

6. Thermochemistry

Chemical reactions, such as $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$, and phase changes, such as $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$, are accompanied by changes in energy. For example, two moles of liquid water has less energy than two moles of hydrogen and one mole of oxygen gases. Consequently, the chemical reaction of hydrogen and oxygen releases energy – ultimately in the form of heat. Chemical reactions are an important source of energy – e.g. heat in homes in winter, mechanical energy in the engine of a car, electrical energy in a cellphone battery. In order to predict the energy released by a given chemical reaction or physical process, chemists have measured the heat released by many processes and developed an energy scale for a wide range of substances. The closely related enthalpy scale is used to determine heat released under standard conditions - see Sec. 5.5. To understand this scale and how to use it requires the introduction of precise terminology.

6.1 System and Properties - Energy

We divide the universe into *system(s)* and *surroundings* (i.e. everything else). A *system* is an amount of a substance or collection of substances with a volume. If the system is in equilibrium (i.e. it is unchanging, or changing slowly), then it also has a temperature and pressure. It has other properties also. Most notably, the system has an energy, the sum total of all potential and kinetic energies of particles in the system. Enthalpy is another property – it is energy plus a small extra term. An energy or enthalpy scale for substances can be constructed from a sufficiently large set of measured energy or enthalpy changes. Changes in energy or enthalpy are determined by measuring the flow of heat to or from the system.

6.2 Heat

Heat is the energy that flows from a hot system to a cold system, when they are in *thermal contact* (this simply means they are touching, and not separated by thermal insulation). Heat flows until the final temperatures of the systems are the same. We use the symbol q to denote heat flow *into* a system, when there is one system of interest. When heat flows *from* the system, q is negative. When there are two systems, we use subscripts to distinguish the properties. When heat flows from system 2 to system 1 their q values are equal in magnitude but opposite in sign;

$$q_2 = -q_1$$

q_1 is positive because heat flowed into system 1, while q_2 is negative.

Temperature measurements are used to determine the amount of heat flow. When heat flows into a system, its temperature generally increases. The temperature change is proportional to the heat transferred, and vice versa. Thus, a measured temperature change can be used to determine the amount of heat transferred via

$$q = C \Delta T$$

C is the heat capacity of the system. It is proportional to the amount of substance – the size of the system. A system twice as big – but otherwise identical – has twice the heat capacity. Consequently, heat capacities for substances are tabulated for substances per mole, or per gram. Specific heat capacity,

$$s = C / m$$

is the heat capacity per gram of substance; i.e. m is the mass in grams. Specific heat capacities are tabulated for various substances. The value for water is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ at 25°C and 1 atm pressure. We will use this value for water under any conditions. This is an approximation that greatly simplifies all our calculations. Copper has a much lower specific heat capacity, $0.385 \text{ J K}^{-1} \text{ g}^{-1}$ at 25°C and 1 atm pressure (we will treat s as independent of temperature for all substances). In terms of specific heat capacity, heat is related to temperature change according to

$$q = ms \Delta T \quad 6.1$$

Example 6.1: How much heat must flow into a 100. g sample of water to raise its temperature from 20.00°C to 25.00°C ? ($s_{\text{water}} = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$)

Approach: Substitute given mass, specific heat capacity and temperature difference into the above formula.

Note that

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 25.00^\circ\text{C} - 20.00^\circ\text{C} = 5.00^\circ\text{C} \text{ or } 5.00 \text{ K}$$

Differences in temperature, ΔT , expressed in $^\circ\text{C}$, can also be written with the unit K. A 1°C difference is the same as 1 K difference.

The heat transferred is

$$\begin{aligned} q &= ms \Delta T \\ &= 100. \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times 5.00 \text{ K} \\ &= 2092 \text{ J} = 2.09 \text{ kJ} \end{aligned}$$

This example demonstrates how a calorimeter works. A chemical reaction or phase transition releases or absorbs heat within a calorimeter. The calorimeter has a well-defined heat capacity. Sometimes you will be given the heat capacity, C . Other times you are given a mass of a substance (usually it is water, or a dilute aqueous solution) and you use ms for the heat capacity. Occasionally, you must add the heat capacities of the (empty) calorimeter and a reacting solution. The temperature change inside the calorimeter is measured to determine how much heat was released or absorbed by the reaction or phase transition.

Example 6.2: A 20.0 g sample of copper at $300.^\circ\text{C}$ is placed within a thermally insulated vessel containing 100. g of water at 20.0°C . What is the final temperature when thermal equilibrium is re-established? ($s_{\text{water}} = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$ and $s_{\text{copper}} = 0.385 \text{ J K}^{-1} \text{ g}^{-1}$)

Approach: Express the heat lost by copper, and the heat gained by water, in terms of the respective changes in temperature. Equate these expressions and solve for the unknown final temperature, T_f . Note that heat *lost* by copper is $-q_{\text{copper}}$.

