Lecture 38: Thermochemistry 1

Read:        BLB 5.3–5.5
HW:          BLB 5:4,6,17,29,37,39,41,53,55

Know:       REVIEW Lectures 2 & 26
• energy
• enthalpy
• enthalpy of reactions
• calorimetry

Check out the grad-u-lator on the Chem110 website

FINAL SKILL CHECK TEST DEADLINE:
MONDAY, APRIL 27

Need help?? Get help!! TAs in CRC (211 Whitmore) and SI—hours on Chem 110 website; my office hours (Mon 12:30-2 & Tues 10:30-12 in 324 Chem Bldg [or 326 Chem])

Final Exam:  MONDAY, May 4, 12:20 pm

Concept Final review session with Sheets: Thursday 4/30 @ 6pm in 108 Forum. Please work through the Concept Exam (on lecture note page) before the review session & bring it with you, along with any questions you may have. This review is meant to complement to the review sessions that your TAs will be holding in which they will go over the practice exams.
Thermochemical equations

**thermochemistry:** the study of the *relationship* between chemical reactions and energy changes

- a **balanced** chemical equation that also includes the **change**

- $\Delta H^\circ$ (delta H standard)
  - standard P (1 bar) & T (usually 25°C)

**NOTE:** this is **NOT** the same as STP for gases!!!

Recall: $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$

- in **chemistry** (!!!)
  - **kilojoule**
    - $1 \text{ kJ} = 10^3 \text{ J}$
  - **calorie**
    - $1 \text{ cal} = 4.184 \text{ J}$
  - **Calorie**
    - $1 \text{ Cal} = 10^3 \text{ cal} = 1 \text{ kcal}$
    - (dietary)
The first law of thermodynamics

energy can be converted between various forms, but **total energy is**

- law of conservation of energy = first law of thermodynamics

- **all energy** lost by a **system** under observation **must** be gained by the **surroundings**

- during energy conversion, some heat is **always** produced
State functions

- **state functions** are independent, -independent (no memory of previous state), and depend only on current state (its T, P, etc.)

- E is a state function

- for Δ elevation, path 1 = path 2

- ΔE for path 1 = ΔE for path 2

- ΔE = E_{final} − E_{initial}
Energy & enthalpy

• when changes occur at **constant pressure** (e.g., those done at bench)

• work \((w)\) arises from expansion or contraction of system \(w = -P\Delta V \quad \Delta V = V_{\text{final}} - V_{\text{initial}}\)

• \(\Delta E = q_p + w_{\text{expansion}}\)

**quantitative definition:**
• \(\Delta E = q_p + w_p = q_p - P\Delta V\)

• So, \(q_p = \Delta E + P\Delta V \equiv \Delta H \quad H \text{ is enthalpy}\)

**qualitative definition:**
• \(H\) is also a state function; \(\Delta H\) is the quantity of thermal energy (heat) absorbed or released by a system at constant pressure

• for many chemical processes, \(P\Delta V\) is small & \(\Delta H \approx \Delta E\)
Examples of enthalpy

• energy transfers accompany:
  physical changes
  chemical changes

• physical changes we’ve seen before…
  
  • freezing & melting
    add heat to ice ⇒
    temperature does not change during melting
    
    $\Delta H_{\text{fusion}}$ (heat of fusion)

  • vaporizing & condensing
    add heat to water ⇒
    temperature does not change during vaporization
    
    $\Delta H_{\text{vaporization}}$ (heat of vaporization)
Enthalpy of reactions: chemical changes

\[ \Delta H = H_{\text{products}} - H_{\text{reactants}} = q_p = \Delta H_{\text{rxn}} \]

• enthalpy is an extensive property (\(\propto\) how much stuff you’ve got)

• \(\Delta H_{\text{rxn}}\) is equal in magnitude \textbf{but opposite in sign} for \(\Delta H\) of reverse reaction; depends on \textbf{states} of reactants & products (e.g., gas, liquid …)

• \(\Delta H < 0\)
  \textbf{exothermic} reaction; \(q_p < 0\)
  heat is
  think of heat as a “\textbf{product}” (will come in handy when we get to equilibrium)

• \(\Delta H > 0\)
  \textbf{endothermic} reaction; \(q_p > 0\)
  heat is
  think of heat as a “\textbf{reactant}” (will come in handy when we get to equilibrium)
Demo: great cotton balls of fire

\[
\text{Na}_2\text{O}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O}_2(\text{aq})
\]
(sodium peroxide)

\[
2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \quad \text{what type of rxn?}
\]

• reaction produces heat (\(\Delta H\) is \(-\)); have high \(\text{O}_2\) concentration and cotton has low ignition temperature … voila!

