Chapter 6: Thermochemistry

6.1 Forms of Energy and Their Interconversion
6.2 Enthalpy: Heats of Reaction and Chemical Change
6.3 Calorimetry: Laboratory Measurement of Heats of Reaction
6.4 Stoichiometry of Thermochemical Equations
6.5 Hess’s Law of Heat Summation
6.6 Standard Heats of Reaction ($\Delta H^0_{\text{rxn}}$)

Announcements
Will Discuss Moving Exam With Other Instructors.

NOW ASSUME EXAM IS AUG 29 AS PLANNED

Hour Exam 2 (Chapter 4-6)
Date: Thursday, August 29, 2013
Room: Chin Tang Room (same as before)
Time: 6PM-7:30PM

Homework
Chapter 4:
9, 11, 13, 15, 17, 19, 23, 27, 33, 39, 42, 43, 44, 51, 57, 59, 61, 66, 71, 83

Chapter 5:
2, 8, 14, 17, 22, 5.31*, 5.41*, 5.43*, 44*, 48, 5.52*, 5.54, 58, 69*, 70*, 72*, (Principles of Chemistry)

Chapter 6:
6, 8, 10, 12, 18, 23, 24, 27*, 36*, 39*, 47*, 48*, 53*, 56*, 59* (Principles of Chemistry)

Thermochemistry involves the monitoring of energy transformations that occur with a chemical reaction.

$\text{CH}_4(g) + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + \text{HEAT}$

- Reaction gives off heat with rise in temperature in the flask
- We say “EXOTHERMIC REACTION”
- Heat is written as a product.

$\text{NH}_4\text{NO}_3 + \text{H}_2\text{O} + \text{HEAT} \rightarrow \text{NH}_4^+ + \text{NO}_3^-$

- Reaction absorbs heat with decrease in temperature
- We say “ENDOTHERMIC REACTION”
- Heat is written as a reactant.

Thermodynamics is a formal accounting system based on observations over centuries that tracks energy changes in a chemical system.

- the theory is developed without knowledge of the atoms and molecules.
- The focus is the “bulk properties” of matter (Temperature, pressure, volume, internal energy, enthalpy, heat capacity).
- It makes sense once you learn the language and basic ideas.
Energy is the capacity to do work or produce heat. Energy can be transformed to different forms.

- **Radiant energy** comes from the sun and is earth’s primary energy source (nuclear fusion).
- **Thermal energy** is the energy associated with the vibration and rotational motion of atoms and molecules.
- **Chemical energy** is the energy stored within the chemical bonds of substances.
- **Nuclear energy** is the energy stored within the neutrons and protons in the atom (E = mc²).
- **Kinetic energy**: energy associated with moving mass
- **Potential energy**: energy available by virtue of an object's position or height above a reference height.

The SI Unit of energy is the Joule (kg m²/s²).

- KE = \( \frac{1}{2} \text{mass} \cdot v^2 = \frac{1}{2} (\text{kg})(\text{m/s})^2 = \text{kg} \cdot \text{m}^2/\text{s}^2 = 1 \text{ joule} \)
- Work = F x d = mass (a) x d = (kg)(m/s²) x (m) = kg m²/s² = 1 joule
- PE = \( \text{mass} gh = (\text{kg})(\text{m/s}^2)(\text{m}) = \text{kg} \cdot \text{m}^2/\text{s}^2 = 1 \text{ joule} \)
  g = acceleration gravity (9.8 m/s²), and h is object's height.

**Know how to play with these conversions**

- 1 calorie (cal) = 4.18 J
- 1000 calorie (cal) = 1 Cal (food calorie)
- 1 British Thermal Unit (BTU) = 1055 Joules

A single Fritos chip snack has a energy content of 5.0 Cal. How many joules is this?

\[ E = 5 \text{ Cal} \times \frac{1000 \text{ cal}}{1 \text{ Cal}} \times \frac{4.18 \text{ J}}{1 \text{ cal}} = 2.1 \times 10^4 \text{ J} \]

What is the kinetic energy (in kilojoules) of a 2300 lb car moving at 55 mi/h?

- KE = \( \frac{1}{2} \text{mv}^2 =? \)
  - 1 Joule = 1 kg·m²/s²
  - 1 mile = 1.609 km = 1609 m
  - 1 lb = 0.454 kg

Thermodynamics uses a specialized vocabulary that we need to get used to.

- **Energy** is the capacity to do work and exchange heat—it can take on many many forms.
- **Work** = Energy = Force x Distance.
- **Internal Energy** is the kinetic energy of molecules in motion (translational, rotational, and vibrational).
- **Heat** is thermal energy transferred between two objects at different temperatures. Heat “flows” only when there is a difference in temperature.
- **Chemical Energy** is energy stored in a chemical bond.

In 1843, James Joule found that heat and work can be interconverted and are manifestations of the same thing, energy. Significant observation & discovery!

Joule found

1 cal heat = 4.1868 J work
Thermodynamic Formalism: A system has a bulk property of matter that we call “internal energy”.

- Reactants and products are the system; everything else is the surroundings.
- We track the energy flow into and out of the system.
- Loss of energy from the system to the surroundings has a negative sign.
- Increase of the system energy from the surroundings has a positive sign.

The \textit{internal energy}, \(E\), of a system is a bulk property of matter that on a microscopic level represents all energy within the system.

\begin{align*}
\text{On a microscopic scale the internal energy is:} \\
\begin{align*}
&\text{Translational kinetic energy.} \\
&\text{Molecular rotation.} \\
&\text{Bond vibration.} \\
&\text{Intermolecular attractions.} \\
&\text{Chemical bonds.} \\
&\text{Electrons.} \\
&\text{Nuclear} \\
&\text{Electrochemical}
\end{align*}
\end{align*}

Thermodynamic Vernacular & Definitions

A \textit{system} is that part of the universe that exchanges matter and energy with its surroundings across a boundary.