The heat lost by copper is

$$\begin{aligned} -q_{\text{copper}} &= -m_{\text{copper}} s_{\text{copper}} \Delta T_{\text{copper}} \\ &= -20.0 \text{ g} \times 0.385 \text{ J K}^{-1} \text{ g}^{-1} \times (T_f - 300.^\circ\text{C}) \\ &= 7.70 \text{ J K}^{-1} (300.^\circ\text{C} - T_f) \end{aligned}$$

The heat gained by water is

$$\begin{aligned} q_{\text{water}} &= m_{\text{water}} s_{\text{water}} \Delta T_{\text{water}} \\ &= 100. \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times (T_f - 20.^\circ\text{C}) \\ &= 418 \text{ J K}^{-1} (T_f - 20.^\circ\text{C}) \end{aligned}$$

Heat lost by copper is gained by water. So

$$\text{or } q_{\text{water}} = -q_{\text{copper}}$$

$$418 \text{ J K}^{-1} (T_f - 20.^\circ\text{C}) = 7.70 \text{ J K}^{-1} (300.^\circ\text{C} - T_f)$$

which rearranges to

$$(418 + 7.70) T_f = 7.70 \times 300. + 418 \times 20.$$

$$T_f = 10670/425.7^\circ\text{C} = 25.1^\circ\text{C}$$

The final temperature has units of $^\circ\text{C}$ because the initial temperatures of copper and water were expressed in $^\circ\text{C}$. Only when dealing with temperature differences do we use $^\circ\text{C}$ in a thermodynamic formula. Otherwise, temperature must be expressed in Kelvin.

When there is a phase transition, heat can be absorbed or released without an accompanying change in temperature. Melting, vaporization and sublimation absorb heat, while the reverse processes – freezing, condensation and deposition – release heat while a constant temperature is maintained.

6.2 Work

The energy of a system can be changed in another way. Work can be done on a system (or *by* a system). Work is mechanical energy transferred when force applies over a distance. A system exchanges work with its surroundings when the boundary between them moves, increasing or decreasing the volume of the system. Consider the gas system depicted in Fig. 6.1. Here, the piston applies a force to a boundary of the gas. The boundary moves down a distance, d . Work is done on the gas, as its boundary moves and its volume decreases.

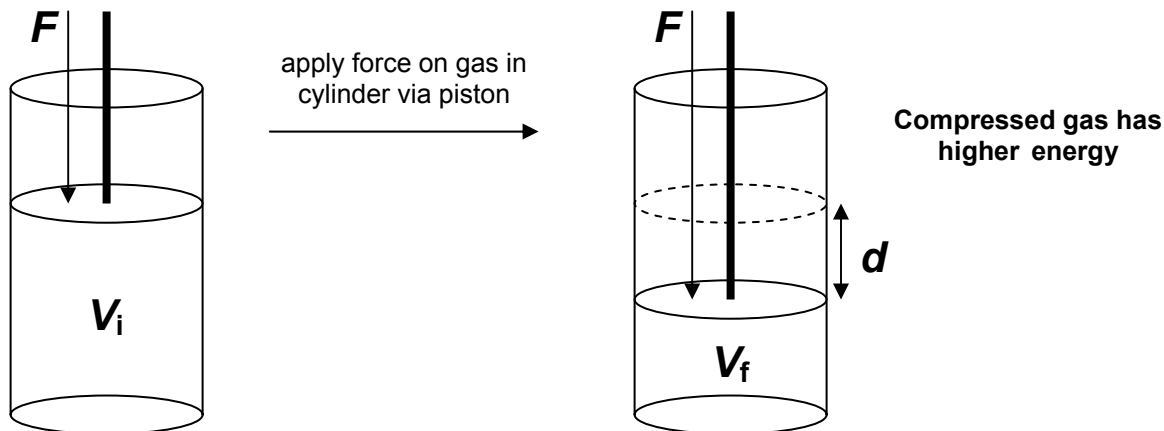


Figure 6.1. Force applied on a gas over a distance decreases the volume of the gas while increasing its energy.

The force on the piston is applied over the distance, d . The work done on the gas is

$$\begin{aligned} w &= F d \\ &= p A d \\ &= -p \Delta V \end{aligned} \quad 6.2$$

where A is the area of the moving boundary and p is the pressure on that boundary (force per unit area). The third line follows from $A d = -\Delta V$; i.e., the volume of the gas *decreases* by this amount, $-\Delta V$ is negative.

