Chapter 10
Thermochemistry

• 10-1 Heat
• 10-2 Calorimetry
• 10-3 Enthalpy
• 10-4 Standard-State Enthalpies
• 10-5 Bond Enthalpies
• 10-6 The First Law of Thermodynamics
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Thermochemistry

• **Heat Capacity**, \( C_p \), is the amount of heat required to raise the temperature of a substance by one degree at constant pressure.

• \( C_p \) is always a positive number
• \( Q \) and \( \Delta T \) must be both negative or positive
• If \( q \) is negative, then heat is evolved or given off and the temperature decreases
• If \( q \) is positive, then heat is absorbed and the temperature increases
Heat Capacity (continued)

- $C_p$ units are energy per temp. change
- $C_p$ units are Joule/°K or JK$^{-1}$

- Molar heat capacity

- Units are J/K/mole or JK$^{-1}$mol$^{-1}$
Specific Heat Capacity

- The word **Specific** before the name of a physical quantity very often means divided by the mass

- **Specific Heat Capacity** is the amount of heat required to raise the temperature of one gram of material by one degree Kelvin (at constant pressure)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat Capacity (J/gK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(l)</td>
<td>0.140</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.739</td>
</tr>
<tr>
<td>O₂</td>
<td>0.719</td>
</tr>
<tr>
<td>H₂O</td>
<td>4.18</td>
</tr>
</tbody>
</table>
Chapter 10
Thermochemistry

• Example (not in book)
  a.) Calculate the molar heat capacity of quartz (SiO$_2$)
  b) Calculate the amount of heat required to raise 45.0 Kg of rock (quartz) by 15°C.

• Strategy
  a) Use relationship $c_p = M c_s$
  b) Use $q = m c_s \Delta T$
Example (not in book)

a.) Calculate the molar heat capacity of quartz (SiO$_2$), if $c_s$SiO$_2$=0.739 J/K/g

b) Calculate the amount of heat required to raise 45.0 Kg of rock (quartz) by 15°C.

Solution

a) Find the molar mass of quartz and Use relationship $c_p=Mc_s$

b) Use $q= mc_s\Delta T$
Exercise 10-1

- Exactly 500.0 kJ of heat is absorbed at a constant pressure by a sample of gaseous helium. The temperature increases by 15.0K.
  
  a.) Compute the heat capacity of the sample

  b.) The mass of the helium sample is 6.42 kg. Compute the specific heat capacity and molar heat capacity of helium.

Strategy

- a.) Use the relationship $C_p = \frac{q}{\Delta T}$
- B.) Use $c_s = \frac{C_p}{m}$ and use $c_p = \frac{C_p}{n}$
Exercise 10-1

- Exactly 500.0 kJ of heat is absorbed at a constant pressure by a sample of gaseous helium. The temperature increases by 15.0K.
  
a.) Compute the heat capacity of the sample
  
b.) The mass of the helium sample is 6.42 kg.
    Compute the specific heat capacity and molar heat capacity of helium.

Solution

  - a.) Use the relationship \( C_p = \frac{q}{\Delta T} \)

  - b.) Use \( c_s = \frac{C_p}{m} \) and use \( c_p = \frac{C_p}{n} \)
Equilibration Temperature

- When 2 bodies are placed in contact, heat is exchanged until they reach a common final temperature.
- Heat gained by the cooler body equals the heat lost by the warmer body.
- If \( q \) is positive, heat is gained.
- If \( q \) is negative, heat is lost.

- Can also write similar equations for \( c_s \)
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Thermochemistry

• Example (not in book)
A 43.9g piece of Copper ($c_s = 0.385 \text{ J g}^{-1} \text{ K}^{-1}$) at 135 °C is plunged into 254g of water ($c_s = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$) at 39 °C. Assuming no heat is lost to the surroundings, what will be the final temperature?

a) 100.0 C
b) 87.0 C
c) 53.1 C
d) 40.5 C
e) None of these
Also Try 10-2 Example and Exercise
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Thermochemistry

• For processes carried out at constant pressure, the heat absorbed equals a change in **Enthalpy**, $H$.

\[ q_p = \Delta H \]

(note p denotes constant pressure)

• **Enthalpy** is a **state property**, which means it depends on its initial and final state, not the path to get there.
Enthalpy of Reaction