The \textit{surrounding} that part of the universe which is not the system.

A \textit{system is defined} when its variable of states (independent variables) are defined.

A \textit{process} is an event in which a physical or chemical change causes a state property of the system to change. When a process occurs matter, heat or work must cross a boundary between the system and surroundings.

A \textit{path} is a specific way to carry out a process from initial state through intermediate states and final state. Work and heat are both path functions.

There are 3-classes of “systems” depending on how each exchanges matter and energy with its surroundings.

- **Open System**: Matter exchanged. Heat or work exchanged.
- **Closed System**: Matter not exchanged. Heat or work exchanged.
- **Isolated System**: No matter exchanged. No heat or work exchanged.

The \textit{1st Law of Thermodynamics} that energy is \textit{neither created nor destroyed in any process}, it is just transformed to other forms of energy across two boundaries.

\[
\Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0
\]

\[
\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}
\]

“The total energy of a system and its surroundings remains constant.”

The \textit{internal energy} of a system can only change by exchange of heat (\(q\)) and mechanical work (\(w\)) with the surroundings.

\[
\Delta E_{\text{sys}} = q + w = q - P\Delta V
\]

Initial State \hspace{2cm} Final State

Initial State \hspace{2cm} Final State
We can only measure a change in internal energy of a system by accounting for heat (q) and mechanical work (w) with the surroundings.

\[ \Delta E_{\text{Sys}} = q + w \]

Measurements are relative to something. What’s the tallest mountain in the world?

1. Mount Everest is king if measured from sea level (8,848 meters)
2. Mauna Kea is when measured from the depths of the Pacific Ocean floor. It rises 10,203 meters.
3. Mt. Chimborazo in the Andes triumphs. Although it stands but 6,267 meters above sea level, its peak is the farthest from the earth’s core.

The internal energy of a system can only change by exchange of heat (q) and mechanical work (w) with the surroundings.

\[ \Delta E_{\text{Sys}} = q + w \]

Mechanical work is known in thermodynamics as \( P \Delta V \).

Work arising from piston moving in a cylinder.

\[ w = P \times \Delta V \]

A chemical reaction can cause a change in internal energy that is accounted for completely by measuring the exchange of heat (q) and mechanical work (w) with the surroundings.

\[ \Delta E_{\text{Sys}} = q + w = q - P \Delta V \]
The internal energy, $U$, can be changed only by exchanging heat ($q$) or work ($w$) with its surroundings.

\[ \Delta E_{\text{sys}} = q + w \]

It's a state function!

The 1st Law of Thermodynamics says that total energy of a system + surroundings remains constant—i.e. energy is neither created nor destroyed just transformed between the two boundaries.

\[ \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0 \]

Determining A Change in Internal Energy

When gasoline burns in a car engine, the heat released causes the products CO$_2$ and H$_2$O to expand, which pushes the pistons outward. Excess heat is removed by the car’s cooling system. If the expanding gases do 451 J of work on the pistons and the system loses 325 J to the surroundings as heat, calculate the change in energy ($\Delta E$) in J, kJ, and kcal.

SOLUTION:

\[ q = -325 \text{ J and } w = -451 \text{ J} \]

\[ \Delta E = q + w = -325 \text{ J} + (-451 \text{ J}) = -776 \text{ J} \]

\[ -776 \text{ J} \text{ to } -776 \text{ kJ} \cdot \frac{10^3 \text{ J}}{1 \text{ kJ}} \]

\[ -776 \text{ kJ} \cdot \frac{4.18 \text{ kcal}}{1 \text{ kJ}} = -0.185 \text{ kcal} \]

Energy can be transformed from one form to another but it can not be destroyed. (1st Law of Thermodynamics)

Potential Energy = $mgh$

Kinetic Energy = $\frac{1}{2} mv^2 = 0$

High PE

No PE

High PE

No PE

We can describe behavior of physical and chemical phenomena as a tendency to seek lower chemical potentials:

H$_2$(g) + O$_2$(g) \rightarrow 2H$_2$O

Acid + Base

Water + salt

$\Delta E$

$\Delta E$
Chemists don’t use internal energy to monitor energy changes in the lab. Instead, we define and use a related quantity called enthalpy.

\[ \Delta E_{sys} = q + w = q - P\Delta V \]

**CASE 1**

At constant pressure:

\[ \Delta E = q_P - P\Delta V \]

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

\[ \Delta H = q_P = \Delta E + P\Delta V \]

**CASE 2**

At constant volume: \( \Delta V = 0 \)

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

\[ \Delta E = q_V \]

An **Exothermic reaction** releases heat to the surroundings, \( \Delta H < 0 \).

\[
2H_2 (g) + O_2 (g) \longrightarrow 2H_2O (l) + heat \quad \Delta H = <0
\]

heat written as a product (given off)

An **Endothermic reaction** absorbs heat from the surroundings into the system, \( \Delta H > 0 \).

\[
\text{heat} + 2\text{HgO} (s) \longrightarrow 2\text{Hg} (l) + O_2 (g) \quad \Delta H = >0
\]

heat written as a reactant (consumed)

There are 3-Cases When \( \Delta H = \Delta E \)

1. In systems containing solids and liquids; there is no volume change (or it is very small); \( \Delta V = 0 \) and \( \Delta H = \Delta E \)

2. In reactions where the number of moles of gas does not change from reactants to products; no work is done.

\[
\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g) \quad \Delta V = 0 \text{ and } \Delta H = \Delta E
\]

3. Reactions in which the number of moles of gas does change but \( q \) is \( \gg \gg \) \( P\Delta V \).

Reworking our Internal Energy Equation, some points of clarification on confusing stuff.