Example 6.3: How much work is done on the air in a bicycle pump when the volume of air is decreased by 50 mL under 5.0 atm pressure?

Approach: Substitute into the above formula for work.

$$\begin{aligned} w &= -p \Delta V \\ &= -5.0 \text{ atm} \times 0.050 \text{ L} = -0.25 \text{ L atm} \\ &= -101.3 \text{ J L}^{-1} \text{ atm}^{-1} \times 0.25 \text{ L atm} \\ &= 25 \text{ J} \end{aligned}$$

The L atm energy units are converted to J by the conversion factor $1.103 \text{ J} = 1 \text{ L atm}$. This is an important step if you need to combine work and heat. Heat is determined in J.

Note that the conversion factor between L atm and J is just the ratio of the two forms of the gas constant.

$$101.3 \text{ J L}^{-1} \text{ atm}^{-1} = \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}}$$

A system can gain or lose energy via work. The system gains energy when work is done on it – i.e. when it is compressed. The system loses energy when work is done by the system – it expands, compressing the surroundings. The sign of the work associated with a process is simply assessed by asking whether the volume of the system increased or decreased during the process. Because gases generally occupy much larger volumes than solids and liquids, the volume of a system is primarily determined by the number of moles of gas in the system. Moreover, changes in volume are generally connected with changes in the number of moles of gas. Thus, work is done by (i.e. $w < 0$) a system undergoing a reaction that increases the number of moles of gas. For example, a system of calcium carbonate decomposing into calcium oxide and carbon dioxide gas does work on the surroundings – i.e., work is done by the system. The energy is lost to the surroundings.



Example 6.4: For which of the following processes is work positive – i.e., work is done on the system?

- (a) $2 \text{ Na}(\text{s}) + 2 \text{ H}_2\text{O}(\text{l}) \rightarrow 2 \text{ NaOH}(\text{aq}) + \text{H}_2(\text{g})$
- (b) $\text{C}_3\text{H}_8(\text{g}) + 5 \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{l})$
- (c) $2 \text{ NI}_3\text{NH}_3(\text{s}) \rightarrow 2 \text{ N}_2(\text{g}) + 3 \text{ I}_2(\text{s}) + 3 \text{ H}_2(\text{g})$
- (d) $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
- (e) $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$

Approach: Count the number of moles of reactant and product gases. Work is positive if the number of moles of gas decreases.

- (a) The only gas here is a product. $\Delta n_{\text{gas}} = n_{\text{product gas}} - n_{\text{reactant gas}} = 1$. Work is done by the system. $w < 0$
- (b) $\Delta n_{\text{gas}} = -2$. Work is done **on** the system. $w > 0$
- (c) $\Delta n_{\text{gas}} = 5$. Work is done by the system. $w < 0$
- (d) $\Delta n_{\text{gas}} = -1$. Work is done **on** the system. $w > 0$
- (e) $\Delta n_{\text{gas}} = 1$. Work is done by the system. $w < 0$

6.4 Energy Conservation – the First Law of Thermodynamics

We have seen that energy can be transferred, either as heat or work, between systems, but is never created or destroyed. This is the *first law of thermodynamics* – energy is conserved. Thus, if the energy of a system changes it is because heat or work has been transferred between the system and surroundings. Specifically,

$$\Delta U = q + w \quad 6.3$$

is the change in energy of the system expressed as the sum of heat flowing into the system and work done on the system - negative values accounting for reverse transfers. The above equation is the first law of thermodynamics in equation form.

Example 6.5: What is the change in energy for the following combinations of q and w ?

- (a) $q = 50 \text{ J}$ and $w = 50 \text{ J}$
- (b) $q = 0 \text{ J}$ and $w = 100 \text{ J}$
- (a) $q = 100 \text{ J}$ and $w = 0 \text{ J}$

Approach: Add heat and work to get ΔU , the change in energy.

- (a) $\Delta U = q + w = 50 \text{ J} + 50 \text{ J} = 100 \text{ J}$
- (b) $\Delta U = q + w = 0 \text{ J} + 100 \text{ J} = 100 \text{ J}$
- (c) $\Delta U = 100 \text{ J}$

Note that the three combinations of q and w listed above produce the same change in the energy. The final energy depends only on the initial energy and the sum of heat and work transfers. In general, every system has a thermodynamic state with well-defined values of all of system properties – the *state functions* (they depend only on the state of the system). There are many paths connecting two final states. Paths correspond to processes that generally involve heat or work transfer. Heat and work are characteristics of processes – they are not state functions.

