

10: Energetics of Chemical Reactions

Foundation

We begin our study of the energetics of chemical reactions with our understanding of mass relationships, determined by the stoichiometry of balanced reactions and the relative atomic masses of the elements. We will assume a conceptual understanding of energy based on the physics of mechanics, and in particular, we will assume the law of conservation of energy. In developing a molecular understanding of the reaction energetics, we will further assume our understanding of chemical bonding via valence shell electron pair sharing and molecular orbital theory.

Goals

The heat released or consumed in a chemical reaction is typically amongst the most easily observed and most readily appreciated consequences of the reaction. Many chemical reactions are performed routinely specifically for the purpose of utilizing the heat released by the reaction.

We are interested here in an understanding of the energetics of chemical reactions. Specifically, we wish to know what factors determine whether heat is absorbed or released during a chemical reaction. With that knowledge, we seek to quantify and predict the amount of heat anticipated in a chemical reaction. We expect to find that the quantity of heat absorbed or released during a reaction is related to the bonding of the molecules involved in the reaction.

Prior to answering these questions, we must first answer a few questions regarding the nature of heat. Despite our common familiarity with heat (particularly in Houston), the concept of heat is somewhat elusive to define. We recognize heat as "whatever it is that makes things hot", but this definition is too imprecise to permit measurement or any other conceptual progress. Exactly how to we define and measure heat?

Observation 1: Measurement of Heat by Temperature

We can define in a variety of ways a temperature scale which permits quantitative measurement of "how hot" an object is. Such scales are typically based on the expansion and contraction of materials, particularly of liquid mercury, or on variation of resistance in wires or thermocouples. Using such scales, we can easily show that heating an object causes its temperature to rise.

It is important, however, to distinguish between heat and temperature. These two concepts are not one and the same. To illustrate the difference, we begin by measuring the temperature rise produced by a given amount of heat, focusing on the temperature rise in 1000 g of water produced by burning 1.0 g of methane gas. We discover by performing this experiment repeatedly that the temperature of this quantity of water always rises by exactly 13.3°C. Therefore, the same quantity of heat must always be produced by reaction of this quantity of methane.

If we burn 1.0 g of methane to heat 500 g of water instead, we observe a temperature rise of 26.6°C. If we burn 1.0 g of methane to heat 1000 g of iron, we observe a temperature rise of 123°C. Therefore, the temperature rise observed as a function of the quantity of material heated as well as the nature of the material heated. Consequently, 13.3°C is not an approximate measure of this quantity of heat, since we cannot say that the burning of 1.0 g of methane "produces" 13.3°C of heat. Such a statement is clearly revealed to be nonsense, so the concepts of temperature and heat must be kept distinct.

Our observations do reveal that we can relate the temperature rise produced in a substance to a fixed quantity of heat, provided that we specify the type and amount of the substance. Therefore, we define a property for each substance, called the **heat capacity**, which relates the temperature rise to the quantity of heat absorbed. We define q to be the quantity of heat, and ΔT to be the temperature rise produced by this heat. The heat capacity C is defined by

$$q = C\Delta T \quad (10.1)$$

This equation, however, is only a definition and does not help us calculate either q or C , since we know neither one.

Next, however, we observe that we can also elevate the temperature of a substance **mechanically**, that is, by doing work on it. As simple examples, we can warm water by stirring it, or warm metal by rubbing or scraping it. (As a historical note, these observations were crucial in establishing that heat is equivalent to work in its effect on matter, demonstrating that heat is therefore a form of energy.) Although it is difficult to do, we can measure the amount of work required to elevate the temperature of 1 g of water by 1°C. We find that the amount of work required is invariably equal to 4.184 J. Consequently, adding 4.184 J of energy to 1 g of water must elevate the energy of the water molecules by an amount measured by 1°C. By conservation of energy, the energy

of the water molecules does not depend on how that energy was acquired. Therefore, the increase in energy measured by a 1°C temperature increase is the same regardless of whether the water was heated or stirred. As such, 4.184 J must also be the amount of energy added to the water molecules when they are **heated** by 1°C rather than stirred. We have therefore effectively measured the heat q required to elevate the temperature of 1 g of water by 1°C . Referring back to the definition of heat capacity, we now can calculate that the heat capacity of 1 g of water must be $4.184\frac{\text{J}}{^{\circ}\text{C}}$. The heat capacity **per gram** of a substance is referred to as the **specific heat** of the substance, usually indicated by the symbol c_s . The specific heat of water is $4.184\frac{\text{J}}{^{\circ}\text{C}}$.

