Thermodynamics and Thermochemistry

Thermodynamics is the study of heat transfer. Thermochemistry is the study of heat transfer in chemical reactions. Chemical reactions that release heat tend to be **product favored.** Once started, product favored reactions proceed almost completely from reactants to products, though some outside assistance may be needed to initiate the reaction.

Heat is the focus of thermochemistry and thermodynamics. Other forms of energy exist including heat, work, kinetic, potential, light, and electrical energy. Below are descriptions of some of these types of energy.

Heat (q) is a form of energy that flows between two objects because of a difference in temperature (T) and that causes molecules to move faster.

Work (w) is the ability to move an object across a distance against an applied force.

Kinetic energy is the energy of motion, so the faster the velocity the higher the kinetic energy. At the same temperature, gases have higher KE than liquids, liquids have higher KE than solids.

Potential energy (PE) is the energy of position. Forming chemical bonds lowers the potential energy of a chemical system releasing kinetic energy in the process.

The Internal Energy (E or U) of a system = KE + PE. U depends on number and type of particles as well as T. Increases in T result in increases in U.

Law of Conservation of Energy states that the internal energy, the sum of KE and PE, is conserved. **Thermodynamics** is the study of heat transfer that depends on the **Law of Conservation of Energy.** Energy is neither created nor destroyed, but energy can change from one type to another.

Heat flows from the hotter object to the cooler object until thermal equilibrium is established. The process can be monitored by the temperature change ΔT

System – object under study
Surroundings – everything else outside the system

Exothermic processes give off heat from the system to the surroundings. The **system** may feel hot to the touch because it is emitting heat (losing PE and releasing it as KE or heat). Over time, the **system** cools down (temperature decreases) because it is losing heat to the **surroundings** which then experience a temperature increase**.** The s**ystem** loses heat so $q_{system} < 0$.

Endothermic processes get heat to the **system** from the **surroundings**. The **system** may feel cool to the touch because it is absorbing heat (gaining PE and absorbing KE or heat). Over time, the **system** warms up (temperature increases) because it is getting heat from the **surroundings** which then experience a temperature decrease. The **system** gets heat so $q_{system} > 0$.

A measure of energy is the calorie, where 1 Calorie = 4.184 J. One calorie is the energy required to raise 1g of water 1°C

Heat capacity is the heat required to raise an object by a number one degree Celsius. Larger objects have more heat capacity than smaller objects of the same composition. The units of heat capacity are J/°C, or equivalently, J/K.

Specific heat capacity is the heat required to raise an object of one gram by one degree Celsius. Because mass is part of the definition of specific heat capacity, large objects have the same specific heat capacity as small objects of the same composition. The units of specific heat capacity are J/(g °C), or equivalently, J/(g K).

First Law of Thermodyanamics
The first law of thermodynamics states that the energy change for a process is the sum of the heat and work terms. Mathematically, the first law of thermodynamics is expressed as the following relationship:

$\Delta E = q + w$

Note that alone q and w are path functions, which means that the amount of heat or the amount of work depends on the number and direction of the individual steps taken to get from the initial state and the final state. ΔE, however, is a state function, which means that the value of ΔE depends only on the initial and final states and not the path taken. ΔE can be calculated as $E_{final} - E_{initial}$.

Many chemical reactions and processes are carried out at constant pressure, and the work term tends to be small. When the work term is small at constant pressure, the energy change for a process can be described by the heat generated or absorbed by the process. The term enthalpy, ΔH, is the change in heat energy. A mathematical expression for the energy change or enthalpy change at constant pressure (when work w≈0) is:

$\Delta E = \Delta H = q_p$ (heat at constant pressure)

Like ΔE, ΔH is a state function which depends only on the initial and final states. ΔH can be calculated as $H_{final} - H_{initial}$. Because it is not possible to know absolute heat for a

process, only the heat change, The enthalpy change is calculated as $\Delta H = \Delta H_{final} - \Delta H_{initial}$.

Calculating Heat with no Change in State
For heat transfer to or from the system without a change in the state of matter,
    $q = m\, Cp\, \Delta T$

$q = q_{system}$ is the heat gained or lost by the system
m = mass
Cp = specific heat capacity (found in tables)
ΔT = temperature change = $T_{final} - T_{initial}$. Final state – initial state is the meaning of Δ.

If a transfer of heat is carried out under constant pressure, then $\Delta H = q_p = q$.

Example: Calculate the heat evolved when a 26.1g sample of aluminum metal, $Cp=0.910J/(g\,°C)$, cools from 101.0°C to 25.0°C.

