Chapter Six   Thermodynamics of Chemistry

The branch of science which includes the study of energy transformations is called **thermodynamics**. Basic to thermodynamics are two "laws" derived from experience, which can be stated as follows:

1.   Energy can neither be created nor destroyed—the energy of the universe is constant.

2.   The entropy of the universe is always increasing.

These generalizations are statements of the first and second laws of thermodynamics.

Applied to chemistry, thermodynamics provides criteria for predicting whether a given reaction can occur. If a reaction is feasible, the extent to which it will proceed under a given set of conditions can be predicted. One great value of thermodynamics is that it is possible to use data from experiments which can be conveniently carried out to arrive at conclusions about experiments which are difficult or even impossible to perform.

§ 6–1   The First Law of Thermodynamics

Conceptions

1. Systems and Surroundings

The part of the material world that the chemist selects for study is called a **system** (The portion of matter which is being investigated is called the *system*). A system in which the amount of matter remains constant is said to be a *closed*

system. An unopened can of beer is a closed system. A system in which the amount of matter changes with time is called an *open system.* The human body is an open system; it continually takes in food and oxygen and eliminates waste products. Systems are chosen by chemists for convenience. A test tube containing sugar would be a convenient system for observing the macroscopic properties of sugar. A chemist interested, for example, in the chemistry of the formation of the earth might even consider the entire world as system. Once the chemist selects a system for study, everything else in the environment is called the *surroundings* (All other objects in the universe which may interact with the system are called the *surroundings*). Frequently a chemist uses a sample for study. A *sample* is a representative portion of a system.

2.   States and State functions

A system is described by identifying its constituents and their quantities, the temperature, the pressure, and perhaps some other relevant conditions, such as the physical states of the substances involved. A complete description of the system defined its **state.** The initial state of a system is its state before it undergoes a change, and the final state describes the system after a change has occurred. In going from the initial state to the final state, a system may exchange energy with its surrounding, and/or its components may change composition; but there can be no change in the total mass of the system. No matter can be lost to or gained from the surroundings.

The properties of a system which uniquely define the state of the system are

called **thermodynamic properties** or **state functions**. For example, consider a system consisting of one mole of an ideal gas. The state of the system is specified by giving any two of the properties pressure, P, volume, V, and temperature, T, of n moles of an ideal gas are related by the equation

$$PV = nRT$$

This equation, expressing the relationship of its state functions, is called the equation of state for an ideal gas. The equations of state for real gases, liquids, solids and solutions are more complicated than that for an ideal gas. Moreover, even for an ideal gas, there are state functions other than P, V, and T. For example, energy is a state function.

The properties of a system which do not depend on the quantity of matter present are called **intensive properties**. For example, density, pressure, and temperature are intensive properties. Properties which are proportional to the quantity of matter in the system are called **extensive properties**. The mass of a sample is an extensive property. Other examples of extensive properties will be described in the following sections.

The First Law of Thermodynamics

Any system in a given state will possess a given quantity of energy, called its internal energy, U. Internal energy is an extensive property. By either releasing energy or by absorbing energy, a system may change from an initial state where its internal energy is U_1 to a different (final) state where its internal energy is U_2. The change in internal energy is

$$U = U_2 - U_1$$

It is seldom necessary (and of little practical use) to know the individual value of energies U_1 and U_2. The *difference* in energy between two states is of prime importance and is usually conveniently determined. The change (increase or decrease) of energy in a given system was determined from its mass, its heat capacity, and the change in temperature. At no time was the total energy of the system considered, only the gain or loss of heat was found.

Energy may be transferred into or out of a system in forms other than heat. For example a chemical system may transfer mechanical energy through expansion of a gaseous product. It is customary to denote all forms of transferred energy other than heat as work, W. Thus when a system changes from one state to another, the change in its internal energy is given by

$$U = Q - W$$

Where Q is the heat *absorbed* by the system and W is the work *done by* the system. For Q, a positive value is understood to indicate a transfer of energy into the system, while a negative value indicates energy transferred out of the system. The quantity W is given a positive value for work transferred *out of* the system. A positive value of U thus indicates an increase in the internal energy of a system, and a negative value indicates a decrease. The relationship $U = Q - W$ is a mathematical statement of the first law of thermodynamics—energy can neither be created nor destroyed.