Determining the heat capacity (or specific heat) of water is an extremely important measurement for two reasons. First, from the heat capacity of water we can determine the heat capacity of any other substance very simply. Imagine taking a hot 5.0 g iron weight at 100°C and placing it in 10.0 g of water at 25°C . We know from experience that the iron bar will be cooled and the water will be heated until both have achieved the same temperature. This is an easy experiment to perform, and we find that the final temperature of the iron and water is 28.8°C . Clearly, the temperature of the water has been raised by 3.8°C . From the definition of heat capacity and the specific heat of water, we can calculate that the water must have absorbed an amount of heat $q = (10.0\text{ g})\left(4.184\frac{\text{J}}{^{\circ}\text{C}}\right)(3.8^{\circ}\text{C}) = 1.59\text{ J}$. By conservation of energy, this must be the amount of heat **lost** by the 1 g iron weight, whose temperature was lowered by 71.2°C . Again referring to the definition of heat capacity, we can calculate the specific heat of the iron bar to be $c_s = \frac{-1.59\text{ J}}{(-71.2^{\circ}\text{C})(5.0\text{ g})} = 0.45\frac{\text{J}}{^{\circ}\text{C}}$. Following this procedure, we can easily produce extensive tables of heat capacities for many substances.

Second, and perhaps more importantly for our purposes, we can use the known specific heat of water to measure the heat released in any chemical reaction. To analyze a previous example, we observed that the combustion of 1.0 g of methane gas released sufficient heat to increase the temperature of 1000 g of water by 13.3°C . The heat capacity of 1000 g of water must be $(1000\text{ g})\left(4.184\frac{\text{J}}{^{\circ}\text{C}}\right) = 4184\text{ J}^{\circ}\text{C}$. Therefore, by the definition of heat capacity, elevating the temperature of 1000 g of water by 13.3°C must require $55,650\text{ J} = 55.65\text{ kJ}$ of heat.

The method of measuring reaction energies by capturing the heat evolved in a water bath and measuring the temperature rise produced in that water bath is called **calorimetry**. This method is dependent on the equivalence of heat and work as transfers of energy, and on the law of conservation of energy. Following this procedure, we can straightforwardly measure the heat released or absorbed in any easily performed chemical reaction. For reactions which are difficult to initiate or which occur only under restricted conditions or which are exceedingly slow, we will require alternative methods.

Observation 2: Hess' Law of Reaction Energies

Hydrogen gas, which is of potential interest nationally as a clean fuel, can be generated by the reaction of carbon (coal) and water:

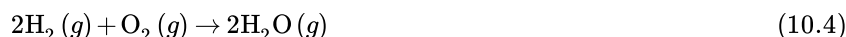


Calorimetry reveals that this reaction requires the **input** of 90.1 kJ of heat for every mole of $\text{C}(s)$ consumed. By convention, when heat is absorbed during a reaction, we consider the quantity of heat to be a positive number: in chemical terms, $q > 0$ for an **endothermic** reaction. When heat is evolved, the reaction is **exothermic** and $q < 0$ by convention.

It is interesting to ask where this input energy goes when the reaction occurs. One way to answer this question is to consider the fact that the reaction converts one fuel, $\text{C}(s)$, into another, $\text{H}_2(g)$. To compare the energy available in each fuel, we can measure the heat evolved in the combustion of each fuel with one mole of oxygen gas. We observe that

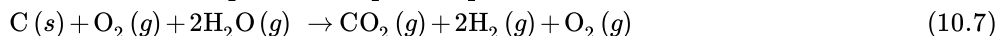


produces 393.5 kJ for one mole of carbon burned; hence $q = -393.5\text{ kJ}$. The reaction



produces 483.6 kJ for two moles of hydrogen gas burned, so $q = -483.6\text{ kJ}$. It is evident that more energy is available from combustion of the hydrogen fuel than from combustion of the carbon fuel, so it is not surprising that conversion of the carbon fuel to hydrogen fuel requires the input of energy.