Solution: Use the values in the equation for calculating heat.
$q = 26.1g \times 0.910\ J/(g\,°C) \times (25.0°C - 101.0°C) = -1805.1J = -1810J$ (to 3SD)
1810J of heat are given off from the aluminum metal.

Calorimetry
If heat from one object is transferred into one or more objects, then the heat for the overall process is given by:
    $q_1 + q_2 + q_3 + ... = 0$

Example: A 42.61g sample of aluminum, $Cp=0.910J/(g\,°C)$, with an initial temperature of 98.9°C is dropped into a coffee cup calorimeter filled with 96.25g of water at an initial temperature of 21.5°C. What is the final temperature of the water?

Solution: Because all of the heat from the aluminum is transferred into the water, use the relationship: $m_{water}\, Cp_{water}\, \Delta T_{water} + m_{Al}\, Cp_{Al}\, \Delta T_{Al} = 0$
$96.25g \times 4.184\ J/(g\,°C) \times (Tf - 21.5°C) + 42.61g \times 0.910J/(g\,°C) \times (Tf - 98.9°C)$

$402.71J/°C \times Tf - 8658.265J + 38.7751J/°C \times Tf - 3834.85739J = 0$

$441.4851J/°C \times Tf - 12493.122J = 0$

$Tf = 28.3°C$

Bomb Calorimetry
In bomb calorimetry, a sample is burned in a device called a bomb calorimeter. After the sample burns, some of the heat from the reaction goes to warm the water in the calorimeter and some of the heat warms the bomb in the calorimeter. In this case, the following equation applies.

$q_{reaction} + q_{calorimeter} + q_{bomb} = 0$

$q_{calorimeter} = m_{water}\, Cp_{water}\, \Delta T_{water}$

q_{bomb} is either given in J/°C or can be calculated if $q_{reaction}$ is known.

Example: Calculate the heat of combustion of octane, a component of automobile fuel when 1.15g of octane burns in a bomb calorimeter and raises the temperature of 1241g of water from 22.28°C to 30.52°C. The heat capacity of the bomb is 795 J/°C.

Solution: The balanced chemical reaction for the combustion of octane is shown below.

$$2C_8H_{18}(g) + 25\ O_2(g) \rightarrow 16\ CO_2(g) + 18\ H_2O\ (g)$$
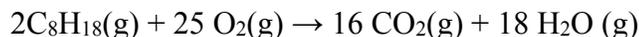
$q_{reaction} + m_{water}\, Cp_{water}\, \Delta T_{water} + q_{bomb} \times \Delta T_{water}$

$q_{reaction} + 1241g \times 4.184\ \text{J/g °C} \times (30.52\ °C - 22.28\ °C)$
     $+ 795\ \text{J/°C} \times (30.52\ °C - 22.28\ °C) = 0$

$q_{reaction} = 49335J = -49300J$ (to 3SD) which represents the heat of combustion ΔH_{comb} for 1.15g of octane. Calculate the heat in kJ per mole of C_8H_{18}:
     -49335J / 1.15g C_8H_{18} × 114.232g C_8H_{18}/ mol C_8H_{18} × 1kJ/1000J= -4900kJ/mol.

Enthalpy and Phase Changes
For phase changes (boiling, melting, sublimation), there is no temperature change, so all the energy goes into ordering (or disordering) the substance for the phase change. In this case, use the heat or enthalpy (ΔH) of vaporization for boiling, the enthalpy of fusion for melting, and the enthalpy of sublimation for subliming. You must keep track of the sign by knowing that melting, boiling, and subliming are endothermic processes (sign of heat is positive for calculations) and that freezing, condensing, and depositing are exothermic processes (sign of heat is negative for calculations).

Enthalpy of vaporization/fusion/sublimation (ΔH_{vap}, ΔH_{fus}, ΔH_{sublim}) values are typically given in tables in units J/g or J/mol.

Calculating Heat for a Process

To calculate the overall energy required to warm water through phase changes or the overall energy released to cool water through phase changes, use

$q_{total} = q_{warmingsolid} + q_{melting} + q_{warmingliquid} + q_{boiling} + q_{warmingvapor}$

$q_{warmingsolid} = m \, Cp_{(ice)} \, \Delta T$

$q_{melting} = \Delta H_{fus} \, (J/g) * m$ or $\Delta H_{fus} \, (J/mol) * n$

$q_{warmingliquid} = m \, Cp_{(water)} \, \Delta T$

$q_{boiling} = \Delta H_{vap} \, (J/g) * m$ or $\Delta H_{vap} \, (J/mol) * n$

$q_{warmingvapor} = m \, Cp_{(steam)} \, \Delta T$

Example: Calculate the heat evolved or needed to cool 12.5g of steam at 120°C to ice at −15°C given that $Cp_{(ice)}$=2.11J/(g°C), ΔH_{fus}=334J/g, $Cp_{(water)}$=4.18J/(g°C), ΔH_{vap}=2260J/g, $Cp_{(steam)}$=2.08J/(g°C).