**Definition of internal energy, \( \Delta E \)**

\[ \Delta E_{sys} = q + w \]

**Definition of Work**

\[ w = \text{work} = -P\Delta V \]

Substituting

\[ \Delta E_{sys} = q + w = q - P\Delta V = q - P(V_f - V_i) \]

Calculate the work (in kilojoules) done during a reaction in which the volume expands from 12.0 L to 14.5 L against an external pressure of 5.0 atm. Watch the conversion of PV units to joules. \( 101.3 \text{ J} = 1 \text{ L atm} \)

\[ P = 5.0 \text{ atm} \quad \Delta V = (14.5 - 12.0) \text{ L} = 2.5 \text{ L} \]

\[ w = -P\Delta V \]

\[ w = -(5.0 \text{ atm})(2.5 \text{ L}) = -12.5 \text{ L atm} \]

\[ (-12.5 \text{ L atm})(101 \text{ J/L atm}) = -1.3 \times 10^3 \text{ J} = -1.3 \text{ kJ} \]
A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands (a) against a vacuum and (b) against a constant pressure of 3.7 atm?

(a) \[ \Delta V = 5.4 \text{ L} - 1.6 \text{ L} = 3.8 \text{ L} \]
\[ W = -0 \text{ atm} \times 3.8 \text{ L} = 0 \text{ L} \cdot \text{atm} = 0 \text{ joules} \]

(b) \[ \Delta V = 5.4 \text{ L} - 1.6 \text{ L} = 3.8 \text{ L} \]
\[ W = -3.7 \text{ atm} \times 3.8 \text{ L} = -14.1 \text{ L} \cdot \text{atm} \]
\[ W = -14.1 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -1430 \text{ J} \]

Imagine a chemical reaction that results in a change in both volume and temperature as shown below.

1) Has any work been done? If so, is its sign positive or negative?
2) Has there been an enthalpy change? If so, what is the sign of \( \Delta H \)? Is the reaction exothermic or endothermic?

Determining A Change in Internal Energy
When gasoline burns in a car engine, the heat released causes the products CO\(_2\) and H\(_2\)O to expand, which pushes the pistons outward. Excess heat is removed by the car’s cooling system. If the expanding gases do 451 J of work on the pistons and the system loses 325 J to the surroundings as heat, calculate the change in energy (\( \Delta E \)) in J, kJ, and kcal.

Learning Check: A Comparison of \( \Delta H \) and \( \Delta E \)
2Na(s) + 2H\(_2\)O(l) \[\rightarrow\] 2NaOH(aq) + H\(_2\) (g) \( \Delta H = -367.5 \) kJ/mol
\[ \Delta E = \Delta H - P \Delta V \]
At 25°C, 1 mole H\(_2\) = 24.5 L at 1 atm
\[ P \Delta V = 1 \text{ atm x 24.5 L} = 2.5 \text{ kJ} \]
\[ \Delta E = -367.5 \text{ kJ/mol} - 2.5 \text{ kJ/mol} = -370.0 \text{ kJ/mol} \]

Chemical energy is transformed to heat (enthalpy) in all chemical reactions. Chemists measure the enthalpies of nearly all chemical reactions and give special names to some of them.

<table>
<thead>
<tr>
<th>Type of Reaction</th>
<th>Example</th>
<th>( \Delta H ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of neutralization</td>
<td>HCl(aq) + NaOH(aq) [\rightarrow] NaCl(aq) + H(_2)O(l)</td>
<td>-56.2</td>
</tr>
<tr>
<td>Heat of ionization</td>
<td>H(_2)O(l) [\rightarrow] H(^+)(aq) + OH(^-)(aq)</td>
<td>56.2</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>H(_2)O(l) [\rightarrow] H(_2)O(l)</td>
<td>6.01</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>H(_2)O(l) [\rightarrow] H(_2)O(g)</td>
<td>44.0*</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td>MgCl(_2)(s) + 2Na(l) [\rightarrow] 2NaCl(s) + Mg(s)</td>
<td>-180.2</td>
</tr>
</tbody>
</table>
Announcements

Hour Exam II:
Date: August 29
Time: 6:00-7:30PM (40 mult. choice  2 Long problems)
Room:  SOM 111 Ching Tan Room
Coverage: Chapters 4-6

Tips:
1) Understand the learning objectives given at the end of each Chapter.
2) Do the homework problems and problems done in class and lecture slides (guaranteed).
3) Note the skipped material posted on blog and in class!
4) Practice the Silberberg quizzes in the links of blog

Chapter 4-6 Excluded Topics

Principle of Chemistry 2nd Edition

Chapter 4:
Nothing excluded. All chapter learning objectives/sample problems/homework are game.

Chapter 5:
Collecting A Gas Over Water p.163 - 165.
Relationship between KE and Temperature: p.170 - 171
Effusion and Diffusion p 172 - 173

Chapter 6:
Constant Volume Calorimeter p 198 - 199
Fossil Fuels and Climate Change p 205 - 207

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A thermochemical equation shows the enthalpy change (\(\Delta H\)) of a chemical reaction and also the reactions stoichiometric factors.

\[ C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H = -2043 \text{ kJ} \]

What does the thermochemical equation tell us?
1) Sign of \(\Delta H\) (exothermic or endothermic).
2) Magnitude of \(\Delta H\): 2043 kJ released & written as product
   \[ C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) + 2043 \text{ kJ} \]
3) \(\Delta H\) is a useful stoichiometric factors for calculations.
   \[ 1 \text{ mol } C_3H_8(g) = -2043 \text{ kJ} \quad 5O_2(g) = -2043 \text{ kJ} \]
   \[ 3CO_2(g) = -2043 \text{ kJ} \quad 4H_2O(l) = -2043 \text{ kJ} \]

Using the Heat of Reaction (\(\Delta H_{\text{rxn}}\)) to Find Amounts

The major source of aluminum in the world is bauxite which is mostly aluminum oxide. Its thermal decomposition can be represented by:

\[ Al_2O_3(s) \rightarrow 2Al(s) + 3/2O_2(g) \quad \Delta H_{\text{rxn}} = 1676 \text{ kJ} \]

If aluminum is produced this way, how many grams of aluminum can form when 1.000 x 10^3 kJ of heat is is used to decompose the oxide?