Of considerable importance is the observation that the heat input in the reaction of coal and water, 90.1 kJ is exactly equal to the **difference** between the heat evolved, -393.5 kJ , in the combustion of carbon and the heat evolved, -483.6 kJ , in the combustion of hydrogen. This is not a coincidence: if we take the combustion of carbon and add it to the **reverse** of the combustion of hydrogen, we get



Canceling the $\text{O}_2(g)$ from both sides, since it is net neither a reactant nor product. The final equation is equivalent to the reaction of carbon and water presented earlier. Thus, taking the combustion of carbon and "subtracting" the combustion of hydrogen (or more accurately, adding the reverse of the combustion of hydrogen) yields the final equation above. And, the heat of the combustion of carbon **minus** the heat of the combustion of hydrogen equals the heat of the reaction between carbon and water.

By studying many chemical reactions in this way, we discover that this result, known as **Hess' Law**, is general.

Hess' Law

The heat of any reaction is equal to the sum of the heats of reaction for any set of reactions which in sum are equivalent to the overall reaction.

(Although we have not considered the restriction, applicability of this law requires that all reactions considered proceed under similar conditions: we will consider all reactions to occur at constant pressure.)

A pictorial view of Hess' Law as applied to the heat of the reaction of carbon and water is illustrative. In Figure 10.1, the reactants $\text{C}(s) + 2\text{H}_2\text{O}(g)$ are placed together in a box, representing the **state** of the materials involved in the reaction prior to the reaction. The products $\text{CO}_2(g) + 2\text{H}_2(g)$ are placed together in a second box representing the state of the materials involved after the reaction. The reaction arrow connecting these boxes is labeled with the heat of this reaction. Now we take these same materials and place them in a third box containing $\text{C}(s)$, $\text{O}_2(g)$, and $2\text{H}_2(g)$. This box is connected to the reactant and product boxes with reaction arrows, labeled by the heats of reaction in the combustion of carbon and the combustion of hydrogen.



Figure 10.1: A pictorial view of Hess' Law.

This picture of Hess' Law reveals that the heat of reaction along the "path" directly connecting the reactant state to the product state is exactly equal to the total heat of reaction along the alternative "path" connecting reactants to products via the intermediate state containing $\text{C}(s)$, $\text{O}_2(g)$, and $2\text{H}_2(g)$. A consequence of our observation of Hess' Law is therefore that the net heat evolved or absorbed during a reaction is independent of the path connecting the reactant to product. (This statement is again subject to our restriction that all reactions in the alternative path must occur under constant pressure conditions.)

A slightly different view of Figure 10.1 results from beginning at the reactant box and following a complete circuit through the other boxes leading back to the reactant box, summing the net heats of reaction as we go. We discover that the net heat transferred (again provided that all reactions occur under constant pressure) is exactly zero. This is a statement of the conservation of energy: the energy in the reactant state does not depend upon the processes which produced that state. Therefore, we cannot extract any energy from the reactants by a process which simply recreates the reactants. Were this not the case, we could endlessly produce unlimited quantities of energy by following the circuitous path which continually reproduces the initial reactants.

By this reasoning, we can define an energy function whose value for the reactants is independent of how the reactant state was prepared. Likewise, the value of this energy function in the product state is independent of how the products are prepared. We choose this function, H , so that the change in the function, $\Delta H = H_{\text{products}} - H_{\text{reactants}}$, is equal to the heat of reaction q under constant pressure conditions. H , which we call the **enthalpy**, is a **state function**, since its value depends only on the state of the materials under consideration, that is, the temperature, pressure, and composition of these materials.