Solution: Cooling gives off heat from the system to the surroundings, so the sign for the heat of will be negative for each step. Calculate the heat evolved for each step and add the heat for each step together to calculate the overall heat lost by the system in the process.

The heat emitted on cooling steam from 120°C to 100°C is:
$q_{coolingvapor} = m \, Cp_{(steam)} \, \Delta T = 12.5g \times 2.08 \, J/(g°C) \times (100°C − 120°C) = −520J$

The heat emitted on condensing steam to liquid water at 100°C is:
$q_{condensing} = −q_{boiling} = −\Delta H_{vap} * m = −2260J/g \times 12.5g = −28250J$

The heat evolved on cooling water from 100°C to 0°C is:
$q_{coolingwater} = m \, Cp_{(water)} \, \Delta T = 12.5g \times 4.18 \, J/(g°C) \times (0°C − 100°C) = −5225J$

The heat evolved on freezing water to ice at 0°C is:
$q_{freezing} = −q_{melting} = −\Delta H_{fus} * m = −334J/g \times 12.5g = −4175J$

Finally, the heat given off on cooling ice at 0°C to ice at −15°C is:
$q_{coolingice} = m \, Cp_{(ice)} \, \Delta T = 12.5g \times 2.11 \, J/(g°C) \times (−15°C − 0°C) = −396J$

The heat given off by the overall process can be calculated by adding the heat given off by each step as follows

$q_{total} = −520J + −28250J + −5225J + −4175J + −396J = −38600J$

Using Enthalpy of Reaction
Given this equation and the associated enthalpy value, several unit factors can be stated.

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ ΔH = −286kJ

The exothermic reaction generates 286kJ of heat per:
- mol of $H_2(g)$ consumed, −286kJ/mol $H_2(g)$
- ½ mol of $O_2(g)$ consumed, −286kJ/mol $O_2(g)$
- mol of $H_2O(g)$ formed, −286kJ/mol $H_2O(g)$

When writing the reverse reaction, change the sign of ΔH.

$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ ΔH = +286kJ

The endothermic reaction uses 286kJ of heat per:
- mol of $H_2O(g)$ consumed, +286kJ/mol $H_2O(g)$
- mol of $H_2(g)$ formed, +286kJ/mol $H_2(g)$
- ½ mol of $O_2(g)$ formed, +286kJ/mol $O_2(g)$

When a reaction is multiplied by a factor, such as 3, multiply ΔH by the same factor.

$3H_2O(l) \rightarrow 3H_2(g) + 3/2\ O_2(g)$ ΔH = +858kJ
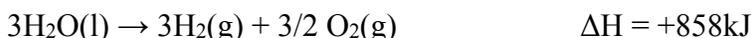
The endothermic reaction uses 858kJ of heat per:
- 3 mol of $H_2O(g)$ consumed, +858kJ/3 mol $H_2O(g)$
- 3 mol of $H_2(g)$ formed, +858kJ/3 mol $H_2(g)$
- 3/2 mol of $O_2(g)$ formed, +858kJ/ [3/2 mol $O_2(g)$]

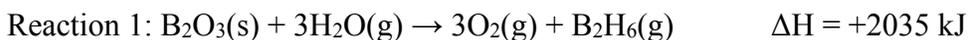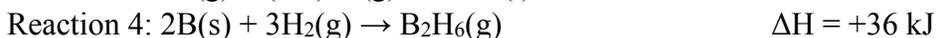**Hess's Law**
When a final reaction is the sum of one or more individual reactions, ΔH for the final reaction is the sum of the ΔH values for the individual reactions. Changing the direction of the reaction flips the sign of ΔH, so that an **exothermic** reaction would become **endothermic**. Multiplying the reaction by a factor affects ΔH by the same factor. The example below explains the decision making process for each reaction in a final reaction that is the sum of four individual steps.