Another reaction demo

\[
\text{Ba(OH)}_2\cdot8\text{H}_2\text{O}(\text{s}) + 2\text{NH}_4(\text{SCN})(\text{s}) \rightarrow \text{Ba(SCN)}_2(\text{aq}) + 2\text{NH}_3(\text{g}) + 10\text{H}_2\text{O}(\text{l})
\]

• mix two solids …

• highly endothermic reaction; \(\Delta H\) is \(+\)

• driving force is increase in disorder (entropy); go from 2 ordered crystals to lots of ions & gases in solution
Example:

\[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) \quad \Delta H = -483.6 \text{ kJ} \]

a. Is this reaction exothermic or endothermic?

b. How much heat is given off per mole of \( \text{O}_2 \)?

c. How much heat is given off per mole of \( \text{H}_2 \)?

d. How much heat will be needed to convert 9.0 g of water into hydrogen and oxygen?

e. How much heat will be given off if 10.0 g of \( \text{H}_2 \) is consumed?
**Example:**
5.00 g of table sugar \( (C_{12}H_{22}O_{11}) \) is completely combusted. How much heat is released? (Then why don’t you combust when you eat candy??)

\[ \Delta H = -1348.2 \text{ kJ} \]

\[ C_{12}H_{22}O_{11}(s) + 12 \ O_2(g) \rightarrow 12 \ CO_2(g) + 11 \ H_2O(g) \]

342 g/mol \hspace{1cm} 32 g/mol \hspace{1cm} 44 g/mol \hspace{1cm} 18 g/mol

5.00 g

Use \( \Delta H_{\text{rxn}} \) as you would any other reactant or product. That is, you need to have a balanced chemical equation & use appropriate molar relationships ...

The negative sign indicates that heat is \textit{released}
Calorimetry (review Lecture 26)

• experimental measure of heat flow; used to determine $\Delta H_{\text{rxn}}$

• review **molar heat capacity & specific heat (capacity)**

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

$q = \text{quantity of heat} \quad C = \text{specific heat}$

$m = \text{mass} \quad \Delta T = T_{\text{final}} - T_{\text{initial}}$

$m \cdot C = \text{heat capacity} \quad (\text{an extensive property})$

• for $\text{H}_2\text{O} \quad C = 4.184 \text{ J/(g °C)}$

*NOTE:* $\text{H}_2\text{O}$ is *usually* part of the surroundings

$q_{\text{surroundings}} = C_{\text{surroundings}} \cdot m \cdot \Delta T$
Coffee cup calorimeter
*(constant pressure calorimetry)*

- heat *lost* by the reaction \( q_{\text{rxn}} \) is **equal** in magnitude to **but opposite** in sign to heat *gained* by the solution \( q_{\text{soln}} \) (and vice versa)

- we can measure **temperature** and calculate **enthalpy (heat lost or gained)** measure \( q_{\text{soln}} \) & calculate \( q_{\text{rxn}} \)

\[
q_{\text{soln}} = - q_{\text{rxn}}
\]

- can calculate \( q_{\text{rxn}} \), which is \( q_p = \Delta H_{\text{rxn}} \)
Quantitative calorimetry

You mix 50 mL of 0.1 M $\text{SO}_3^{2-}(aq)$ and 50 mL 0.1 M $\text{OCl}^-(aq)$ and observe that the temperature increases from 20.0°C to 33.6°C. What is $\Delta H$ for this reaction? Assume all heat capacity is from the water, and density of solution is 1.0 g/mL.