The concept of a state function is somewhat analogous to the idea of elevation. Consider the difference in elevation between the first floor and the third floor of a building. This difference is independent of the path we choose to get from the first floor to the third floor. We can simply climb up two flights of stairs, or we can climb one flight of stairs, walk the length of the building, then walk a second flight of stairs. Or we can ride the elevator. We could even walk outside and have a crane lift us to the roof of the building, from which we can climb down to the third floor. Each path produces exactly the same elevation gain, even though the distance traveled is significantly different from one path to the next. This is simply because the elevation is a "state function". Our elevation, standing on the third floor, is independent of how we got to the third floor, and the same is true of the first floor. Since the elevation thus is a state function, the elevation gain is independent of the path.

Now, the existence of an energy state function H is of considerable importance in calculating heats of reaction. Consider the prototypical reaction in Figure 10.2a, with reactants R being converted to products P . We wish to calculate the heat absorbed or

released in this reaction, which is ΔH . Since H is a state function, we can follow any path from R to P and calculate ΔH along that path. In Figure 10.2b, we consider one such possible path, consisting of two reactions passing through an intermediate state containing all the atoms involved in the reaction, each in elemental form. This is a useful intermediate state since it can be used for any possible chemical reaction. For example, in Figure 10.1, the atoms involved in the reaction are C, H, and O, each of which are represented in the intermediate state in elemental form. We can see in Figure 10.2b that the ΔH for the overall reaction is now the difference between the ΔH in the formation of the products P from the elements and the ΔH in the formation of the reactants R from the elements.

a. 
b. 

Figure 10.2: Calculation of ΔH

The ΔH values for formation of each material from the elements are thus of general utility in calculating ΔH for any reaction of interest. We therefore define the **standard formation reaction** for reactant R, as



and the heat involved in this reaction is the **standard enthalpy of formation**, designated by ΔH_f° . The subscript f , standing for "formation", indicates that the ΔH is for the reaction creating the material from the elements in standard state. The superscript $^\circ$ indicates that the reactions occur under constant standard pressure conditions of 1 atm. From Figure 10.2b, we see that the heat of any reaction can be calculated from

$$\Delta H_f^\circ = \Delta H_{f, \text{products}}^\circ - \Delta H_{f, \text{reactants}}^\circ \quad (10.9)$$

Extensive tables of ΔH_f° have been compiled and published. This allows us to calculate with complete confidence the heat of reaction for any reaction of interest, even including hypothetical reactions which may be difficult to perform or impossibly slow to react.

Observation 3: Bond Energies in Polyatomic Molecules

The **bond energy** for a molecule is the energy required to separate the two bonded atoms to great distance. We recall that the total energy of the bonding electrons is lower when the two atoms are separated by the bond distance than when they are separated by a great distance. As such, the energy input required to separate the atoms elevates the energy of the electrons when the bond is broken.

We can use diatomic bond energies to calculate the heat of reaction ΔH for any reaction involving only diatomic molecules. We consider two simple examples. First, the reaction



is observed to be endothermic with heat of reaction $70 \frac{\text{kJ}}{\text{mol}}$. Note that this reaction can be viewed as consisting entirely of the breaking of the H_2 bond followed by the formation of the HBr bond. Consequently, we must input energy equal to the bond energy of H_2 ($436 \frac{\text{kJ}}{\text{mol}}$), but in forming the HBr bond we recover output energy equal to the bond energy of HBr ($366 \frac{\text{kJ}}{\text{mol}}$). Therefore the heat of the overall equation at constant pressure must be equal to the difference in these bond energies, $70 \frac{\text{kJ}}{\text{mol}}$.

Now we can answer the question, at least for this reaction, of where the energy "goes" during the reaction. The reason this reaction absorbs energy is that the bond which must be broken, H_2 , is stronger than the bond which is formed, HBr. Note that energy is released when the HBr bond is formed, but the amount of energy released is less than the amount of energy required to break the H_2 bond in the first place.