• If a chemical reaction occurs at constant pressure then
• \((\text{Heat absorbed}) = q_p = \Delta H\)
• \(\Delta H\) may be either positive or negative
  – If \(\Delta H\) positive \(= \Delta H > 0 = q > 0\)
    Means heat is absorbed
    And is called Endothermic
  – If \(\Delta H\) negative \(= \Delta H < 0 = q < 0\)
    Means heat is given off
    And is called Exothermic
CO (g) + \( \frac{1}{2} \) O\(_2\) (g) \( \rightarrow \) CO\(_2\) (g) \( \Delta H = -283\)kJ

An exothermic reaction

If doubled (x2), double \( \Delta H \)
2CO (g) + O\(_2\) (g) \( \rightarrow \) 2CO\(_2\) (g) \( \Delta H = -566\)kJ

If the original reaction is reversed
CO\(_2\) (g) \( \rightarrow \) CO (g) + \( \frac{1}{2} \) O\(_2\) (g) \( \Delta H = +283\)kJ

An endothermic reaction

You can Try Example 10-5
Phase Changes

• Phase changes are not chemical reactions but involve enthalpy change

• Note that there are no $T$ units, these occur at constant temperatures for freezing, fusion, vaporization or condensation
Typical Exam question

How much heat energy is needed to decompose 9.74g of HBr (g) (M =80.9 g/mol) into its elements?

\[ \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr (g)} \]

\[ \Delta H = -72.8 \text{ kJmol}^{-1} \]

Strategy:
• Decomposition is actually the reverse reaction
• \( \Delta H \) to burn 2 moles of HBr is 72.8kJ/mol
Typical Exam question

How much heat energy is needed to decompose 9.74g of HBr (g) (M = 80.9 g/mol) into its elements?

\[ \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr (g)} \]

\[ \Delta H = -72.8 \text{ kJ mol}^{-1} \]

Solution:

\[ 2\text{HBr (g)} \rightarrow \text{H}_2 + \text{Br}_2 \]

\[ \Delta H = +72.8 \text{ kJ mol}^{-1} \]
Hess’s Law

• Sometimes it's difficult or even impossible to conduct some experiments in the lab.

• Because **Enthalpy (H) is a State Property**, it doesn’t matter what path is taken as long as the initial reactants lead to the final product.

• Hess’s Law is about adding or subtracting equations and enthalpies.

• **Hess’s Law**: *If two or more chemical equations are added to give a new equation, then adding the enthalpies of the reactions that they represent gives the enthalpy of the new reaction.*
Hess’s Law

Unknown C (graphite) + 1/2 O₂ (g) → CO (g) ΔH = ?

This is Hess’s Law. It always works no matter how complicated the path.
Standard State
Enthalpies

- Designated using a superscript ° (pronounced naught)
- This is needed because Enthalpy varies with temperature
- Is written as $\Delta H^\circ$

$\Delta H^\circ_{25^\circ C}$ or $\Delta H^\circ_{298.15^\circ K}$ or $\Delta H^\circ$

- If no temperature is indicated in the subscript, assume 25°C.
- OFB text appendix D lists standard enthalpies of formation for a variety of chemical species at 1 atm and 25°C.
Standard State Enthalpies

• $\Delta H^\circ$ is the sum of products minus the sum of the reactants

• For a general reaction
  $a \text{ A} + b \text{ B} \rightarrow c \text{ C} + d \text{ D}$
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• Exercise 10-7

Suppose hydrazine and oxygen react to give dinitrogen pentaoxide and water vapor:

\[ 2 \text{N}_2\text{H}_4 \text{ (l)} + 7 \text{O}_2 \text{ (g)} \rightarrow 2 \text{N}_2\text{O}_5 \text{ (s)} + 4 \text{H}_2\text{O} \text{ (g)} \]

Calculate the \( \Delta H \) of this reaction, given that the reaction:
\[ \text{N}_2 \text{ (g)} + \frac{5}{2} \text{O}_2 \text{ (g)} \rightarrow \text{N}_2\text{O}_5 \text{ (s)} \]
has a \( \Delta H \) of -43 kJ.
10-7 Exercise

\[2N_2H_4 (l) + 7O_2 (g) \Rightarrow 2N_2O_5 (s) + 4H_2O (g)\]