\[
\text{SO}_3^{2-}(aq) + \text{OCl}^-(aq) \rightarrow \text{SO}_4^{2-}(aq) + \text{Cl}^-(aq) \quad \Delta H = ???
\]

\[
\begin{array}{ll}
50.0 \text{ mL} & 50.0 \text{ mL} \\
0.10 \text{ M} & 0.10 \text{ M}
\end{array}
\]

\[
C_{\text{H}_2\text{O}} = 4.184 \text{ J/(g } ^\circ\text{C)}
\]

\[
\Delta T = 33.6^\circ\text{C} - 20.0^\circ\text{C} = 13.6^\circ\text{C}
\]

Is there a limiting reagent problem?? Always check if you are given amounts of $>1$ reagent!!
Example:
100 mL of 0.5 M HCl is mixed with 50 mL of 1.0 M NaOH in a coffee-cup calorimeter. What is the final temperature of this solution? The initial temperature is 21.5°C. Assume that the total volume of solution is 150 mL, that its density is 1.0 g/mL, and that its specific heat of the solution is the same as that for pure water [4.184 J/(g K)]. Is this an exothermic or endothermic process?

\[
\text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl} \quad \Delta H = -54 \text{ kJ}
\]

100 mL 50 mL
0.5 M 1.0 M

\[T_i = 21.5^\circ\text{C} \quad V_{\text{soln}} = 150 \text{ mL}\]

\[T_f = ?? \quad d = 1.0 \text{ g/mL}\]

\[C = 4.184 \text{ J/(g K)} \quad C = 4.184 \text{ J/(g K)}\]

Does this answer make sense??? If heat is evolved during a reaction, the temperature of the surroundings (here, solution) MUST increase!!
Think about this more until it makes sense...
Bomb calorimeter
(constant volume calorimetry)

• heat evolved during combustion is absorbed by calorimeter contents causing a rise in water temperature

• \( q_{\text{rxn}} = - C_{\text{cal}} \times \Delta T \)

\( C_{\text{cal}} = \text{heat capacity of bomb calorimeter} \)

**NOTE:** because bomb calorimetry is at constant volume (not constant pressure), heat transferred is \( \Delta E \), not \( \Delta H \)
**Example:**
A 1.35 g sample of caffeine (C₈H₁₀N₄O₂) is burned in a constant-volume calorimeter that has a heat capacity of 7.85 kJ/°C. The temperature increases from 24.65°C to 29.04°C. Determine the amount of heat released and the molar energy of combustion of caffeine.

\[ C₈H₁₀N₄O₂(s) + O₂(g) \rightarrow CO₂(g) + H₂O(g) + N₂(g) \]
194 g/mol 32 g/mol 44 g/mol 18 g/mol 28 g/mol
1.35 g

\[ q \text{ released} = ?? \]
\[ \Delta E (kJ/mol \text{ caffeine}) = ?? \]

\[ C_{\text{cal}} = 7.85 \text{ kJ/°C} \]
\[ T_i = 24.65°C \]
\[ T_f = 29.04°C \]
\[ \Delta T = 4.39°C \]
Before next class:

Read: BLB 5.6–5.7; 8.8
HW: BLB 5:63,67a,b,69,73,75,83,85; 8:65a,67a,c,92a
18:72a,b, 74
Sup 5:1–7; 8:11–13

Know:
• Hess’s Law
• heats of formation
• enthalpy of reactions

review: Does this make sense??

<table>
<thead>
<tr>
<th>TABLE 5.1</th>
<th>Sign Conventions for $q$, $w$, and $\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>For $q$</td>
<td>+ means system gains heat</td>
</tr>
<tr>
<td>For $w$</td>
<td>+ means work done on system</td>
</tr>
<tr>
<td>For $\Delta E$</td>
<td>+ means net gain of energy by system</td>
</tr>
<tr>
<td></td>
<td>− means work done by system</td>
</tr>
<tr>
<td></td>
<td>− means net loss of energy by system</td>
</tr>
</tbody>
</table>

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Good luck studying for finals! Please start now.

Answers:
p. 9: (a) exothermic; (b) $-483.6$ kJ; (c) $-241.8$ kJ; (d) $120.9$ kJ;
(e) $-1209$ kJ
p. 10: $-19.71$ kJ
p. 13: $\Delta H = -1138$ kJ
p. 14: $25.8^\circ$C; exothermic
p. 16: $q_{rxn} = -34.5$ kJ; $\Delta E = -4958$ kJ/mol