Enthalpy changes and calorimetry

Enthalpy changes in reactions
Calorimetry and heat measurement
Hess’s Law
Heats of formation
Learning objectives

• Describe the standard state for thermodynamic functions
• Explain sign of enthalpy change for changes of state
• Calculate enthalpy changes for reactions
• Use specific heat and heat capacity in calorimetric problems
• Apply Hess’ law to calculations of enthalpy change
• Use standard heat of formation in calculations of enthalpy of reaction
• Use bond energies to estimate heats of reaction
The importance of state

• The heat change in a reaction will depend upon the states of the reactants and/or products
• States must be specified
  – $\Delta H(1) = -2043 \text{ kJ}$
    
    \[
    C_3H_8(g) + 5O_2(g) = 3CO_2(g) + 4H_2O(g)
    \]
  – $\Delta H(2) = -2219 \text{ kJ}$
    
    \[
    C_3H_8(g) + 5O_2(g) = 3CO_2(g) + 4H_2O(l)
    \]
• Additional heat is released in (2) because condensation of H$_2$O releases 176 kJ
Thermodynamic standard state

- Heat changes will also depend upon P and T
- The Standard State:
  Most stable form of a substance at 1 atm pressure and 25°C (usually); 1 M concentration for solutions
- Conventionally, enthalpy change under standard conditions is represented by: $\Delta H^o$
- Any thermodynamic function referring to standard conditions is identified by $^o$
Calculating $\Delta U$ from $\Delta H^o$

- Reaction between $N_2$ and $H_2$ at $P = 40$ atm and $\Delta V = 1.12$ L

$$N_2(g) + 3H_2(g) = 2NH_3(g) \quad \Delta H^o = -92.2 \text{ kJ}$$

- What is $\Delta U$?

$$\Delta U = \Delta H - P\Delta V$$

$$\Delta U = -92.2kJ - (40 \times -1.12 \text{ Latm}) \left( 101 \frac{J}{\text{Latm}} \right) \left( \frac{1kJ}{1000J} \right)$$

$$\Delta U = -92.2kJ - (-4.52kJ) = -87.7kJ$$

$\Delta U > \Delta H$

- Internal energy change is less negative by amount of work done by surroundings on compressing system
Enthalpies of change of state

- Conversion of a substance from one state to another involves heat input or output
- Heat is absorbed when breaking bonds
  - Solid → liquid → gas
- Heat is released when making bonds
  - Gas → liquid → solid
- Heat of fusion, vaporization etc. (formerly known as “latent” heats – heat consumed with no change in T)
State functions ignore path

- Transition from solid to gas may lie through liquid phase...
- Or transition may be direct – sublimation
- Enthalpy change is the same by either route

$$\Delta H_{\text{subl}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vap}}$$
Heat of reaction

- Enthalpy change for a reaction is commonly known as heat of reaction.
- *Exothermic* refers to reaction where heat is given out by system (we warm our hands): $\Delta H < 0$.
- *Endothermic* refers to reaction where heat is absorbed by system and surroundings get cool (hands get cold): $\Delta H > 0$.
- **NOTE SIGNS OF $\Delta H$!**

![Diagram of heat of reaction with chemical equations: $2 \text{H}_2(g) + \text{O}_2(g)$ and $2 \text{H}_2\text{O}(g)$ with $\Delta H < 0$ (exothermic).]
Calculations with $\Delta H^\circ$

- $\Delta H^\circ$ may be quoted for a given equation or for one mole of a reactant or product.
- Either way, it can be used to calculate the heat change for a given amount of substance.
Example

- What is the heat evolved from the combustion of 15.5 g of \( \text{C}_3\text{H}_8 \)?

\[
\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) = 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \quad \Delta H = -2219 \text{ kJ} / \text{mol}
\]

- Combustion of one mole of \( \text{C}_3\text{H}_8 \) yields - 2219 kJ
- Molar mass of \( \text{C}_3\text{H}_8 \) = 44.0 g/mol
- No moles in 15.5 g = 15.5/44.0 = 0.352 mol
- Heat produced = - 2219 x 0.352 = - 782 kJ
Worked example of heat of combustion
Calorimetry: the universe in the palm of your hand

- Heat change in process measured by temperature change of water in calorimeter (surroundings)
- Insulation confines heat exchange to process and calorimeter – universe becomes the calorimeter
Heat capacity and specific heat

- **Heat capacity, C:**
  Heat required to raise temperature of body by 1ºC (extensive)

  \[ C = \frac{q}{\Delta T} \]

- **Specific heat (capacity), c (σ):**
  Heat required to raise 1 gram of the substance by 1ºC (intensive)

  \[ q = c \cdot \Delta T \cdot m \]
Interactive calorimetry exercise

- Calculate some heat changes using virtual calorimeter
- Heats of solution
Constant pressure and constant volume

- Heat capacity can be defined at constant pressure and constant volume

\[ C_P = \frac{q}{\Delta T} \quad \text{and} \quad C_V = \frac{q}{\Delta T} \]