Example: Calculate ΔH for this final reaction
$2B(s) + (3/2)O_2(g) \rightarrow B_2O_3(s)$ ΔH = ?

possibly using these four individual reactions

Reaction 1: $B_2O_3(s) + 3H_2O(g) \rightarrow 3O_2(g) + B_2H_6(g)$ ΔH = +2035 kJ
Reaction 2: $H_2O(l) \rightarrow H_2O(g)$ ΔH = +44 kJ

Reaction 3: $H_2(g) + (1/2)O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286$ kJ
Reaction 4: $2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$ $\Delta H = +36$ kJ

Solution: Note what side the reactants and products are on in the final reaction as well as the coefficients as you review each individual reaction. Key individual reactants and products are displayed in bold text.
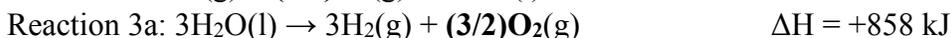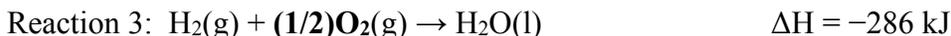
With Reaction 1, $B_2O_3(s)$ appears as a product in the final reaction with a coefficient of one, so reverse the direction of Reaction 1 and change the sign of ΔH. Note that $B_2O_3(s)$ does not appear in any other individual reaction, so this is a good reaction to begin the process.
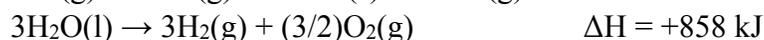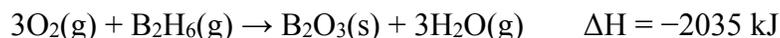
Reaction 1: **$B_2O_3(s)$** + $3H_2O(g) \rightarrow 3O_2(g) + B_2H_6(g)$ $\Delta H = +2035$ kJ
Reaction 1a: $3O_2(g) + B_2H_6(g) \rightarrow$ **$B_2O_3(s)$** + $3H_2O(g)$ $\Delta H = -2035$ kJ

For Reaction 2, H_2O does not appear in the final reaction so skip this reaction for now.
Reaction 2: $H_2O(l) \rightarrow H_2O(g)$ $\Delta H = +44$ kJ

In Reaction 3, $(1/2)O_2(g)$ appears as a reactant, and it is needed as a reactant in the final reaction. Reaction 1a already provides $3O_2(g)$ as a reactant, yet only $(3/2)$ $O_2(g)$ are needed in the final reaction. Because the third reaction is the only other source of $O_2(g)$, reverse the direction of Reaction 3 and multiply it by three to leave the correct moles of $O_2(g)$ as a reactant after adding Reaction 1a to Reaction 3a.
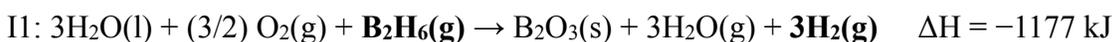
Reaction 3: $H_2(g) +$ **$(1/2)O_2(g)$** $\rightarrow H_2O(l)$ $\Delta H = -286$ kJ
Reaction 3a: $3H_2O(l) \rightarrow 3H_2(g) +$ **$(3/2)O_2(g)$** $\Delta H = +858$ kJ

The first intermediate result (I1) and ΔH value after adding Reaction 1a to Reaction 3a are

     $3O_2(g) + B_2H_6(g) \rightarrow B_2O_3(s) + 3H_2O(g)$ $\Delta H = -2035$ kJ
     $3H_2O(l) \rightarrow 3H_2(g) + (3/2)O_2(g)$ $\Delta H = +858$ kJ

I1: $3H_2O(l) + (3/2)$ $O_2(g) + B_2H_6(g) \rightarrow B_2O_3(s) + 3H_2O(g) + 3H_2(g)$ $\Delta H = -1177$ kJ

Looking at Reaction 4, $2B(s)$ appears as a reactant, and it appears as a reactant in the final reaction with a coefficient of two. Note also that $3H_2$ and $B_2H_6(g)$ will cancel when Reaction 4 is added to I1.
Reaction 4: **$2B(s)$** + $3H_2 \rightarrow B_2H_6(g)$ $\Delta H = +36$ kJ
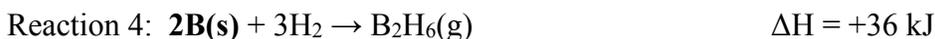
The second intermediate result (I2) and ΔH value after adding Reaction I1 to Reaction 4 are

I1: $3H_2O(l) + (3/2)$ $O_2(g) +$ **$B_2H_6(g)$** $\rightarrow B_2O_3(s) + 3H_2O(g) +$ **$3H_2(g)$** $\Delta H = -1177$ kJ
4: **$2B(s) + 3H_2$** $\rightarrow$ **$B_2H_6(g)$** $\Delta H = +36$ kJ

