right] \left[ \frac{kJ}{1000 \text{J}} \right] (298 \text{K}) = -3268 \text{kJ}
\]

**E) Heats of Reaction**

Heat of reaction under the condition of constant volume: \( q_v = \Delta E \)

Heat of reaction under the condition of constant pressure: \( q_p = \Delta H \)

1) **Heat of Combustion**

The heat change associated with the burning of a compound.

**Example:**

\[
2 \text{C}_4\text{H}_{10} (g) + 13 \text{O}_2 (g) \rightarrow 8 \text{CO}_2 (g) + 10 \text{H}_2\text{O} (l) \quad \Delta H^\text{comb}_\text{O} = -5314 \text{kJ}
\]

The heat of combustion is measured in a bomb calorimeter.
A weighed sample of a compound is placed in the bomb. The bomb is charged with 25 atm of \( \text{O}_2 \) and ignited. The heat given up by the reaction \( (q_{\text{reaction}} < 0) \) is absorbed by the calorimeter \( (q_{\text{cal}} > 0) \).

\[
q_{\text{reaction}} = -q_{\text{cal}}
\]

The change in temperature of the calorimeter is measured and the heat absorbed \( (q_{\text{cal}} = C_{\text{cal}} \Delta T) \) by the calorimeter is calculated. Since the volume of the bomb in which the reaction takes place is constant,

\[
q_{\text{reaction}} = q_v = \Delta E = -(C_{\text{calor}} + C_{\text{water}}) \Delta T = -C_{\text{cal}} \Delta T = -q_{\text{cal}}
\]

\[
q_{\text{reaction}} = \Delta E = -C_{\text{cal}} \Delta T
\]

where \( C_{\text{calor}} \) is the heat capacity of the calorimeter components (bomb, bucket, thermometer, etc.) and \( C_{\text{water}} \) is the heat capacity of the water in the bucket.

The heat of reaction under the condition of constant pressure is calculated with the following equation.

\[
\Delta H = \Delta E + \Delta nRT
\]

2) Heat of Formation

The heat change associated with the formation of a compound from its elements in their most stable form.

**Example:**

\[
\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g}) \quad \Delta H^\circ_f = -93.38 \text{ kJ}
\]

The numeric value for the heat of a reaction is dependent on the temperature and pressure at which the reaction is carried out. If we are to compare heats of reaction, then these heats must be measured under the same conditions. For this reason a standard set of
conditions has been chosen for reporting heats of reaction. These conditions are that the reactants and products are in their standard states.

**Standard State of:**

- **gas**
- **liquid**
- **solid**

**Physical State:**

- pure gas
- pure liquid
- pure, crystalline solid

**Pressure:**

- partial pressure
- 1 atm
- 1 atm

**Temperature:**

- 25°C
- 25°C
- 25°C

The heat change associated with the formation of a compound in its standard state from its elements (most stable form) in their standard states is called the standard enthalpy of formation, \( \Delta H^\circ_f \).

By definition the \( \Delta H^\circ_f \) for an element is its most stable form is zero.

A table of heats of formation for compounds can be found in the text.

**Example:** Table of Standard Enthalpies of Formation

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H^\circ_f ) (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O (l)</td>
<td>-285.84</td>
</tr>
<tr>
<td>NH(_3) (g)</td>
<td>-46.69</td>
</tr>
<tr>
<td>CO(_2) (g)</td>
<td>-393.51</td>
</tr>
<tr>
<td>H(_2)O (g)</td>
<td>-241.8</td>
</tr>
<tr>
<td>H(_2) (g)</td>
<td>0.0</td>
</tr>
<tr>
<td>H (g)</td>
<td>217.94</td>
</tr>
</tbody>
</table>

The thermochemical equations for these \( \Delta H^\circ_f \) are known by definition.

**Example:** Write the thermochemical equation for \( \Delta H^\circ_f (\text{CO}_2 \ (\text{g})) = -393.51 \text{ kJ/mole} \).