Example

In a certain process, 2848J of heat is absorbed by a system while the system is doing work corresponding to 1235J. What is the value of U for the process?

Since work is done by the system, W has a positive value:

$$U = Q - W = 2848 - 1235 = 1613 \text{ J}$$

When a system changes from one state to another, the magnitude of the change in internal energy, U, depends only on the initial and final states, and not on the path or process by which the change takes place. If this fact were not true, it would be possible for a system to change from an initial to a final state along one path, then change back to the initial state along another path, and have a net quantity of energy left over. Since the system would then be in its original state, the process would be repeated over and over again. With each repetition some energy would be gained, and the effect would be the creation of energy, which is in contraction to the first law of thermodynamics. In changing from an initial state to a final state, both Q and W could have many different values, depending on the path, but $Q - W$ is invariable and independent of the path. Therefore U depends only on the initial state and the final state, as is expected since U is a state function.

§ 6–2   Thermochemistry

Enthalpy

1. Q_V (The heat is changed at constant temperature)

$$\Delta U = Q_V - W = Q_V - P\ \Delta V = Q_V$$

2. Q_P (The heat is absorbed at constant pressure)

The change in internal energy for a system undergoing a chemical reaction at constant pressure is given by

$$\Delta U = Q_P - W = Q_P - P\ \Delta V \qquad \text{(expansion work only)}$$

Where the subscript P denotes that the heat is absorbed at constant pressure. Rear-ranging and expanding gives

$$Q_P = \Delta U + P\ \Delta V = (U_2 - U_1) + P(V_2\text{-}V_1)$$

Collecting terms for the initial and final states gives

$$Q_P = (U_2 + P\ V_2) - (U_1 + PV_1)$$

It can be shown that the product PV has the dimensions of energy; thus $(U + PV)$ also has the dimensions of energy. It is convenient to define a new state function called **enthalpy, H,** as follows:

$$\boldsymbol{H = U + P\ V}$$

Then

$$Q_P = H_2 - H_1 = \Delta H \qquad \text{(expansion work only)}$$

$$(= \Delta U + P\ \Delta V = Q_v + \Delta nRT)$$

The change in enthalpy is merely the heat absorbed in a process occurring at constant pressure in which the only possible work is expansion against the atmosphere. Since U, P, and V are state functions, it is apparent that H is also a state function; that ΔH is depends only on the initial and final states of the system involved.

The concept of enthalpy is so useful that it is applied to a wide variety of types of reactions and processes. Special names and symbols are often used to denote the enthalpy of certain of these, such as enthalpy of formation (H_f),enthalpy of combustion (H_{comb}), and enthalpy of sublimation (H_{sub}). It must be defined below, are merely different examples of specific enthalpy changes.
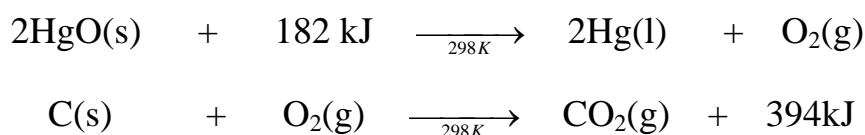
3. The relationship between Q_v and Q_P

$$H = U + P V = H = U + nRT$$

$$H = Q_P = U + nRT = Q_v + nRT$$

Enthalpy Changes in Chemical Reactions

The term heat of reaction—more precisely, **enthalpy of reaction**—is often used to denote that in a given chemical process, a definite quantity of energy is absorbed or released per mole of some substance undergoing change. Reactions which occur with the evolution of energy are said to be **exothermic**; reactions in which energy is absorbed are **endothermic**. The quantities of energy evolved in an exothermic reaction or absorbed in an endothermic reaction depend on the quantities of reactants undergoing change.