I2: $3H_2O(l) + 2B(s) + (3/2)\ O_2(g)$ $\rightarrow B_2O_3(s) + 3H_2O(g)$ $\Delta H = -1141\ kJ$
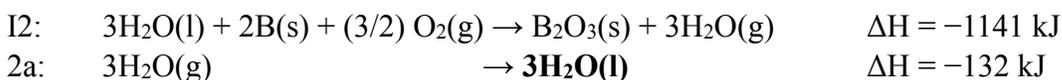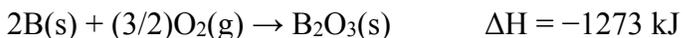
Comparing I2 to the final reaction, three water molecules appear on each side in I2 but not in the final reaction. Reaction 2 has $H_2O(l)$ as a reactant with a coefficient of one. I2 has $H_2O(l)$ as a reactant with a coefficient of three, so reverse Reaction 2 and multiply the reaction and ΔH value by three so that $H_2O(l)$ will cancel. Note that $H_2O(g)$ will also cancel leaving the final reaction and the final ΔH value.

Reaction 2: **$H_2O(l) \rightarrow H_2O(g)$** $\Delta H = +44\ kJ$
Reaction 2a: **$3H_2O(g) \rightarrow 3H_2O(l)$** $\Delta H = -132\ kJ$

Add I2 to Reaction 2a to get the final answer and ΔH value.

I2: $3H_2O(l) + 2B(s) + (3/2)\ O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$ $\Delta H = -1141\ kJ$
2a: $3H_2O(g)$ $\rightarrow$ **$3H_2O(l)$** $\Delta H = -132\ kJ$
_____
Final: $2B(s) + (3/2)O_2(g) \rightarrow B_2O_3(s)$ $\Delta H = -1273\ kJ$

The final reaction and ΔH value are
$2B(s) + (3/2)O_2(g) \rightarrow B_2O_3(s)$ $\Delta H = -1273\ kJ$

Calculate $\Delta H°_{rxn}$ using Standard Enthalpy Values
When all the standard enthalpy values for the species in a chemical reaction are known at standard conditions (°), the following equation can be used to calculate the enthalpy change for a reaction.

$\Delta H°_{rxn} = \Sigma\Delta H°_{f(products)} - \Sigma\Delta H°_{f(reactants)}$

$\Delta H°_{f(products)}$ are the enthalpy of formation values for the products times the number of moles of product formed in the chemical equation. $\Delta H°_{f(reactants)}$ are the enthalpy of formation values for the reactants times the number of moles of reactant used in the chemical equation.

Standard conditions (°) are a pressure of 1 atm, temperature of 25 °C, concentration of 1M, all species in their standard states, and complete conversion of reactants to products. Refer to the information in the table for specific information about standard conditions. The $\Delta H°_f$ is 0 for an element in its standard state. For example, $O_2(g)$ and C(s, graphite) would have $\Delta H°_f$ values of 0, but the $\Delta H°_f$ value for C(s, diamond) would not be zero because diamond is not the standard state of carbon. The enthalpy value for C(diamond) is 1.8kJ/mol.

Example: Calculate the enthalpy change for the following reaction using standard enthalpy values found in a table of thermodynamic values.

$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$ $\Delta H°_{rxn} =$

Solution: Look up the values for $C_2H_6(g)$, $CO_2(g)$, and $H_2O(g)$ in a table of thermodynamic values. The enthalpy of formation, $\Delta H°_f$, for $O_2(g)$ is 0 because it is an element in its standard state.

$\Delta H°_f[C_2H_6(g)] = -83.85$ kJ/mol
$\Delta H°_f[O_2(g)] = 0$ kJ/mol
$\Delta H°_f[CO_2(g)] = -393.51$ kJ/mol
$\Delta H°_f[H_2O(g)] = -241.83$ kJ/mol

$\Delta H°_{rxn} = \{6 \times \Delta H°_f[H_2O(g)] + 4 \times \Delta H°_f[CO_2(g)]\} - \{2 \times \Delta H°_f[C_2H_6(g)] + 7 \times \Delta H°_f[O_2(g)]\}$

$\Delta H°_{rxn} = \{6 \text{ mol} \times -241.83 \text{ kJ/mol} + 4 \text{ mol} \times -393.51 \text{ kJ/mol}\} -$
          $\{2 \text{ mol} \times -83.85 \text{ kJ/mol} + 7 \text{ mol} \times 0 \text{ kJ/mol}\}$

$\Delta H°_{rxn} = -2587.32$ kJ

Like all enthalpies of reaction, $\Delta H°_{rxn}$ means -2587.32 kJ / 2 mol C_2H_6. Similar relationships apply for the other reactants and products (-2587.32 kJ per 7 mol of $O_2(g)$ used, per 4 mol $CO_2(g)$ formed, and per 6 mol $H_2O(g)$ of formed).