• What values to use?
  – \(\Delta H_f^\circ N_2O_5 (s)\) given \(\Delta H^\circ = -43.1 \text{ kJmol}^{-1}\)
  – \(\Delta H_f^\circ H_2O (g)\) look up in App. D
  – \(\Delta H_f^\circ N_2H_4 (l)\) look up in App. D
  – \(\Delta H_f^\circ O_2 (g)\) look up in App. D

• \(\Delta H_f^\circ = -1154.74 \text{ kJmol}^{-1}\)
Typical Exam question

Given the following thermo chemical equations, calculate the standard enthalpy of formation for propane, \( \text{C}_3\text{H}_8 \) (g)

1. \( \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \)
   \( \Delta H^\circ = (-393) \text{ kJmol}^{-1} \)

2. \( \text{H}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \)
   \( \Delta H^\circ = (-286) \text{ kJmol}^{-1} \)

3. \( \text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \)
   \( \Delta H^\circ = (-2452) \text{ kJmol}^{-1} \)

Answers

A. (3131) \text{ kJmol}^{-1}

B. 129

C. 4775

D. (1773)

E. None of these
General

\[ aA + bB \rightarrow cC + dD \]

\[ \Delta H^\circ = c\Delta H^\circ C + d\Delta H^\circ D - a\Delta H^\circ A - b\Delta H^\circ B \]
Bond Enthalpies

- The breaking of chemical bonds in stable substances often generates highly reactive products (or intermediates)

\[ \text{CH}_4 \rightarrow \cdot \text{CH}_3 + \cdot \text{H} \quad \Delta H^\circ = + 439 \text{ kJmol}^{-1} \]

- Called Bond Enthalpy
- OFB Table 10-3 p 462 gives Average Bond Enthalpies

### Table 10–3
Average Bond Enthalpies

<table>
<thead>
<tr>
<th>Bond Enthalpya (kJ mol(^{-1}))</th>
<th>H—</th>
<th>C—</th>
<th>C=</th>
<th>C≡</th>
<th>N—</th>
<th>N=</th>
<th>N≡</th>
<th>O—</th>
<th>O=</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>436</td>
<td>413</td>
<td>391</td>
<td>463</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>413</td>
<td>348</td>
<td>615</td>
<td>812</td>
<td>292</td>
<td>615</td>
<td>891</td>
<td>351</td>
<td>728</td>
</tr>
<tr>
<td>N</td>
<td>391</td>
<td>292</td>
<td>615</td>
<td>891</td>
<td>161</td>
<td>418</td>
<td>945</td>
<td>139</td>
<td>498</td>
</tr>
<tr>
<td>O</td>
<td>463</td>
<td>351</td>
<td>728</td>
<td>139</td>
<td>498</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>339</td>
<td>259</td>
<td>477</td>
<td>185</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>F</td>
<td>563</td>
<td>441</td>
<td>270</td>
<td>185</td>
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</tr>
<tr>
<td>Cl</td>
<td>432</td>
<td>328</td>
<td>200</td>
<td>203</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Br</td>
<td>366</td>
<td>276</td>
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<td>203</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>299</td>
<td>240</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

• **Average** Bond Enthalpies

\[
\begin{align*}
C_2H_6 & \rightarrow \cdot C_2H_5 + \cdot H \quad \Delta H^\circ = + 410 \text{ kJmol}^{-1} \\
CHF_3 & \rightarrow \cdot CF_3 + \cdot H \quad \Delta H^\circ = + 429 \text{ kJmol}^{-1} \\
CHCl_3 & \rightarrow \cdot CCl_3 + \cdot H \quad \Delta H^\circ = + 380 \text{ kJmol}^{-1} \\
CHBr_3 & \rightarrow \cdot CBr_3 + \cdot H \quad \Delta H^\circ = + 377 \text{ kJmol}^{-1}
\end{align*}
\]

\[\text{average } \Delta H^\circ \text{C-H} = + 412 \text{ kJmol}^{-1}\]

• Applications of Bond Enthalpy

– Given a reaction
– 1\textsuperscript{st} Step is break all bonds to give free atoms in the gas phase (Endothermic)
– 2\textsuperscript{nd} Step is form new bonds for the products. (Exothermic)
• Applications of Bond Enthalpy
  – Given a reaction
  – 1\textsuperscript{st} Step is break all bonds to give free atoms in the gas phase (Endothermic)
  – 2\textsuperscript{nd} Step is form new bonds for the products. (Exothermic)
Exercise 10-10