SOLUTION:

\[ g \text{ Al} = 1000 \text{ kJ} \times \frac{2 \text{ mol Al}}{1676 \text{ kJ}} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 32.2 \text{ g Al} \]

Using the thermochemical equation calculate how much heat is evolved (or what is the enthalpy) when 266 g of white phosphorus (P_4) is combusted in air? (Molar mass: P_4 is 123.9 g/mol).

\[ P_4(s) + 5O_2(g) \rightarrow P_4O_{10} (s) \quad \Delta H_{\text{rxn}} = -3013 \text{ kJ} \]
Using the thermochemical equation calculate how much heat is evolved (or what is the enthalpy) when 266 g of white phosphorus (P<sub>4</sub>) is combusted in air? The molar mass of P<sub>4</sub> is 123.9 g/mol.

\[
P_4(\text{s}) + 5O_2(\text{g}) \rightarrow P_2O_{10}(\text{s}) \quad \Delta H_{\text{rxn}} = -3013 \text{ kJ/mol}
\]

\[
\Delta H = H(\text{products}) - H(\text{reactants})
\]

\[
\Delta H_{\text{rxn}} = \frac{266 \text{ g } P_4}{123.9 \text{ g } P_4} \times 3013 \text{ kJ} = -6470 \text{ kJ}
\]

**Rules For Manipulating Thermochemical Equations.**

1. The stoichiometric coefficients always refer to the number of moles of a substance—it’s extensive!

2. If you reverse a reaction, the sign of \( \Delta H \) changes

3. If you multiply both sides of the equation by a factor \( n \), then \( \Delta H \) must change by the same factor \( n \).

4. The physical states of all reactants and products must be specified in thermochemical equations.

**Changes in internal energy, \( \Delta E \) can also be summarised in an Energy Reaction Diagram.**

This system does work on its surroundings. Energy is lost by the system = \( \Delta E < 0 \).

**A state function** is a math function whose magnitude depends only on the initial and final states and not on the path taken to between the two states.

The change in a state function is zero when the system returns to its original condition. For non-state functions, the change is **not zero** if the path returns to the original condition.

Temperature is a state function. Its value does not depend the path to get there. Whether we start with boiling water at 100˚C, or frozen water at 0˚C, once the water is at 50˚ the difference in temperature is 50˚C.

- The change in a state function is zero when the system returns to its original condition. For non-state functions, the change is **not zero** if the path returns to the original condition.
A chemical system possesses a state function called internal energy (and enthalpy too). A chemical reaction causes a change in internal energy (or enthalpy) equal to the difference in heat transfer into or from the system and the work done by or on the system.

Why Are State Functions Important?
- A state function tells us that the function has one unique value between any two arbitrary states. This fact makes thermodynamics powerful and useful.

Because ΔH is a state function, its value depends only on the final and initial state and not the path. This gives us a powerful way to predict enthalpy of many chemical reactions.

CH₄ (g) + 2O₂ ==> CO₂ + 2H₂O
ΔH₁ = -607 kJ
CO(g) + 2H₂O + 1/2 O₂(g) ==> CO₂ + 2H₂O
ΔH₂ = -283 kJ
CH₄ (g) + 2O₂ ==> CO₂ + 2H₂O
ΔH₃ = ? kJ

Enthalpy, H

Thermochemistry is concerned primarily with calculating ΔHrxn (the heat of a reaction).

Hess’s Law States: The enthalpy change for any reaction is equal to the sum of the enthalpy changes for any individual step in the reaction.

CH₄ (g) + 2O₂ ==> CO₂ + 2H₂O + 1/2 O₂
ΔH₁ = -607 kJ
CO(g) + 2H₂O + 1/2 O₂(g) ==> CO₂ + 2H₂O
ΔH₂ = -283 kJ
CH₄ (g) + 2O₂ ==> CO₂ + 2H₂O
ΔH₃ = ? kJ

Because enthalpy is a state function, its value only depends on the final and initial state and not the path. This gives us a powerful way to predict enthalpy of many chemical reactions.

Energy level diagrams are useful pictorials of the thermodynamic transitions that take place during a chemical reaction.

2-Ways or Problem Types For Hess Law Enthalpy Calculations
1) standard state data
2) formation equation
3) Calculation of ΔH°rxn

Multiple Thermochemical Equations To Rearrange--Use Rules!

ΔH°rxn = Σ nᵢ ΔH°ᵢ(products) - Σ mᵢ ΔH°ᵢ(reactants)
Hess’s Law States: The enthalpy change for a chemical reaction is equal to the sum of the enthalpy changes for any individual step in the reaction.

We can use known thermochemical equations to generate $\Delta H$ of an unknown chemical reaction.