Since -393.51 kJ is the heat change for the formation of one mole of CO\(_2\) from the most stable forms of elemental carbon and hydrogen, then

\[
\text{C (s)} + \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) \quad \Delta H^\circ_f = -393.51 \text{ kJ}
\]

3) Hess’s Law

The heat change at constant temperature and pressure for a particular chemical reaction is constant and independent of the path taken from reactants to products.

Consider the formation of CO\(_2\) by two different pathways.
The heat change is the same for both pathways to CO₂.

4) Calculation of enthalpies that cannot be measured from enthalpies that have been measured

Procedure:
Step #1: Write down the thermochemical equation for which you wish to calculate the $\Delta H$ (or other thermodynamic function) as the summary equation.

Step #2: Arrange given thermochemical equations (equations with known values for $\Delta H$ or other thermodynamic function) so that the sum of the equations is the summary equation.

Step #3: Write down an appropriate value for the $\Delta H$ (or other thermodynamic function) associated with each thermochemical equation in Step #2. If the thermochemical equation is the reverse of the given equation, change the sign of the $\Delta H$.

Step #4: Add up the values for the $\Delta H$s (or other thermodynamic functions) in Step #3.

Example: Calculate the enthalpy of formation, $\Delta H^\circ_f$, for benzene, C₆H₆, at 25°C given

$$C_6H_6 (l) + 15/2 O_2 (g) \rightarrow 6 CO_2 (g) + 3 H_2O (l) \quad \Delta H^\circ_{comb} = -3267.7 \text{ kJ}$$

and $\Delta H^\circ_f (CO_2 (g)) = -393.51 \text{ kJ/mole}$; $\Delta H^\circ_f (H_2O (l)) = -285.84 \text{ kJ/mole}$.

Note: The thermochemical equations associated with the enthalpies of formation for CO₂ and H₂O are known by definition.

$$C (s) + O_2 (g) \rightarrow CO_2 (g) \quad \Delta H^\circ_f = -393.51 \text{ kJ}$$

$$H_2 (g) + \frac{1}{2} O_2 (g) \rightarrow H_2O (l) \quad \Delta H^\circ_f = -285.84 \text{ kJ}$$
Alternate Method for Calculating $\Delta H$

$$
\Delta H^\circ_{\text{reaction}} = \sum v_{\text{product}} \Delta H^\circ_f (\text{product}) - \sum v_{\text{reactant}} \Delta H^\circ_f (\text{reactant})
$$

where $v$, called the mole number, is the stoichiometric coefficient in the thermochemical equation.

Example: Calculate the enthalpy of formation, $\Delta H^\circ_f$, for benzene, $\text{C}_6\text{H}_6$, at 25°C given

$$
\begin{align*}
\text{C}_6\text{H}_6 (l) + 15/2 \text{O}_2 (g) & \rightarrow 6 \text{CO}_2 (g) + 3 \text{H}_2\text{O} (l) & \Delta H^\circ_{\text{comb}} = -3267.7 \text{ kJ} \\
\text{and } \Delta H^\circ_f (\text{CO}_2 (g)) & = -393.51 \text{ kJ/mole} ; \Delta H^\circ_f (\text{H}_2\text{O} (l)) = -285.84 \text{ kJ/mole}
\end{align*}
$$

$$
\begin{align*}
\Delta H_{\text{comb}} & = v_{\text{CO}_2} \Delta H^\circ_f (\text{CO}_2 (g)) + v_{\text{H}_2\text{O}} \Delta H^\circ_f (\text{H}_2\text{O} (l)) - v_{\text{C}_6\text{H}_6} \Delta H^\circ_f (\text{C}_6\text{H}_6 (l)) - v_{\text{O}_2} \Delta H^\circ_f (\text{O}_2 (g)) \\
& = (6 \text{ mole})(-393.51 \text{ kJ/mole}) + (3 \text{ mole})(-285.84 \text{ kJ/mole}) - (1 \text{ mole})(-3267.7 \text{ kJ}) - (15/2 \text{ mole})(0 \text{ kJ/mole}) \\
& = -3267.7 \text{ kJ} \\
\Delta H^\circ_f (\text{C}_6\text{H}_6 (l)) & = 49.12 \text{ kJ/mole}
\end{align*}
$$