The second example is similar:



This reaction is exothermic with $\Delta H^\circ = -103 \frac{\text{kJ}}{\text{mol}}$. In this case, we must break an H_2 bond, with energy $436 \frac{\text{kJ}}{\text{mol}}$, and a Br_2 bond, with energy $193 \frac{\text{kJ}}{\text{mol}}$. Since two HBr molecules are formed, we must form two HBr bonds, each with bond energy $366 \frac{\text{kJ}}{\text{mol}}$. In total, then, breaking the bonds in the reactants requires $629 \frac{\text{kJ}}{\text{mol}}$, and forming the new bonds releases $732 \frac{\text{kJ}}{\text{mol}}$, for a net release

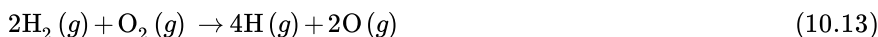
of $103 \frac{\text{kJ}}{\text{mol}}$. This calculation reveals that the reaction is exothermic because, although we must break one very strong bond and one weaker bond, we form two strong bonds.

There are two items worth reflection in these examples. First, energy is released in a chemical reaction due to the **formation** of strong bonds. Breaking a bond, on the other hand, always requires the **input** of energy. Second, the reaction of H_2 and Br_2 does not actually proceed by the two-step process of breaking both reactant bonds, thus forming four free atoms, followed by making two new bonds. The actual process of the reaction is significantly more complicated. The details of this process are irrelevant to the energetics of the reaction, however, since, as we have shown, the heat of reaction ΔH does not depend on the path of the reaction. This is another example of the utility of Hess' Law.

We now proceed to apply this bond energy analysis to the energetics of reactions involving polyatomic molecules. A simple example is the combustion of hydrogen gas discussed previously. This is an explosive reaction, producing 483.6 kJ per mole of oxygen. Calculating the heat of reaction from bond energies requires us to know the bond energies in H_2O . In this case, we must break not one but two bonds:



The energy required to perform this reaction is measured to be $926.0 \frac{\text{kJ}}{\text{mol}}$. The reaction of hydrogen and oxygen can proceed by a path in which we first break two H_2 bonds and one O_2 bond, then we follow the reverse of the decomposition of water twice:



Therefore, the energy of the final equation must be the energy required to break two H_2 bonds and one O_2 bond minus twice the energy of the decomposition of water. We calculate that $\Delta H^\circ = 2 \times (436 \frac{\text{kJ}}{\text{mol}}) + 498.3 \frac{\text{kJ}}{\text{mol}} - 2 \times (926.9 \frac{\text{kJ}}{\text{mol}}) = -483.5 \frac{\text{kJ}}{\text{mol}}$. It is clear from this calculation that the formation of water is strongly exothermic because of the very large amount of energy released when two hydrogen atoms and one oxygen atom form a water molecule.

It is tempting to use the heat of the decomposition of water to calculate the energy of an O–H bond. Since breaking the two O–H bonds in water requires $926.9 \frac{\text{kJ}}{\text{mol}}$, then we might infer that breaking a single O–H bond requires $\frac{926.9}{2} \frac{\text{kJ}}{\text{mol}} = 463.5 \frac{\text{kJ}}{\text{mol}}$. However, the reaction



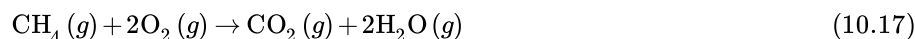
has $\Delta H^\circ = 492 \frac{\text{kJ}}{\text{mol}}$. Therefore, the energy required to break an O–H bond in H_2O is not the same as the energy required to break the O–H bond in the OH diatomic molecule. Stated differently, it requires more energy to break the first O–H bond in water than is required to break the second O–H bond.

In general, we find that the energy required to break a bond between any two particular atoms depends upon the molecule those two atoms are in. Considering yet again oxygen and hydrogen, we find that the energy required to break the O–H bond in methanol (CH_3OH) is $437 \frac{\text{kJ}}{\text{mol}}$, which differs substantially from the energy of the first O–H bond in water. Similarly, the energy required to break a single C–H bond in methane (CH_4) is $435 \frac{\text{kJ}}{\text{mol}}$, but the energy required to break all four C–H bonds in methane is $1663 \frac{\text{kJ}}{\text{mol}}$, which is not equal to four times the energy of one bond. As another such comparison, the energy required to break a C–H bond is $400 \frac{\text{kJ}}{\text{mol}}$ in trichloromethane (HCCl_3), $414 \frac{\text{kJ}}{\text{mol}}$ in dichloromethane (H_2CCl_2), and $422 \frac{\text{kJ}}{\text{mol}}$ in chloromethane (H_3CCl).