6.5 Enthalpy

Enthalpy is state function like energy (volume, pressure, temperature, etc). It is closely related to energy and we sometimes speak of energy of enthalpy as though they were interchangeable. Enthalpy, H , is just energy, U , plus an extra term:

$$H = U + p V \quad 6.4$$

The extra term is the energy required to "make room" for the system in an environment with constant pressure, p . Solids and liquids occupy small spaces and the associated $p V$ term in the enthalpy is generally negligible. Gases occupy much larger volumes. The $p V$ term is small, but not negligible, for gases.

Enthalpy is introduced because it is common to perform heat measurements under constant pressure conditions. Calorimetry is used to measure heat. If the experiment takes place under constant pressure conditions, the change in energy is not equal to the measured q . The first law gives

$$\begin{aligned} \Delta U &= q + w \\ &= q - p \Delta V \end{aligned}$$

Under constant pressure conditions, the volume can change.

Bomb calorimeters are calorimeters with *constant volume*. Heat measurements made with bomb calorimeters directly give ΔU (the work term is zero);

$$\Delta U = q + 0 = q_V \quad 6.5$$

where q_V denotes heat for a constant volume process. However, bomb calorimeters require a strong, rigid (steel) container to withstand large pressure differences resulting from chemical reactions inside the calorimeter. Constant pressure calorimeters, known as coffee cup calorimeters, are much safer – but do not give ΔU directly. This is not a problem, however.

Under constant pressure conditions,

$$p \Delta V = \Delta(p V)$$

Work is thus the change in a state function (pressure \times volume), when pressure is constant. This allows the first law to be rearranged to

$$\begin{aligned} \Delta U &= q + w \\ \Delta U &= q - p \Delta V \\ \Delta U + \Delta(p V) &= q \\ \Delta(U + p V) &= q \end{aligned}$$

or

$$\Delta H = q = q_p \quad 6.6$$

where q_p denotes heat for a constant pressure process, and $H = U + p V$ as introduced above. Here, we see that heat measured in a coffee cup calorimeter gives the change in enthalpy, a state function. It is sufficient (and convenient) to construct an enthalpy scale by doing a series of coffee cup calorimeter experiments. Each experiment measures the enthalpy difference between the reactants and products for some reaction – i.e., the *enthalpy of reaction*.

Example 6.6: The neutralization of 100. mL 0.200 M NaOH solution with 100. mL 0.200 HCl solution is performed in a coffee cup calorimeter. The temperature of the combined solution rises from 20.00°C to 21.34°C. What is the enthalpy of this reaction in kJ mol^{-1} ? Assume the solution has density 1.00 g mL^{-1} and specific heat capacity $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ – i.e., the properties of pure water at 20.00°C.

Approach: Determine the heat transferred from the temperature change and the heat capacity (use mass \times specific heat capacity here). Write a net balanced chemical reaction and determined the number of moles reacted. Divide the heat by the number of moles to get the enthalpy of reaction in kJ mol^{-1} . The sign is negative because heat is released by the reaction and the temperature increased.

To use

$$q = m s \Delta T$$

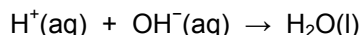
we need the total mass of solution.

$$\begin{aligned} m &= V d \\ &= (100. + 100. \text{ mL}) \times 1.00 \text{ g mL}^{-1} = 200. \text{ g} \end{aligned}$$

Therefore,

$$\begin{aligned} q &= 200. \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} (21.34 - 20.00) \text{ K} \\ &= 1120 \text{ J} = 1.12 \text{ kJ} \end{aligned}$$

The net balanced reaction is



The number of moles of $\text{H}^+(\text{aq})$ is the volume of the HCl solution \times its concentration – i.e. $0.100 \text{ L} \times 0.200 \text{ mol L}^{-1} = 0.0200 \text{ mol}$. The number of moles of OH^- is the same. They both react to completion. Therefore the number of moles reacted – the extent of reaction – is 0.0200 mol .

The enthalpy of reaction is

$$\begin{aligned}\Delta H &= -1.12 \text{ kJ} / 0.0200 \text{ mol} \\ &= -56.0 \text{ kJ mol}^{-1}\end{aligned}$$

The sign reversal in the last step - recognizing that the reaction releases heat - can be confusing for students. The sign reversal results because the heat that determines ΔH is the heat that must be released to return the contents of the calorimeter to the initial temperature. The system – the calorimeter and its contents – would lose heat in this imagined process, a process not actually carried out since the calorimeter is thermally insulated. Nevertheless, the heat associated with the imagined process is calculated exactly as above, except that the sign of ΔT is reversed. In this process, 21.34°C is the initial temperature and 20.00°C is the final temperature. The heat determined in this way gives the enthalpy of reaction at 20.00°C .

In the above example, the reaction released heat and ΔH is negative. This is an *exothermic* reaction. Processes with positive ΔH absorb energy – they are called *endothermic* processes. For example, the dissolution of ammonium nitrate in water is endothermic.