F) Molar Heat Capacity

1) $C_v$: Heat Capacity for a Constant Volume Process

Consider increasing the temperature of one mole of an ideal monoatomic gas by $\Delta T$ degrees in a constant volume process.

$$
\begin{align*}
E_2 & = \frac{3}{2} R(T + \Delta T) \\
\Delta E & = E_2 - E_1 = \frac{3}{2} R\Delta T = q_v \\
\end{align*}
$$

The amount of heat required to raise the temperature of the gas by $\Delta T$ degrees in a constant volume process.
\[ C_v = \frac{q_v}{\Delta T} = \frac{\Delta E}{\Delta T} \quad (3) \]

\( C_v \) for an ideal monatomic gas is

\[ C_v = \frac{3}{2} R = 12.47 \frac{J}{\text{mole-K}} \]

Values of \( C_v \) for some other gases

<table>
<thead>
<tr>
<th>Compound</th>
<th>( C_v ) (J/mole-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>20.33</td>
</tr>
<tr>
<td>( \text{Cl}_2 )</td>
<td>25.10</td>
</tr>
<tr>
<td>( \text{HCl} )</td>
<td>21.00</td>
</tr>
</tbody>
</table>

Rearranging eq 3

\[ \Delta E = C_v \Delta T \quad (4) \]

Eq 4 is valid for one mole of a real gas in a constant volume process and *for one mole of an ideal gas under all conditions.*

2) \( C_p \): Heat Capacity for a Constant Pressure Process

For a constant pressure process the change in volume of one mole of an ideal gas is the result of a change in temperature.

\[ P \Delta V = P(V_2 - V_1) = R(T_2 - T_1) = R \Delta T \quad (5) \]

The heat absorbed by one mole of an ideal gas in a constant pressure process

\[ q_p = \Delta H = \Delta E + P \Delta V \quad (6) \]

\[ \text{and} \]

\[ C_p = \frac{q_p}{\Delta T} = \frac{\Delta H}{\Delta T} \quad (7) \]

Rearranging eq 7

\[ \Delta H = C_p \Delta T \quad (8) \]

Eq 8 is valid for one mole of a real gas in a constant pressure process and *for one mole of an ideal gas under all conditions.*

Substituting eqs 4, 5, and 8 into eq 6

\[ C_p \Delta T = C_v \Delta T + R \Delta T \]

and dividing by \( \Delta T \)

\[ C_p = C_v + R \quad (9) \]
Eq 9 is valid only for an ideal gas.

**Example:** Calculate $C_p$ for an ideal monatomic gas if $C_v$ is 12.47 J/mole-$K$.

\[
C_p = C_v + R = 12.47 \frac{J}{\text{mole-K}} + 8.314 \frac{J}{\text{mole-K}} = 20.78 \frac{J}{\text{mole-K}}
\]

**SUMMARY:**

- **When an ideal gas is the thermodynamic system,**
  \[
  \Delta E = nC_v \Delta T \quad \text{and} \quad \Delta H = nC_p \Delta T
  \]
  \[
  \Delta E = q + w \quad \text{and} \quad C_p = C_v + R
  \]
  where $n$ is the number of moles of the ideal gas.

- **When a chemical reaction is the thermodynamic system,**
  \[
  q_{\text{reaction}} = \Delta E = -C_{\text{cal}} \Delta T \quad \text{and} \quad \Delta H = \Delta E + \Delta nRT
  \]
  and
  \[
  \Delta E = q + w
  \]