The physical states of the reactants and products must be specified to describe a reaction completely. For example, the process represented by the equation

$$2HgO(s) \quad + \quad 182 \text{ kJ} \quad \xrightarrow{298K} \quad 2Hg(l) \quad + \quad O_2(g)$$

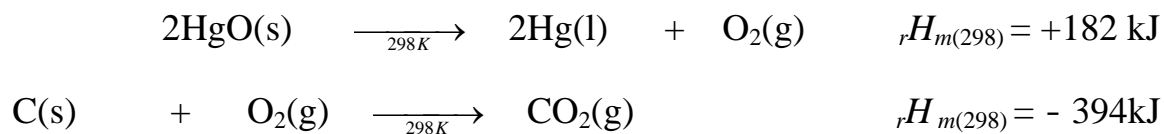$$C(s) \quad + \quad O_2(g) \quad \xrightarrow{298K} \quad CO_2(g) \quad + \quad 394kJ$$

When a chemical reaction occurs at constant pressure and involves no work other than perhaps expansion against the atmosphere, the heat of reaction is equal

to the enthalpy change, H. The terms *heat of reaction and enthalpy change* are sometimes used interchangeably, but for reactions carried out at other than constant pressure, the heat of reaction is not in general equal to the enthalpy change.

Since energy is given off in an exothermic reaction, the enthalpies of the products total less than the enthalpies of the reactants. Hence the sign of H is negative, indicating a decrease in enthalpy. Conversely, in an endothermic reaction, energy must be provided from outside the system, and there is an increase in enthalpy in going from the initial state to the final state. The sign of H is positive. As two examples, the chemical systems described above can be written with their enthalpy changes as

$$2HgO(s) \xrightarrow{298K} 2Hg(l) + O_2(g) \qquad _rH_{m(298)} = +182 \text{ kJ}$$

$$C(s) + O_2(g) \xrightarrow{298K} CO_2(g) \qquad\qquad _rH_{m(298)} = -394 \text{kJ}$$

Enthalpies of Formation

1. Definition

Knowledge of the enthalpy change for a given reaction permits the evaluation of the reaction as a source of energy. For example, fuels for jet planes or for rockets must yield large quantities of energy per gram of fuel. Even more important, in the design of industrial chemical plants, calculations of the energy requirements of the various processes and their related costs must be made. Often, a process is designed so that the heat liberated in an exothermic step in the process is used to augment the energy requirements for an endothermic step.

Enthalpy changes for many reactions can be determined experimentally. However, for many others it is either inconvenient or impossible to measure enthalpy changes directly under a given set of conditions. In such cases the enthalpy change must be calculated from other available data.

Since it is the *change* in enthalpy which is important, it is not necessary to know absolute values of the enthalpies of the substances involved in a reaction. Therefore, one can adopt some arbitrary point of reference, or **standard state**. From which the enthalpy changes can be measured. The standard state (not to be confused with STP) of each element and each compound is defined as its most stable physical form at 1 atm pressure and at a specified temperature, usually 298K. by convention, *each element in its standard state is assigned an enthalpy value of zero*. The enthalpy change that occurs when 1 mole of a compound in its standard state is formed from its elements in their standard states is called the **standard enthalpy of formation** of the compound and is designated by the symbol $_f H_m^o$. The superscript, ^{o}, indicates that all the reactants and all the products are in their standard states. ($_f H_m^o$: kJ.mol^{-1})

2. Applications

Enthalpies of formation of various substances are presented in Table 6–1 (P$_{258}$). It should be noted that the enthalpy change for the dissociation of a compound into its constituent elements is equal in magnitude but opposite in sign to the enthalpy of formation of the compound.

Because H for a reaction is independent of the path of the reaction, the

standard enthalpy change for any reaction may be calculated as the difference between the sum of the enthalpies of formation of all the products and the related sum for all the reactants:

$$_rH_m{}^o \ = \ \sum_i \ v_i \ {}_fH_m{}^o{}_{(Products)} \ - \sum_i \ v_i \ {}_fH_m{}^o{}_{(reactants)}$$

This principle is illustrated in P_{259} (Example 6–5).