This process is endothermic because strong ionic bonds in the reactant were broken in order to form weaker intermolecular forces (solvation of the separated ions) in solution. Other endothermic processes include melting, vaporization, sublimation and bond breaking. Bonds (covalent, ionic or intermolecular) are stronger in a solid, than in a liquid. In the gas phase intermolecular forces are essentially absent.

Exothermic reactions are reactions that break weaker bonds to form stronger bonds. Condensation (the reverse of vaporization) is exothermic because it forms intermolecular bonds in the liquid without breaking any bonds.

Having measured a number of enthalpies of reaction, how do we go on to construct an enthalpy scale? The key is that because enthalpy is a state function, we can get the enthalpy of a specific reaction (the "target" reaction) by adding the enthalpies of reaction for a series of reactions as long as they begin with the specified reactants and end with the specified products. This is called *Hess' Law*.

The simplest application of *Hess' Law* is to combine a reaction with its reverse. In this case, the final products are just the reactants. $\Delta H = 0$ for the closed path. Therefore,

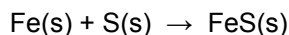
$$\Delta H = \Delta H_{\text{forward}} + \Delta H_{\text{reverse}} = 0$$

or

$$\Delta H_{\text{reverse}} = -\Delta H_{\text{forward}}$$

If a reaction must be scaled (e.g. doubled) so the stoichiometric coefficients match what is required to get the target reaction, then the enthalpy of the reaction is scaled by the same factor. For example, burning twice as much gas produces twice as much heat. If multiple reactions are combined to form a target reaction then their ΔH values are added together.

Example 6.7: Determine the enthalpy of the following reaction given the data below.



n	Reaction	ΔH_n (kJ mol ⁻¹)
1	2 Fe(s) + O ₂ (g) → 2 FeO(s)	-544.0
2	2 S(s) + 3 O ₂ (g) → 2 SO ₃ (g)	-791.4
3	FeO(s) + SO ₃ (g) → FeSO ₄ (s)	-260.7
4	FeS(s) + 2 O ₂ (g) → FeSO ₄ (s)	-828.4

Approach: Manipulate and combine the given reactions as needed so they add up to the target reaction; perform the same manipulations to the ΔH values for each reaction. The target reaction ΔH is the combination of the given ΔH data after they have been manipulated. Look for the target reaction reactants and products in the given reaction.

Reaction 1 has reactant 2 Fe(s) among reactants. Scale reaction 1 by 1/2 to match the Fe(s) coefficient in the target reaction. Reaction 2 has 2 S(s) among reactants. Again, scale by 1/2. Reaction 4 has FeS(s) as a reactant, whereas FeS(s) is a product in the target reaction. Reverse reaction 4. Reaction 3 is needed to cancel out compounds that do not participate in the target reaction. Note that the ΔH values must be adjusted similarly.

		ΔH_n (kJ mol ⁻¹)
1/2 × Rxn 1	Fe(s) + 1/2 O ₂ (g) → FeO(s)	-272.0
1/2 × Rxn 2	S(s) + 3/2 O ₂ (g) → SO ₃ (g)	-395.7
-Rxn 4	FeSO ₄ (s) → FeS(s) + 2 O ₂ (g)	828.4
Rxn 3	FeO(s) + SO ₃ (g) → FeSO ₄ (s)	-260.7
	<u>Fe(s) + S(s) → FeS(s)</u>	<u>-100.0</u>

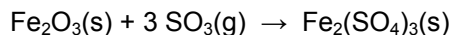
It is useful to have a more systematic approach to determining an enthalpy of reaction from known data. It turns out that the enthalpy of any reaction can be determined from a table of all formation reactions. The formation reaction of a compound is the reaction that forms the compound from its elements in their *standard state*. The standard state of an element is its stable form at 1.00 atm pressure and 25°C. Stable form refers to the stable allotrope (structure) of the element and the stable phase. The standard state of most elements is a solid. The noble gases, hydrogen, nitrogen, oxygen, fluorine and chlorine are gases, while bromine is a liquid. The standard state of carbon is graphite, C(graphite), not diamond, C(diamond).

Any reaction, under *standard conditions* (1.00 atm pressure and 25°C), can be written as the sum of the formation reactions of all products (weighted by the stoichiometric coefficients) plus the sum of the reverse formation reactions of all reactant (again, with stoichiometric weightings). Consequently, the enthalpy of reaction can correspondingly be expressed in terms of enthalpies of formation:

$$\Delta H^\circ = \sum_{\text{products, P}} c_P \Delta H_f^\circ[\text{P}] - \sum_{\text{reactants, R}} c_R \Delta H_f^\circ[\text{R}] \quad 6.7$$

The superscript “°” refers to standard conditions. The terms c_P and c_R are the stoichiometric coefficients of products and reactants, respectively.