These observations are somewhat discouraging, since they reveal that, to use bond energies to calculate the heat of a reaction, we must first measure the bond energies for all bonds for all molecules involved in that reaction. This is almost certainly more difficult than it is desirable. On the other hand, we can note that the bond energies for similar bonds in similar molecules are close to one another. The C–H bond energy in any one of the three chloromethanes above illustrate this quite well. We can estimate the C–H bond energy in any one of these chloromethanes by the average C–H bond energy in the three chloromethane molecules, which is $412 \frac{\text{kJ}}{\text{mol}}$. Likewise, the average of the C–H bond energies in methane is $\frac{1663}{4} \frac{\text{kJ}}{\text{mol}} = 416 \frac{\text{kJ}}{\text{mol}}$ and is thus a reasonable approximation to the energy required to break a single C–H bond in methane.

By analyzing many bond energies in many molecules, we find that, in general, we can approximate the bond energy in any particular molecule by the average of the energies of similar bonds. These average bond energies can then be used to estimate the heat of a reaction without measuring all of the required bond energies.

Consider for example the combustion of methane to form water and carbon dioxide:



We can estimate the heat of this reaction by using average bond energies. We must break four C–H bonds at an energy cost of approximately $4 \times 412 \frac{\text{kJ}}{\text{mol}}$ and two O₂ bonds at an energy cost of approximately $2 \times 496 \frac{\text{kJ}}{\text{mol}}$. Forming the bonds in the products releases approximately $2 \times 742 \frac{\text{kJ}}{\text{mol}}$ for the two C=O double bonds and $4 \times 463 \frac{\text{kJ}}{\text{mol}}$ for the O–H bonds. Net, the heat of reaction is thus approximately $\Delta H^\circ = 1648 + 992 - 1486 - 1852 = -698 \frac{\text{kJ}}{\text{mol}}$. This is a rather rough approximation to the actual heat of combustion of methane, $-890 \frac{\text{kJ}}{\text{mol}}$. Therefore, we cannot use average bond energies to predict accurately the heat of a reaction. We can get an estimate, which may be sufficiently useful. Moreover, we can use these calculations to gain insight into the energetics of the reaction. For example, the combustion of methane is strongly exothermic, which is why methane gas (the primary component in natural gas) is an excellent fuel. From our calculation, we can see that the reaction involved breaking six bonds and forming six new bonds. The bonds formed are substantially stronger than those broken, thus accounting for the net release of energy during the reaction.

Review and Discussion Questions

Assume you have two samples of two different metals, X and Z. The samples are exactly the same mass. Both samples are heated to the same temperature. Then each sample is placed into separate glasses containing identical quantities of cold water, initially at identical temperatures below that of the metals. The final temperature of the water containing metal X is greater than the final temperature of the water containing metal Z. Which of the two metals has the larger heat capacity? Explain your conclusion.

If each sample, initially at the same temperature, is heated with exactly 100 J of energy, which sample has the higher final temperature?

Explain how Hess' Law is a consequence of conservation of energy.

Consider the reaction



Draw Lewis structures for each of N₂O₄ and NO₂. On the basis of these structures, predict whether the reaction is endothermic or exothermic, and explain your reasoning.

Why is the bond energy of H₂ not equal to ΔH_f° of H₂? For what species is the enthalpy of formation related to the bond energy of H₂?

Suggest a reason why ΔH for the reaction



is not equal to ΔH° for the reaction



Determine whether the reaction is exothermic or endothermic for each of the following circumstances:

The heat of combustion of the products is greater than the heat of combustion of the reactants.

The enthalpy of formation of the products is greater than the enthalpy of reaction of the reactants.

The total of the bond energies of the products is greater than the total of the bond energies for the reactants.

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