Hess' Law

1. Conception

The procedure of algebraically combining equations for several processes and adding the corresponding energies in order to obtain the energy of yet another process is sometimes called **Hess' law.** To use this procedure, it is necessary to collect equations containing all of the species involved as reactants and products, and to combine them in such a manner that only the desired reactants and products remain. Since energy and enthalpy are both extensive properties, if other than 1 mole of a given reactant or product is involved, the enthalpy change per mole must be multiplied by the number of moles of that substance. This important principle makes it worthwhile to collect data on the enthalpies of all types of reactions.

2. Applications

P_{255}　(Example 6–4)

Enthalpies of Combustion

The enthalpy change which occurs when 1 mole of a substance reacts completely with oxygen gas at a given temperature is known as the **enthalpy of**

combustion, $_cH_m^o$ (kJ.mol^{-1}), of the substance at that temperature. Enthalpies of combustion are conveniently determined in a bomb calorimeter, as described below. Some enthalpies of combustion are listed in Table 6–2 (P$_{260}$). Values of $_cH_m^o$ are particularly useful for determining values for $_fH_m^o$ for organic compounds. If the values of $_fH_m^o$ of the products of the combustion reaction are known, the $_fH_m^o$ of the compound may be calculated by means of Hess' law. This procedure is very useful in the case of compounds which cannot be conveniently synthesized by direct combination of their constituent elements.

$$\sum_i v_i \ _cH_m^o \text{(reactants)} \ = \ _rH_m^o \ + \sum_i v_i \ _cH_m^o \text{(Products)}$$

$$\Rightarrow \qquad _rH_m^o \ = \sum_i v_i \ _cH_m^o \text{(reactants)} \ - \sum_i v_i \ _cH_m^o \text{(Products)}$$

Estimate $_rH_m^o$ from Bond-energy

From a theoretical point of view, chemical reactions may be regarded as involving the breaking of some bonds and the formation of others. For example, the reaction of 1 mole of propane with oxygen

$$CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 \ + \ 4H_2O$$
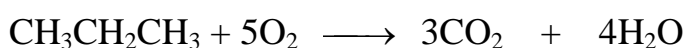
Involves the breaking of 2 moles of carbon-to-carbon bonds, 8 moles of carbon-to-hydrogen bonds, and 5 moles of oxygen-to-oxygen bonds, as well as the formation of 6 moles of carbon-to-oxygen bonds and 8 moles of hydrogen-to-oxygen bonds. The observed enthalpy change must reflect the differences in the strengths of the various bonds. The fact that the reaction is exothermic suggests a model in which, on the average, bonds between oxygen and carbon and between oxygen and hydrogen are stronger than bonds between

carbon and hydrogen, between carbon and carbon, and between oxygen and oxygen. Enthalpy data can be used to compare bond strengths in this manner.

$$_{r}H_{m}{}^{o} \;=\; \sum BE_{(reactants)} \;-\sum BE_{(Products)}$$

§6–3 The Chemical Reaction's Direction

Free Energy and Entropy—Criteria for Spontaneous Change

A major objective of chemists is to understand and control chemical reactions—to know whether or not under a given set of conditions two substances will react when mixed, to predict the extent to which a given reaction will proceed before equilibrium is established, and to determine whether or not a given reaction will be endothermic or exothermic.

The enthalpy change in a chemical reaction is a measure of the difference in energy content of the products and reactants. It is tempting to assume that exothermic reactions will proceed spontaneously upon mixing the reactants and that endothermic reactions do not occur spontaneously. However, there are endothermic reactions which do proceed spontaneously. For example, ammonium chloride decomposes perceptibly at room temperature and appreciably at high temperatures:

$$NH_4Cl(s) \;\longrightarrow\; NH_3(g) \;+\; HCl(g) \qquad H_{298}{}^{o} = \; 176kJ$$
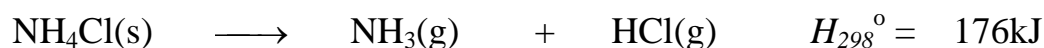
An Endothermic reaction between ions which occurs spontaneously at room temperature is the reaction of magnesium ion with carbonate ion:

$$Mg^{2+}(aq) \;+\; CO_3{}^{2-}(aq) \;\longrightarrow\; MgCO_3(s) \qquad H_{298}{}^{o} = \; 25kJ$$
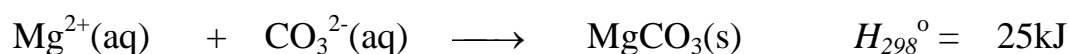
Obviously the enthalpy change is not the only factor responsible for the tendency

of a system to undergo spontaneous change.

The transfer of heat energy from an object at a higher temperature to one at a lower temperature is a familiar example of a spontaneous process. It must be recalled that heat is a unique form of energy in that at constant temperature, heat cannot be completely converted to any other form of energy. The heat content, or enthalpy, of any system must be considered in two parts:

1. That which is free to be converted to other forms of energy.

2. That which is necessary to maintain the system at the specified temperature and thus is unavailable for conversion.

This concept can be expressed in the form of an equation:

Enthalpy = free energy + unavailable energy

Expressed in symbols, the equation becomes

$$H = G + TS$$

Where H is the enthalpy, and G is the free energy. The term denoting unavailable energy is expressed as the product of absolute temperature, T, and a factor which is called entropy, represented by the letter S. Above the temperature absolute zero, every substance possesses a finite (nonzero) entropy. The nature of entropy will be discussed in the next section.

In any process H is the difference between the enthalpy of the final state of a system and the enthalpy of the initial state of the system. The following equations can be written to express the enthalpies of two different states:

For state 2: $H_2 = G_2 + T_2S_2$

For state 1: $H_1 = G_1 + T_1S_1$

Therefore,

$$H = H_2 - H_1 = (G_2 - G_1) + (T_2S_2 - T_1S_1)$$

$$H = G + (TS)$$

For a process occurring at constant temperature, in which $T_2 = T_1 = T$, the equation becomes

$$H = G + T S \qquad (\text{constant } T)$$

This equation, which expresses the limitation on the conversion of heat energy to other forms of energy, is a statement of the **second law of thermodynamics**.

Like enthalpy change(H), the free energy change(G) and the entropy change (S) are thermodynamic functions; that is, their magnitudes depend only on the initial and final states of the system an are independent of the manner in which the system changes from its initial state to its final state. In addition, H,

G and S are extensive properties; that is, their numerical magnitudes depend on the number of moles of substances involved in the system.

If a process is to occur spontaneously, it must not require energy from outside the system. (The process might be endothermic, but in such cases energy is provided from the system itself.) In fact, free energy should be released by the system, so that the final state of the system will have less available energy than its initial state. In more concise terms, any spontaneous process must be accompanied by a *decrease* in free energy.

It is customary to solve the equation representing the second law of

thermodynamics explicitly for G as follows:

$$G = H – T S \qquad (\text{constant } T)$$

And to apply the following criteria for spontaneous change and for the equilibrium state:

1. If G is negative, the given process may occur spontaneously.

2. If G is positive, the indicated process cannot occur spontaneously; instead the reverse of the indicated process may occur.

3. If G is zero, neither the indicated process nor the reverse process can occur spontaneously. The system is in a state of equilibrium (see Chapter 8). The indicated process is said to be a reversible one because a very small change in conditions can make G either positive or negative

The Nature of Entropy

Some processes which increase the randomness of a given system, thus increasing the entropy of the system, include the following:

1. Breaking down large molecules into smaller ones.

2. Increasing the number of moles of gas in the system.

3. Melting a solid.

4. Evaporating a pure liquid.

5. Mixing two or more pure substances, including dissolving one substance in another.

Some processes which generally cause a decrease in the entropy of a system include:

1. Association of small molecules into larger ones.

2. Reaction of gas to form a liquid or solid.

3. Condensation of a gas.

4. Freezing of a liquid.

5. Crystallization of a dissolved substance.

6. Reaction in solution leading to the formation of a precipitate.

Of course, in any actual system undergoing change, processes tending to increase the entropy and processes tending to decrease the entropy may occur simultaneously. In such cases the overall entropy change will be the net result of the various individual processes.