<table>
<thead>
<tr>
<th>Multiple Thermochemical Equations</th>
<th>Measured $\Delta H_{\text{rxn}}$ values summarized in a Table</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_4(g) + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$</td>
<td>$\Delta H_1 = \ ?$ kJ</td>
</tr>
<tr>
<td>$\text{CO}(g) + 2\text{H}_2\text{O} + 1/2 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$</td>
<td>$\Delta H_2 = -607 \text{ kJ}$</td>
</tr>
<tr>
<td>$\text{CO}(g) + 2\text{H}_2\text{O} + 1/2 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$</td>
<td>$\Delta H_3 = -283 \text{ kJ}$</td>
</tr>
</tbody>
</table>

Two gaseous pollutants that form in auto exhaust are CO and NO. An environmental chemist is studying ways to convert them to less harmful gases through the following equation:

$$\text{CO}(g) + \text{NO}(g) \rightarrow \text{CO}_2(g) + 1/2\text{N}_2(g) \quad \Delta H = \ ?$$

Given the following information, calculate the unknown $\Delta H$:

$\text{CO}(g) + 1/2\text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H_A = -283.0 \text{ kJ}$

$\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \quad \Delta H_B = 180.6 \text{ kJ}$

Multiply Equation B by 1/2 and reverse it.

$$\text{NO}(g) + 1/2\text{O}_2(g) \rightarrow \text{NO}_2(g) \quad \Delta H = 90.25 \text{ kJ}$$

Calculate the standard enthalpy of formation of $\text{CS}_2(l)$ given that:

$$\text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H^{\text{rxn}}_{\text{f CO}_2} = -393.5 \text{ kJ}$$

$$\text{S(rhombic)} + \text{O}_2(g) \rightarrow \text{SO}_2(g) \quad \Delta H^{\text{rxn}}_{\text{f SO}_2} = -296.1 \text{ kJ}$$

$$\text{CS}_2(l) + 3\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{SO}_2(g) \quad \Delta H^{\text{rxn}}_{\text{f CS}_2} = -1072 \text{ kJ}$$
Calculate the standard enthalpy of formation of CS₂ (l) given that:

\[ \text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H^\circ_{\text{rxn}} = -393.5 \ \text{kJ} \]

\[ \text{S(rhombic)} + \text{O}_2(g) \rightarrow \text{SO}_2(g) \quad \Delta H^\circ_{\text{rxn}} = -296.1 \ \text{kJ} \]

\[ \text{CS}_2(l) + 3\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{SO}_2(g) \quad \Delta H^\circ_{\text{rxn}} = -1072 \ \text{kJ} \]

1. Write the enthalpy of formation reaction for CS₂

\[ \text{C(graphite)} + 2\text{S(rhombic)} \rightarrow \text{CS}_2(l) \]

2. Add the given rxns so that the result is the desired rxn.

\[ \text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H^\circ_{\text{rxn}} = -393.5 \ \text{kJ} \]

\[ 2\text{S(rhombic)} + 2\text{O}_2(g) \rightarrow 2\text{SO}_2(g) \quad \Delta H^\circ_{\text{rxn}} = -296.1 \times 2 \ \text{kJ} \]

\[ + \text{CO}_2(g) + 2\text{SO}_2(g) \rightarrow \text{CS}_2(l) + 3\text{O}_2(g) \quad \Delta H^\circ_{\text{rxn}} = +1072 \ \text{kJ} \]

\[ \text{C(graphite)} + 2\text{S(rhombic)} \rightarrow \text{CS}_2(l) \quad \Delta H^\circ_{\text{rxn}} = -393.5 + (2\times-296.1) + 1072 = 86.3 \ \text{kJ} \]

Thermochemistry is concerned primarily with calculating \( \Delta H^\circ_{\text{rxn}} \) (the heat of a reaction).

There are 2-Ways or 2-Problem Types

For Hess Law Enthalpy Calculations

1) standard state
2) formation equation
3) Calculation of \( \Delta H^\circ_{\text{rxn}} \)

\[ \Delta H^\circ_{\text{rxn}} = \sum n_i \Delta H^\circ_i(\text{products}) - \sum m_i \Delta H^\circ_i(\text{reactants}) \]

Physicists and chemists define a standard thermodynamic “standard state” and denote with a superscript degree sign, \( \Delta H^\circ \)

**Thermodynamic Standard State Means:**
- 1 atmosphere pressure
- 25°C = 298.15K
- 1 Molar concentration for solutions

\[ \Delta H^\circ_{\text{rxn}} \rightarrow \Delta H^\circ_{\text{rxn}} \]

**Conditions of P, T, [] are given in problem and stated**

The superscript indicates thermodynamic standard state: P = 1 atm, T = 298, [1M]

**Note: fractional coefficients allowed**

It is not possible to measure the “absolute enthalpy”. We define an arbitrary scale with the standard enthalpy of formation (\( \Delta H^\circ_f \)) as a reference point.

1) The standard enthalpy of formation, \( \Delta H^\circ_f \) of any element in its most stable form is zero.

\[ \Delta H^\circ_f \] (O²) = 0

\[ \Delta H^\circ_f \] (C, graphite) = 0

\[ \Delta H^\circ_f \] (O³) = 142 kJ/mol

\[ \Delta H^\circ_f \] (C, diamond) = 1.90 kJ/mol

\[ \Delta H^\circ_f \] (S₈, rhombic) = 0 kJ/mol

\[ \Delta H^\circ_f \] (H₂O(l)) = 0 kJ/mol

**The standard enthalpy of formation, \( \Delta H^\circ_f \) of many compounds is tabulated in many handbooks. This gives us predictive capability and is someone useful in the real world.**

The Standard Enthalpy of Formation, \( \Delta H^\circ_f \), is the enthalpy change associated with the formation of 1 mole of product from its naturally occurring elements under standard state conditions.