• Estimate the Standard Enthalpy of reaction for the gas-phase reaction that forms methanol from methane and water and compare it with the $\Delta H^\circ_r$ obtained from the data in Appendix D.

$$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g}) + \text{H}_2(\text{g})$$
\[ \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g}) + \text{H}_2(\text{g}) \]

\[ \text{C-H} \quad + \quad \text{O-H} \quad \rightarrow \quad \text{C-O-H} \quad + \quad \text{H-H} \]

<table>
<thead>
<tr>
<th>Broken</th>
<th>Formed</th>
<th>Endothermic</th>
<th>Exothermic</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 C-H</td>
<td>3 C-H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 O-H</td>
<td>1 O-H</td>
<td>1 C-O</td>
<td>1 H-H</td>
</tr>
<tr>
<td>kJmol(^{-1})</td>
<td>kJmol(^{-1})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \Delta H = \Delta H \text{ bonds broken} + \Delta H \text{ bonds formed} \]

\[ = +2578 + (-2489) = +89 \text{ kJmol}^{-1} \text{ (estimated)} \]

Using Appendix D \( \Delta H = 116 \text{ kJmol}^{-1} \)
Chapter 10
Thermochemistry

• **First Law of Thermodynamics**
  The change in the internal energy of a system is equal to the work done on it plus the heat transferred to it.
  \[ \Delta E = q + w \]

• **Second Law of Thermodynamics**
  In a real spontaneous process the Entropy of the universe (meaning the system plus its surroundings) must increase.
  \[ \Delta S_{\text{universe}} > 0 \]

• **Third Law of Thermodynamics**
  In any thermodynamic process involving only pure phases at equilibrium, the entropy change, \( \Delta S \), approaches zero at absolute zero temperature; also the entropy of a crystalline substance approaches zero.
  \[ \Delta S = 0 \text{ at } 0^\circ \text{K} \]
First Law of Thermodynamics

\[ \Delta E = q + w \]

- \( q \) was previously defined as the Heat Absorbed by a system
- If \( q > 0 \), heat is absorbed
- If \( q < 0 \), heat is given off
- \( w \) is the work done on the body

Recall

- \( w = F \times d \)
- \( w = \Delta E_{\text{Kinetic}} = \Delta \left( \frac{1}{2}mv^2 \right) \)
- \( w = \Delta E_{\text{potential}} = mg\Delta h \)

- In chemistry this kind of mechanical work is Pressure-Volume work (P-V)
• Force exerted by heating $= P_1 A$
  – Where $P_1$ is the pressure inside the vessel
  – Where $A$ is the Area of the piston
• $P_{\text{ext}} = P_1$ if balanced
• $\Delta V = A \Delta h$
• $W = -P_{\text{ext}} \Delta V$
  – Units are atm·L or L atm
  – Where 1 L atm = 101.325 Joules
\[ W = -P_{\text{ext}} \Delta V \]

- **Expansion**
  - \( \Delta V > 0 \) therefore \( w < 0 \)
  - The system does work on the surroundings

- **Compression**
  - \( \Delta V < 0 \) therefore \( w > 0 \)
  - The surroundings have done work on the system

- **Try Example and Exercise 10-11**
  - Calculate the work done on a gas and express it in Joules
Typical exam questions (1-4)
A gas is compressed from 39.92L to 12.97L at a constant pressure of 5.00 atm. In the course of this compression 9.82 kJ of energy is released

Q1 The heat q for this process is

a 135 kJ
b -135 kJ
c -9.82 kJ
d 9.82 kJ
e can not be determined
A gas is compressed from 39.92L to 12.97L at a constant pressure of 5.00 atm. In the course of this compression 9.82 kJ of energy is released.

**Q2** The work w for this process is

a. 135 L atm
b. -135 L atm
c. -9.82 L atm
d. 9.82 L atm
e. cannot be determined
A gas is compressed from 39.92L to 12.97L at a constant pressure of 5.00 atm. In the course of this compression 9.82 kJ of energy is released.

\[ \Delta E \]

\[ \begin{align*}
\text{a} & : -23.47 \text{ kJ} \\
\text{b} & : 3.86 \text{ kJ} \\
\text{c} & : 23.47 \text{ kJ} \\
\text{d} & : 125 \text{ kJ} \\
\text{e} & : \text{none of these}
\end{align*} \]
A gas is compressed from 39.92L to 12.97L at a constant pressure of 5.00 atm. In the course of this compression 9.82 kJ of energy is released