- For solids and liquids they are similar
- For gases the values differ by R (the ideal gas constant):

\[ C_P = C_V + R \]
Molar heat capacity

- Related to specific heat (sometimes known as specific heat capacity) is the molar heat capacity, $C_m$: the heat required to raise the temperature of 1 mole of a substance by 1°C.

$$q = C_m \cdot \Delta T \cdot \text{moles}$$
Some examples

- The heat capacity of water is much larger than many other substances
  - Consequence of strong H-bonding
- Important consequences for climate, the quality of life, and life itself

<table>
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<th>Substance</th>
<th>S.H. (J/g °C)</th>
<th>S.H. (J/mol °C)</th>
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<tr>
<td>Air</td>
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<td>Mercury</td>
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<td>Water (s)</td>
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</tr>
<tr>
<td>Water (l)</td>
<td>4.179</td>
<td>75.3</td>
</tr>
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</table>
Hess’s law and the many pathways

- Enthalpy being a state function means that enthalpy change for process is independent of pathway.
- Hess’s law states that:
  
  Overall enthalpy change for reaction equals sum of enthalpy changes for individual steps.
Application: determining $\Delta H$ for unknown process in terms of $\Delta H$ for known process

• Consider the reaction

$$N_2(g) + 3H_2(g) = 2NH_3(g) \ldots \Delta H_1$$

Proceeds in two steps

$$N_2(g) + 2H_2(g) = N_2H_4(g) \ldots \Delta H_2$$

$$N_2H_4(g) + H_2(g) = 2NH_3(g) \ldots \Delta H_3$$

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

• Reaction 1 is sum of reactions 2 + 3
Obtain $\Delta H_2$ from $\Delta H_1$ and $\Delta H_3$

• $\Delta H_2$, which is hard to determine experimentally, is obtained using $\Delta H_1$ and $\Delta H_3$

• $\Delta H_2$ is endothermic, the others are exothermic
Combustion of CH$_4$ by alternate routes

- **Route 1**: $\Delta H_1$, complete combustion to CO$_2$
- **Route 2**: $\Delta H_2 + \Delta H_3$, intermediate product is CO
- Different pathways, same enthalpy
  \[ \Delta H_1 = \Delta H_2 + \Delta H_3 \]
Standard heats of formation

- Standard heat of formation, \( \Delta H_f^\circ \):
  - The enthalpy change for the formation of 1 mole of a substance in its **standard state** from its constituent elements in their **standard states**

- \( \Delta H_f^\circ \) for elements in most stable state is by definition 0
• Reactions are often hypothetical
  - $\Delta H^\circ_f (\text{CH}_4)$ is -74.8 kJ/mol although direct reaction between C and H$_2$ does not occur
• Important to know which is the standard state for any substance
• $\Delta H^\circ_f$ values are tabulated for many substances
Heats of reaction, $\Delta H_f^{\circ}$, and Hess’s law

• Application of $\Delta H_f^{\circ}$ to calculation of heats of reaction ($\Delta H_f^{\circ}_{\text{RXN}}$)

• For reaction:

\[ aA + bB = cC + dD \]

• Products – reactants

\[
\Delta H_f^{\circ}_{\text{reaction}} = \left[ c\Delta H_f^{\circ}(C) + d\Delta H_f^{\circ}(D) \right] - \left[ a\Delta H_f^{\circ}(A) + b\Delta H_f^{\circ}(B) \right]
\]
Worked example of heat of reaction

\[ \Delta H_{rxn} = \Delta H_f (CO_2) + \Delta H_f (H_2O) - \Delta H_f (C_3H_8) \]
Estimating $\Delta H^\circ_f$ using bond energies

- What if $\Delta H^\circ_f$ value(s) for reaction is (are) unknown?
- Estimate enthalpy change as difference between bonds broken (energy cost) and bonds made (energy gain)
  - $\Delta H^\circ_{RXN} = D(\text{reactant bonds}) - D(\text{product bonds})$
  - (Bond energies are positive values)
• Consider reaction:

\[ CH_4(g) + 3Cl_2(g) = CHCl_3(g) + 3HCl(g) \]

• On reactant side:
  – 3 C-H bonds and 3 Cl-Cl bonds are broken

• On product side:
  – 3 C-Cl bonds and 3 H-Cl bonds are made

\[ \Delta H^\circ = \left[ 3D_{Cl-Cl} + 3D_{C-H} \right] - \left[ 3D_{H-Cl} + 3D_{C-Cl} \right] \]

\[ \Delta H^\circ = \left[ 3 \times 243 + 3 \times 410 \right] - \left[ 3 \times 432 + 3 \times 330 \right] kJ = -327 kJ \]

• Reaction is exothermic
  – H-Cl bond is much stronger than Cl-Cl
Worked example of heat of reaction from bond energies
More than enthalpy

- Some reactions are exothermic
- Some reactions are endothermic
- Both kinds of reaction can occur spontaneously. Or not. Why?
- The enthalpy is not the arbiter of spontaneity
- There is more to energy than heat
- We must also consider entropy
- Stay tuned for the Second Law...