Spontaneous Endothermic Reactions

The relationship

$$\Delta G = \Delta H - T \Delta S$$

Explains why very exothermic reactions are spontaneous even if there is an accompanying decrease in entropy. For such reactions, ΔH is a sufficiently large negative-quantity that ΔG remains negative despite the fact that is positive. If there is a relatively large positive entropy change, the term $-T \Delta S$ will more than compensate for a small positive value of ΔH, and ΔG will be negative. Consider the reaction

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g) \qquad \Delta H_{298}^o = 176kJ$$
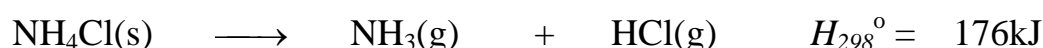
In this case, owing to the formation of 2 moles of gaseous products per mole of solid NH_4Cl reacted, there is a relatively large increase in entropy. The term $-T$

S more than compensates for the positive value of H, and accordingly, G is negative. Because this is a spontaneous change, the energy used up in the reaction must come from within the system itself. If no energy is added to maintain the temperature, there will be a drop in temperature. That is, thermal energy of the system is used to provide the energy needed for the endothermic process.

Entropy Changes In Changes of Phase

The transition of a pure substance from one physical state to another (a phase change) which occurs at a fixed temperature is a reversible process. For example, at 0 and 1 atm pressure, a system composed of ice and water is in a state of equilibrium. If the pressure on the system is increased very slightly, ice will melt. Conversely, a very small decrease in pressure causes the water to freeze. Applying the criterion that $G = 0$,

$$H_{transition} = T \quad S$$

Hence the entropy change for such a reversible process can be determined using the relationship

$$S = \frac{\Delta H_{transition}}{T}$$

Absolute Entropies—The Third Law of Thermodynamics

If data for enthalpy change and entropy change are available for a given reaction, the relationship

$$G = \quad H - T \quad S$$

Permits calculation of the free energy change for the reaction. Unfortunately, for

most chemical reactions there is no convenient way to measure S directly. However there is a way of calculating S. A postulate known as the **third law of thermodynamics** states that the *entropies of all pure crystalline solids are zero at 0 K*. (The specifications *pure* and *crystalline* are necessary because mixtures and noncrystalline solids have some degree of randomness even at 0 K.) By the methods of calculus it is possible to calculate the difference between the entropies of a given substance at two temperatures from heat capacity data. The heat capacities as a function of temperature have been determined for a wide variety of substances, and extensive compilations are now available. Entropy changes for the process of raising the temperature of various substances from 0 K to any higher temperature have been calculated. Since the initial value is 0, the calculated entropy values are the **absolute entropies**, S^o, of the respective substances. Typical data are given in Table 6-3(P$_{269}$). Note that consistent with the nature of entropy, gases have higher entropies than solids, while liquids have intermediate values. Solid elements which are hard, such as boron, have lower entropies than solid elements which are soft, such as sodium. Among compounds, the entropy increases with the increasing number of atoms per molecule or formula unit.

Note that both elements and compounds have nonzero entropies at 25 . As a corollary, the absolute entropy of a compound is not the entropy of formation from its elements. The entropy change for any process is given by

$$_rS_m{}^o = \sum_i v_i S_m{}^o{}_{(Products)} - \sum_i v_i S_m{}^o{}_{(reactants)}$$

Hence for the formation of a compound,

$$S_f{}^o = S_m{}^o{}_{\text{(compound)}} - \sum_i \nu_i S_m{}^o{}_{\text{(elements)}}$$

Standard Free Energy Change

The free energy change of a process in which the reactants in their standard states are converted into products in their standard states is called the standard free energy change, ΔG^o. By convention, the standard free energy of formation of every element in its standard state at 298 K and 1 atm is taken to be zero. The free energy of formation of a compound is defined as the free energy change for the reaction of the elements in their standard states to form the compound in its standard state. Standard free energies of formation of several compounds are listed in Table 6–4 (P_{273}).