- Examples:

\[ \text{H}_2(g) + \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H^\circ_f = -285.8 \ \text{kJ/mol} \]

\[ 3\text{C(s)} + 4\text{H}_2(g) \rightarrow \text{C}_3\text{H}_8(g) \quad \Delta H^\circ_f = -103.85 \ \text{kJ/mol} \]

\[ \text{Ag(s)} + \text{1/2Cl}_2(g) \rightarrow \text{AgCl(s)} \quad \Delta H^\circ_f = -127.0 \ \text{kJ/mol} \]

- Note: 1 mol product!

- Are familiar molecular gases as \( \text{O}_2, \text{N}_2, \text{F}_2, \text{H}_2 \) etc as at 25°C

- Elemental Carbon exists as solid graphite \( C(\text{graph}) \) at 25°C

- Elemental Sulfur exists as \( S_8 \) as a solid at 25°C

- Water is \( \text{H}_2\text{O}(l) \) in its standard state (not ice or water vapor)

Tabulated Values of \( \Delta H^\circ_f \) From Silberberg Textbook

<table>
<thead>
<tr>
<th>Formula</th>
<th>( \Delta H^\circ_f ) (kJ/mol)</th>
<th>Formula</th>
<th>( \Delta H^\circ_f ) (kJ/mol)</th>
<th>Formula</th>
<th>( \Delta H^\circ_f ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(s)</td>
<td>0</td>
<td>Cl₂(g)</td>
<td>0</td>
<td>Ag(s)</td>
<td>0</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>-635.1</td>
<td>HCl(g)</td>
<td>-92.3</td>
<td>AgCl(s)</td>
<td>-127.0</td>
</tr>
<tr>
<td>CaCO₃(s)</td>
<td>-1206.9</td>
<td>H₂(g)</td>
<td>218</td>
<td>Na(s)</td>
<td>0</td>
</tr>
<tr>
<td>C(graphite)</td>
<td>0</td>
<td>H₂O(g)</td>
<td>0</td>
<td>Na(g)</td>
<td>107.8</td>
</tr>
<tr>
<td>C(diamond)</td>
<td>1.9</td>
<td>N₂(g)</td>
<td>0</td>
<td>NaCl(s)</td>
<td>-411.1</td>
</tr>
<tr>
<td>CO(g)</td>
<td>-110.5</td>
<td>NO(g)</td>
<td>90.3</td>
<td>S(s)</td>
<td>0</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>-393.5</td>
<td>NO₂(g)</td>
<td>-45.9</td>
<td>S₈(rhombic)</td>
<td>0</td>
</tr>
<tr>
<td>CH₄(g)</td>
<td>-74.9</td>
<td>O₂(g)</td>
<td>0</td>
<td>S₈(monoclinic)</td>
<td>0.3</td>
</tr>
<tr>
<td>CH₂O₂H(l)</td>
<td>-238.6</td>
<td>H₂O(g)</td>
<td>-241.8</td>
<td>SO₃(g)</td>
<td>-296.8</td>
</tr>
<tr>
<td>HCN(g)</td>
<td>135</td>
<td>H₂O(l)</td>
<td>-285.8</td>
<td>SO₂(g)</td>
<td>-396.0</td>
</tr>
<tr>
<td>CS₂(l)</td>
<td>87.9</td>
<td></td>
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<td></td>
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<tr>
<td>Cl(g)</td>
<td>121.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Writing Heat of Formation $\Delta H^0_f$ Equations

Write balanced equations for the formation of 1 mol of the following compounds from their elements in their standard states and include $\Delta H^0_f$.

(a) Silver chloride, AgCl, a solid at standard conditions.
(b) Calcium carbonate, CaCO$_3$, a solid at standard conditions.
(c) Hydrogen sulfide, H$_2$S, a gas at standard conditions.

PLAN: Remember 1 mole of product is formed and fractions are allowed as coefficients!

<table>
<thead>
<tr>
<th>Method</th>
<th>Reactants</th>
<th>Products</th>
<th>$\Delta H^0_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Ag(s) + 1/2Cl$_2$(g)</td>
<td>AgCl(s)</td>
<td>$-127.0$ kJ</td>
</tr>
<tr>
<td>(b)</td>
<td>Ca(s) + C(graphite) + 3/2O$_2$(g)</td>
<td>CaCO$_3$(s)</td>
<td>$-1206.9$ kJ</td>
</tr>
<tr>
<td>(c)</td>
<td>O$_2$(g) + 1/2N$_2$(g)</td>
<td>NO$_2$(g)</td>
<td>$33.9$ kJ</td>
</tr>
</tbody>
</table>

Thermochemistry is concerned primarily with calculating $\Delta H^0_{rxn}$ (the heat of a reaction).

There are 2-Ways or 2-Problem Types For Hess Law Enthalpy Calculations

1) standard state
2) formation equation
3) Calculation of $\Delta H^0_{rxn}$

Multiple Thermochemical Equations To Rearrange--Use Rules!

$\Delta H^0_{rxn} = \sum n_i \Delta H^0_f(products) - \sum m_i \Delta H^0_f(reactants)$

METHOD 2: The enthalpy of any reaction, $\Delta H^*_{rxn}$, can be obtained by using $\Delta H^f_i$ and the following equation:

$\Delta H^*_{rxn} = \sum n_i \Delta H^f_i(products) - \sum m_i \Delta H^f_i(reactants)$

where $\sum$ means "the sum of".

$n_i$ is the respective stoichi coefficient for $i^{th}$ product
$m_i$ is the respective stoichi coefficient for each $i^{th}$ reactant

IT'S EASIER TO APPLY THAN IT LOOKS! We look up $\Delta H^f_i$ values for products and reactants from a table and multiple by stoichiometric coefficients.