For example, the enthalpy of reaction of



is

$$\Delta H^\circ = \Delta H_f^\circ[\text{Fe}_2(\text{SO}_4)_3(\text{s})] - \Delta H_f^\circ[\text{Fe}_2\text{O}_3(\text{s})] - 3\Delta H_f^\circ[\text{SO}_3(\text{g})]$$

Note that an element in the standard state has an enthalpy of formation of zero, $\Delta H_f^\circ = 0$. The formation reaction in this case is a non-reaction.

The equation for enthalpy of reaction in terms of enthalpies of formation can be depicted graphically.

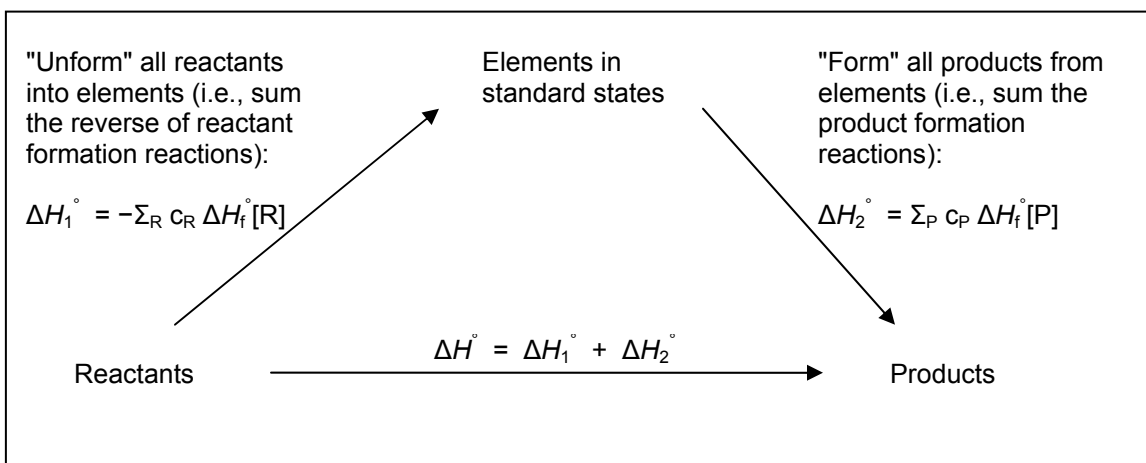
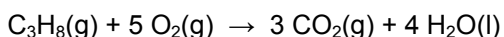


Figure 6.2. Graphical depiction of the expression of enthalpy of reaction in terms of enthalpies of formation – Equation 6.7 above.

Example 6.8: Determine the enthalpy of combustion of propane from the given enthalpies of formation.

Compound	ΔH_f° (kJ mol ⁻¹)
CO ₂ (g)	-393.5
H ₂ O(l)	-285.8
C ₃ H ₈ (g)	-103.8

Approach: Write down the balanced chemical reaction. Combine the enthalpies of formation as described above – products minus reactants.



$$\begin{aligned} \Delta H^\circ &= 3\Delta H_f^\circ[\text{CO}_2(\text{g})] + 4\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] - \Delta H_f^\circ[\text{C}_3\text{H}_8(\text{g})] \\ &= 3(-393.5) + 4(-285.8) - (-103.8) \text{ kJ mol}^{-1} = -2219.9 \text{ kJ mol}^{-1} \end{aligned}$$

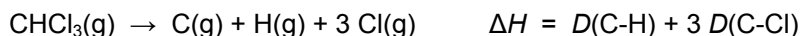
Note that the enthalpy of formation of oxygen is left out of the equation because it is zero.

A table of enthalpies of formation is not the only enthalpy we can construct. It is also convenient to determine enthalpies of reaction using *bond enthalpies*. A bond enthalpy is the enthalpy of a bond dissociation reaction – a reaction breaking a type of bond. For example, the bond enthalpy of the Cl-Cl bond, $D(\text{Cl-Cl})$, is ΔH for the dissociation of Cl₂ gas into Cl atoms:



Bond dissociation is an endothermic process. Bonds are broken – this requires energy – while no bonds are formed. D is always positive.