If the standard free energies of formation of all the reactants and products are known, ΔG^o for a reaction can be calculated as the difference between the sum of the free energies of formation of the products minus the corresponding sum for the reactants. In Figure 6–1, this generalization is shown in a manner analogous to the use of Hess' law.

The standard free energy of formation of a compound, $_fG_m{}^o$ (Δ_fG^o), is a measure of the stability of the substance. For example, if a compound has a large negative value of $_fG_m{}^o$, the compound cannot be readily decomposed into its elements. Indeed, that compound is likely to be formed as a product in any reaction in which its constituent elements are involved. On the other hand, a compound for which $_fG_m{}^o$ is positive will tend to be unstable with respect to

decomposition into its elements. Moreover, it will tend to be consumed in almost any reaction, being converted into substances having lower free energies of formation.
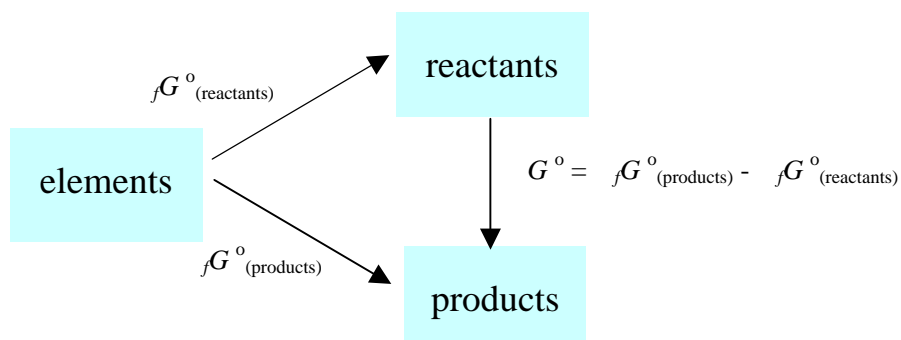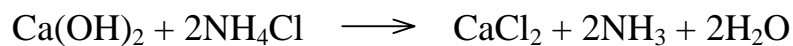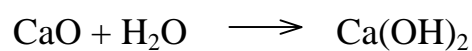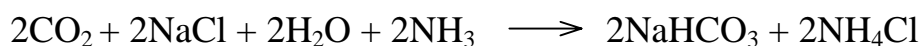

Figure 6–1.   Relationship Between G^o of a Reaction

and $_fG^o$ of Reactants and products

Exercises

1. When 12.0 grams of carbon reacted with oxygen to form CO and CO_2 at 25 and constant pressure, 75.0kcal of heat was liberated and no carbon remained. Calculate the mass of oxygen which reacted.

2. Calculate the enthalpy of combustion of 100.0 grams of CO at 125 .

3. Calculate the heat produced when 1.00 gallon of octane,C_8H_{18}, reacts with oxygen to form carbon monoxide and water vapor at 25 . (The density of octane is 0.7025 g/ml; 1.00 gallon = 3.785 liters.)

4. Assuming no loss of heat to the surroundings, determine the final temperature of the water produced from 2.00 moles of H_2 and 1.00 moles of O_2 initially at

25 which are allowed to react to form $H_2O(g)$.

5. The Solvay process for the industrial production of Na_2CO_3 involves the following reactions:

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$2CO_2 + 2NaCl + 2H_2O + 2NH_3 \longrightarrow 2NaHCO_3 + 2NH_4Cl$$

$$2NaHCO_3 \xrightarrow{heat} Na_2CO_3 + CO_2 + H_2O$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$

(a) Calculate ΔH for each step in the process. (b) Determine the overall ΔH for the process. (c) Write an equation for the net reaction. (d) Calculate ΔH for the net reaction, and compare this result to that of part (b).