Example: Suppose $aA + bB \rightarrow cC + dD$ $\Delta H^*_{rxn} = ?$

$\Delta H^0_{rxn} = \Delta H^f_i(Products) - \Delta H^f_i(Reactants)$

$\Delta H^0_{rxn} = [c\Delta H^f_i(C) + d\Delta H^f_i(D)] - [a\Delta H^f_i(A) + b\Delta H^f_i(B)]$
Nitric acid, whose worldwide annual production is about 8 billion kilograms, is used to make many products, including fertilizer, dyes, and explosives. The first step in the industrial production process is the oxidation of ammonia:

\[ 4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g) \]

Calculate \( \Delta H^\circ \text{rxn} \) from \( \Delta H^\circ_i \) values.

**PLAN:** Look up the \( \Delta H^\circ_i \) values in Appendix and use Hess’s Law to find \( \Delta H^\circ \text{rxn} \).

\( \Delta H^\circ_i \text{NH}_3(g) = -46.3 \text{ kJ/mol} \)

\( \Delta H^\circ_i \text{O}_2(g) = 0 \)

\( \Delta H^\circ_i \text{H}_2\text{O}(g) = -241.8 \text{ kJ/mol} \)

\( \Delta H^\circ_i \text{NO}(g) = 90.4 \text{ kJ/mol} \)

\[ \Delta H^\circ \text{rxn} = -904 \text{ kJ} \]

Benzene (C\(_6\)H\(_6\)) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.

\[ 2\text{C}_6\text{H}_6(l) + 15\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \]

Calculate \( \Delta H^\circ \text{rxn} \) from \( \Delta H^\circ_i \) values.

**SOLUTION:**  \( \Delta H^\circ \text{rxn} = \Sigma n\Delta H^\circ_i \text{(products)} - \Sigma m\Delta H^\circ_i \text{(reactants)} \)

\( \Delta H^\circ \text{rxn} = [4(\Delta H^\circ_i \text{NO}(g) + 6(\Delta H^\circ_i \text{H}_2\text{O}(g)))] - [4(\Delta H^\circ_i \text{NH}_3(g) + 5(\Delta H^\circ_i \text{O}_2(g))] \)

\( = (4 \text{ mol})(90.4 \text{ kJ/mol}) + (6 \text{ mol})(-241.8 \text{ kJ/mol}) - \)

\( [4 \text{ mol})(-46.3 \text{ kJ/mol}) + (5 \text{ mol})(0 \text{ kJ/mol})] \)

\( \Delta H^\circ \text{rxn} = -904 \text{ kJ} \)

### Calculating Using Contrived Equations

\[ 6\text{C}(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) \quad \Delta H^\circ_i = (-393.5 \text{ kJ}) \]

\[ 3\text{H}_2(g) + \frac{3}{2}\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(l) \quad \Delta H^\circ_i = (-285.8 \text{ kJ}) \]

\[ \text{C}_6\text{H}_6(l) \rightarrow 6\text{C}(s) + 3\text{H}_2(g) \quad \Delta H^\circ_i = (-94.04 \text{ kJ}) \]

\[ \Delta H^\circ \text{comb} = [6(-393.5 \text{ kJ}) + 3(-285.8 \text{ kJ})] - [(-94.04 \text{ kJ})] = -3,267.4 \text{ kJ} \]

\[ \Delta H^\circ \text{rxn} = \Sigma n_i \Delta H^\circ_i \text{(products)} - \Sigma m_i \Delta H^\circ_i \text{(reactants)} \]

that’s for one mole of benzene only!

\[ 2 \text{C}_6\text{H}_6(l) + 15\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \quad \Delta H^\circ \text{comb} = 2 \times -3,267 \text{ kJ/mol} \]

### Enthalpies (\( \Delta H \)) of chemical reactions can be determined using the physics of heat transfer a lab method called **calorimetry**.

**Must Understand the Physics of HEAT**

**ABSORPTION: KEY RIFF** = heat absorbed by a substance depends on the material’s specific heat capacity, mass and temperature change.

\[ q = C \Delta T = s \cdot m \Delta T \]

\[ \sum_{i=1}^{n} q_i = 0 \]

No heat enters or escapes!
Principle 1: The amount of heat, $q$, transferred from an object at higher temperature to an object at lower temperature is proportional to the difference in temperature of the two objects!

$$q \propto \Delta T$$

$$q = C \Delta T$$ $C$ = constant of material called heat capacity

**The heat capacity** ($C$) of a material is the amount of heat ($q$) required to raise the temperature by one degree Celsius or Kelvin (units of J/°C or J/K or cal/°C).

Heat transferred = $q \propto (T_{\text{final}} - T_{\text{initial}})$

$$q = C \Delta T$$

- Material dependent constant “heat capacity”
- Temperature difference between objects

$$C = \frac{q}{\Delta T}$$ units of energy per degree (J/°C, J/K, cal/°C, cal/K)

**Principle 2:** The heat capacity, $C$, of any material is found to be proportional to mass of a substance under question.

$$C \propto m$$

$$C = m \cdot s$$ $s$ = constant called the specific heat capacity

**The specific heat** ($s$) of a substance is the amount of heat ($q$) required to raise the temperature of one gram of the substance by one degree Celsius. (How thermally sensitive a substance is to the addition of energy!)

$$q = C \Delta T$$

$$C = m \cdot s$$ (1) (2)

Substituting (2) into 1 gives:

Heat ($q$) absorbed or released:

$$q = s \cdot m \Delta T$$

**The specific heat capacity** of a substance is the amount of heat ($q$) required to raise the temperature of one gram of the substance by one degree Celsius.