Q4 $\Delta H$ for the process is

a -9.82 kJ  

b -7.09 kJ  

c 3.83 kJ  

d 9.82 KJ  

e none of these
Enthalpy and Energy

- 1st Law of Thermodynamics
  \[ \Delta E = q + w \]
  - At constant volume \( \Delta V = 0 \)
  - Thus \( w = -P_{\text{ext}} \Delta V = 0 \)
  \[ \Delta E = q_v \text{ (constant volume)} \]

- Recall as previously stated
  \[ \Delta H = q_p \text{ (constant pressure)} \]

- Enthalpy is defined as
  \[ H = E + PV \]

- or Expressed as a change in Enthalpy
  \[ \Delta H = \Delta E + \Delta(PV) \]

- Rearrange
  \[ \Delta E = \Delta H + \Delta(PV) \]

- If \( PV = nRT \) is the ideal gas law
  \[ \Delta(PV) = \Delta(nRT) = RT \Delta n_g \]
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$\Delta(PV) = RT \Delta n_g$

- $\Delta n_g$ is the change in the total chemical amount of gases in a reaction
- $\Delta n_g = $ Total moles of product gases minus the Total moles of reactant gases
Example

- Calculate the internal energy @ 25°C for the following reaction

\[ \text{C(graphite)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}(g) \]

\[ \Delta H = -110.5 \text{ kJ} \]
Example

- Calculate the internal energy at 25°C for the following reaction

\[
\text{C(graphite)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(}g\text{)}
\]

\[
\Delta H = -110.5 \text{ kJ}
\]
Chapter 10
Thermochemistry Summary

Heat Capacity = \( C_p = \frac{q}{\Delta T} = \frac{\text{heat absorbed}}{\Delta T} \)
where \( C_p \) denotes Heat Capacity at constant pressure
\( \Delta T = T_f - T_i \)

Molar Heat Capacity
\( c_p = \frac{C_p}{n} \) units are JK\(^{-1}\)mol\(^{-1}\)

Specific Heat Capacity
\( c_s = \frac{C_p}{m} \) units are JK\(^{-1}\)g\(^{-1}\)

Equilibration Temperature
\[ q_1 = -q_2 \]
\[ n_1c_{p1}\Delta T_1 = -n_2c_{p2}\Delta T_2 \]
\[ n_1c_{p1}(T_f - T_i)_1 = -n_2c_{p2}(T_f - T_i)_2 \]
• **Enthalpy, H.**

\[ q_p = \Delta H \]

(note p denotes constant pressure)

• **Enthalpy** is a **state property**, which means it depends on its initial and final state, not the path to get there.

  – If **\( \Delta H \) positive** = \( \Delta H > 0 = q > 0 \)
    Means heat is absorbed
    And is called **Endothermic**

  – If **\( \Delta H \) negative** = \( \Delta H < 0 = q < 0 \)
    Means heat is given off
    And is called **Exothermic**

• **Hess’s Law:** *If two or more chemical equations are added to give a new equation, then adding the enthalpies of the reactions that they represent gives the enthalpy of the new reaction.*
Standard State Enthalpies

- $\Delta H^\circ$ is the sum of products minus the sum of the reactants
- For a general reaction
  \[ a\, A + b\, B \rightarrow c\, C + d\, D \]

\[
\Delta H^\circ = c\Delta H_f^\circ (C) + d\Delta H_f^\circ (D) - a\Delta H_f^\circ (A) - b\Delta H_f^\circ (B)
\]

Bond Enthalpies

$\Delta H = \Delta H$ bonds broken + $\Delta H$ bonds formed

First Law of Thermodynamics

The change in the internal energy of a system is equal to the work done on it plus the heat transferred to it.

\[ \Delta E = q + w \]
Enthalpy and Energy

- Enthalpy is defined as
  \[ H = E + PV \]

- or Expressed as a change in Enthalpy
  \[ \Delta H = \Delta E + \Delta(PV) \]

- For gases, If PV = nRT is the ideal gas law
  \[ \Delta(PV) = \Delta(nRT) = RT \Delta n \]
Chapter 10
Thermochemistry

• Examples / exercises
  10-1, 10-2, 10-5, 10-6, 10-7, 10-8, 10-9, 10-10, 10-11, 10-12

• HW Problems
  11, 13, 19, 23, 33, 37, 40, 43, 49, 53, 59, 63