For molecules with more than one bond, ΔH for the dissociation of the molecule into atoms is the sum of all bond enthalpies – one for each bond in the molecule. For example,

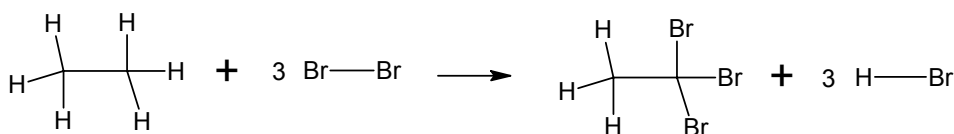
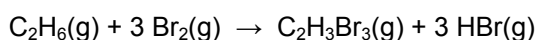


The enthalpy of any gas phase reaction can be written as the sum of all reactant bond enthalpies minus the sum of all product bond enthalpies:

$$\Delta H = \sum_{\text{reactant bonds, r}} n_r D[r] - \sum_{\text{product bonds, p}} n_p D[p] \quad 6.8$$

where n_r is the number of occurrences of bond type r (e.g. C-Cl bond) in all reactant species. Similarly, n_p is the number of occurrences of bond type p among products.

The enthalpy of reaction for



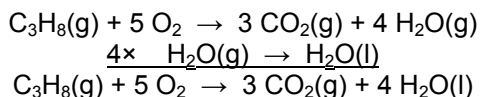
is approximated by

$$\begin{aligned} \Delta H &= D[\text{C-C}] + 6D[\text{C-H}] + 3D[\text{Br-Br}] - D[\text{C-C}] - 3D[\text{C-H}] - 3D[\text{C-Br}] - 3D[\text{H-Br}] \\ &= 3D[\text{C-H}] + 3D[\text{Br-Br}] - 3D[\text{C-Br}] - 3D[\text{H-Br}] \end{aligned}$$

Note that some of the bonds are unchanged from reactant to product. The associated bond enthalpies cancel out leaving only the broken and formed bonds.

The structures of reactants and products must be drawn in order to identify the bonds present. Single, double and triple bonds are tabulated separately, as they have different bond enthalpies. In general, enthalpies of reaction determined from bond enthalpies are only approximate. This is because tabulated bond enthalpies are average bond enthalpies for each bond type – each distinct occurrence of a bond has a slightly different dissociation enthalpy.

The use of bond enthalpies to estimate reaction enthalpies is restricted to gas phase reactions. However, bond enthalpies can be used to determine enthalpies of reaction for reactions with liquids and/or solids, if the bond enthalpy data is supplemented with enthalpies of vaporization and/or sublimation. The target reaction is written as a gas phase reaction plus necessary phase transitions, making use of Hess' Law. For example, the combustion of propane at 25 °C can be written as the sum of a gas phase reaction and the condensation of water:



Therefore, the enthalpy of combustion of propane is just

$$\Delta H = \Delta H_{\text{gas phase reaction}} - 4\Delta H_{\text{vap}}[\text{H}_2\text{O}]$$

where

$$\Delta H_{\text{gas phase reaction}} \cong 2D[\text{C-C}] + 8D[\text{C-H}] + 5D[\text{O=O}] - 3 \times 2D[\text{C=O}] - 4 \times 2D[\text{O-H}]$$

The equation for enthalpy of reaction in terms of bond enthalpies can be depicted graphically.

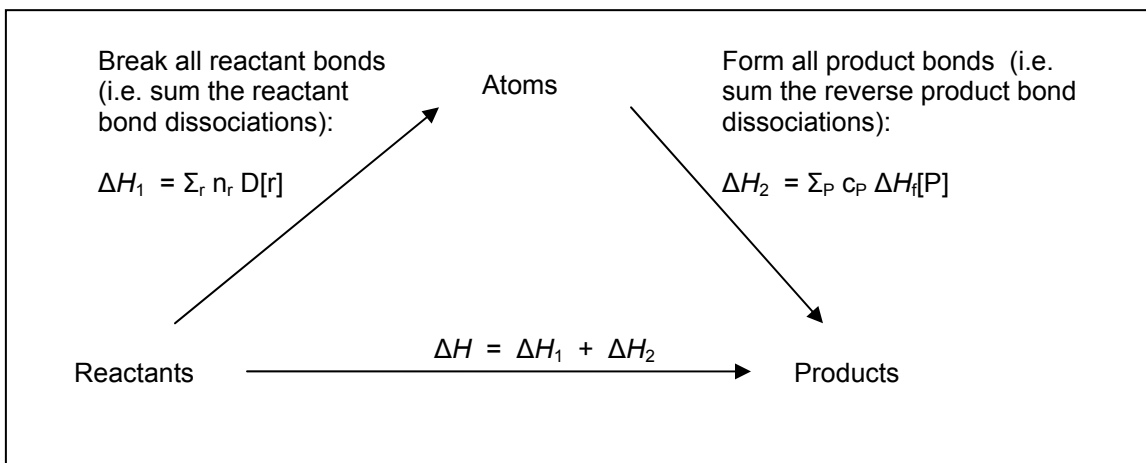
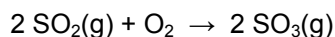


Figure 6.3. Graphical depiction of the expression of enthalpy of reaction in terms of bond enthalpies – Equation 6.8 above.