**Enthalpies ($\Delta H$)** of chemical reactions can be determined using a lab method called calorimetry.

Understand two concepts and you can solve any heat problem in chemistry or physics.

1. **Law of Conservation of Energy**

$$q_{\text{system}} + q_{\text{surroundings}} = 0$$

$$\sum_{i=1}^{n} q_i = 0$$ shorthand notation

2. **Specific Heat Capacity of Substances**

$$q = s \cdot m \Delta T = C \Delta T$$

Heat ($q$) absorbed depends on specific heat capacity, mass and temperature change.
How much heat, \( q \), is required to raise the temperature of 1000 kg piece of iron, (2) a separate 1000 kg of water from 25 to 75°C? Note that the specific heat capacity of iron is 0.45 J/g °C

Heat (\( q \)) absorbed or released:

\[
q = s \cdot m \cdot \Delta T
\]

\[
q_{\text{Fe}} = 1.00 \times 10^3 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times (75° - 25°) \times 0.45 \frac{\text{J}}{\text{g °C}} = 2.25 \times 10^7 \text{ J}
\]

\[
q_{\text{H}_2\text{O}} = 1.00 \times 10^3 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times (75° - 25°) \times 4.18 \frac{\text{J}}{\text{g °C}} = 2.09 \times 10^8 \text{ J}
\]

Coffee Cup Calorimeter

A simple cheap calorimeter—pressure is constant—so we are measuring: \( \Delta H = q_p = \Delta E + P \Delta V \)

- Well insulated and therefore isolated.
- Calorimeter and other parts are assumed to not absorb heat (not true but assumed)
- Heat will come from a chemical reaction, and is denoted: \( q_{\text{rxn}} \)
- Energy Conservation is key: Sum the heats

\[
\sum_{i=1}^{n} q_i = 0
\]

\[
q_{\text{cal}} + q_{\text{therm}} + q_{\text{solution}} + q_{\text{rxn}} = 0
\]

\[
q_i = C_i \Delta T = m_i s_i \Delta T
\]

Determine the specific heat capacity of lead when 150.0 grams of lead pellets at 100.0°C are added to 50.0 ml of water held at 22.0°C. The final temperature of the insulated calorimeter is 28.8°C. Assume the container and thermometer do not absorb heat.

\[
q_{\text{water}} = mc \Delta T = (50.0 \text{ g})(4.184 \text{ J/g °C})(28.8 - 22.0)\circ\text{C} = 1.40 \times 10^3 \text{ J}
\]

\[
q_{\text{lead}} = mc \Delta T = (150.0 \text{ g})(0.13 \text{ Jg}^{-1}\text{C}^{-1})(28.8 - 100.0)\circ\text{C} = -1.40 \times 10^3 \text{ J}
\]

A 237 g piece of molybdenum, initially at 100.0 °C, is dropped into an insulated container with 244 g of water at 10.0 °C. When the system comes to thermal equilibrium, the temperature of the system is 15.3 °C. What is the specific heat of molybdenum?
A 237 g piece of molybdenum, initially at 100.0 °C, is dropped into an insulated container with 244 g of water at 10.0 °C. When the system comes to thermal equilibrium, the temperature of the system is 15.3 °C. What is the specific heat of molybdenum?

\[ \sum_{i=1}^{n} q_i = 0 \]
\[ q_{mb} + q_{water} = 0 \]
\[-q_{mb} = -s_{mb} m_{mb} \Delta T = s_{wtr} m_{wtr} \Delta T = q_{water} \]

\[ 4.184 \frac{J}{g°C} \times 244g \times (15.3 - 10.0) °C = -s \frac{J}{g°C} \times 237g \times (15.3 - 100.0) °C \]

\[ s = \frac{4.184 \frac{J}{g°C} \times 244g \times 5.3°C}{237g \times 84.7°C} = 0.27 \frac{J}{g°C} = 0.27 \frac{J}{gK} \]

Coffee-Cup Calorimetry

Suppose 60.1 g of water at 97.6 °C is poured into a coffee cup containing 50.3 g of water at 24.7 °C. Suppose the final temperature of the combined water samples reaches 62.8 °C. What is the calorimeter heat capacity given that the specific heat capacity of water is 4.184 J/g °C

\[ HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq) \quad \Delta H = ? \text{kJ/mol} \]

A student mixes 50.0 mL of 1.00 M HCl and 50.0 mL of 1 M NaOH in a coffee-cup calorimeter and finds the mixture goes from 21.00 °C to 27.50 °C. Calculate the Heat of Neutralization for the reaction, assuming that the calorimeter and thermometer absorbs a negligible quantity of heat and that the total volume of the solution is additive; that the water density is 1.000 g/mL and its specific heat capacity is that of water = 4.18 J/g K.

\[ HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq) \quad \Delta H = ? \text{kJ} \]

\[ \Delta H = \frac{q_{rxn}}{n} \]

\[ q_{rxn} = m \times s \times \Delta T \]

\[ q_{rxn} = 100.0 \text{mL} \times \frac{1000 \text{ g}}{\text{mL}} \times 4.184 \frac{J}{g°C} \times (27.50 - 21.00) °C = 2720 \text{ J} \]

\[ q_{rxn} = -2720 \text{ J} \]

\[ \text{enthalpy change per mol HCl} = \Delta H \text{per mol} = \frac{q}{n} = \frac{-2720}{\text{mol HCL}} \]

\[ \text{mol HCl} = 0.0500 \text{ L} \times \text{HCl} \times 1.00 \frac{\text{mol HCl}}{\text{L HCl}} = 0.0500 \text{ mol HCl} \]

\[ \Delta H = \frac{-2720}{0.0500 \text{ mol HCl}} = -54.4 \frac{\text{kJ}}{\text{mol HCl}} \]