Example 6.9: Approximate the enthalpy of combustion of oxidation of $\text{SO}_2(\text{g})$ to form $\text{SO}_3(\text{g})$ from the given bond enthalpies.

Bond	D (kJ mol^{-1})
S=O	515
O=O	495

Approach: Write down the balanced chemical reaction. Combine the enthalpies of formation as described above – reactant bonds minus product bonds.



$$\begin{aligned} \Delta H &\cong 2 \times 2D[\text{S=O}] + D[\text{O=O}] - 2 \times 3D[\text{S=O}] \\ &= D[\text{O=O}] - 2D[\text{S=O}] \\ &= 495 - 2(515) \text{ kJ mol}^{-1} = -535 \text{ kJ mol}^{-1} \end{aligned}$$

Problems:

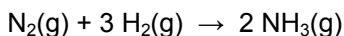
- 6.1 How much heat is released when 100. g of ethanol cools from 50.0°C to 20.0°C ? ($s_{\text{ethanol}} = 2.44 \text{ J K}^{-1} \text{ g}^{-1}$)
- 6.2 How much heat is required to produce steam at $150.^\circ\text{C}$ from 200. mL of liquid water at $20.^\circ\text{C}$? ($s[\text{H}_2\text{O}(\text{l})] = 4.18 \text{ J K}^{-1} \text{ g}^{-1}$, $s[\text{H}_2\text{O}(\text{g})] = 1.85 \text{ J K}^{-1} \text{ g}^{-1}$ and $\Delta H_{\text{vap}}^\circ[\text{H}_2\text{O}] = 44.0 \text{ kJ mol}^{-1}$)
- 6.3 When 8.16 g of $\text{NH}_4\text{NO}_3(\text{s})$ is dissolved in 100. mL of water, in a calorimeter, the temperature is observed to drop from 19.5°C to 15.9°C . What is the enthalpy change for this dissolution process?

6.4 The energy of a gas increases by 125 J, after its volume decreases by 2.00 L under 1.00 atm pressure. How much heat was absorbed/released by the gas?

6.5 For which of the following processes is (i) $q > 0$ (i.e. endothermic), or (ii) $w > 0$ (i.e., work is done on the system)?

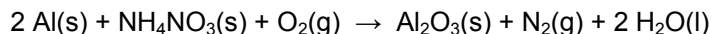
- (a) $\text{Hg(l)} \rightarrow \text{Hg(g)}$
- (b) $\text{Br}_2\text{(g)} \rightarrow 2 \text{Br(g)}$
- (c) $\text{H(g)} + \text{Cl(g)} \rightarrow \text{HCl(g)}$
- (d) $\text{C(g)} \rightarrow \text{C(s)}$
- (e) $2 \text{S(s)} + 3 \text{O}_2\text{(g)} \rightarrow 2 \text{SO}_3\text{(g)}$

6.6 Determine the enthalpy of the following reaction from the given data:



n	Reaction	ΔH_n (kJ mol ⁻¹)
1	$2 \text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{H}_2\text{O(g)}$	-483.6
2	$\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{NO(g)}$	182.6
3	$4 \text{NH}_3\text{(g)} + 5 \text{O}_2\text{(g)} \rightarrow 4 \text{NO(g)} + 6 \text{H}_2\text{O(g)}$	-260.7

6.7 Determine the enthalpy of the reaction below, known as the "mother of all bombs" reaction,



from the given data. How much heat is released per gram of reactant (excluding oxygen – it is supplied by the atmosphere? What is the final temperature of 1.0 L of water at 20. °C, if it is heated by reaction of 10. g of this reactant?

Compound	ΔH_f° (kJ mol ⁻¹)
$\text{NH}_4\text{NO}_3\text{(s)}$	-356.6
$\text{Al}_2\text{O}_3\text{(s)}$	-1675.7
$\text{H}_2\text{O(l)}$	-285.8

6.8 Estimate the enthalpy of the oxidation of ethanol with hypochlorous acid using the given data.



$$\Delta H_{\text{vap}}^\circ [\text{CH}_3\text{CH}_2\text{OH}] = 38.6 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{vap}}^\circ [\text{CH}_3\text{COOH}] = 23.7 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{vap}}^\circ [\text{H}_2\text{O}] = 44.0 \text{ kJ mol}^{-1}$$

Bond	D (kJ mol ⁻¹)
C-C	345
C-H	415
C-O	360
C=O	750
O-H	460
Cl-O	220
Cl-H	430