

Chemical Thermodynamics

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1 Heat and Work

In thermodynamics, we divide the universe into two halves: the *system* and its *surroundings*. In addition, we usually stipulate that the boundary of the system is impermeable to matter (i.e., the mass of the system is constant) but that heat can be freely exchanged with the surroundings. In addition, we allow the system to perform work on its surroundings, or vice-versa.

The concept of work is a topic primarily in physics; however, we can review it here. When a force acts over a distance, it performs work. The work done by a force of 1 Newton acting over 1 meter is defined as 1 Joule.

In mechanics, when a given amount of work is performed upon an object, we assert that the object has gained that amount of kinetic energy (or lost, if the work is negative). However, in thermodynamics, we note that work is equivalent not only to energy, but also to *heat*. Consider a gram of water, which is heated so that its temperature rises by 1 °C. In such a case, we say that the water has gained 1 calorie of heat; this is the definition of the calorie. We can assert the equivalence of heat and work by defining a simple scalar conversion between calories and Joules:

$$1 \text{ cal} = 4.184 \text{ J}$$

2 The First Law of Thermodynamics

The first law of thermodynamics is essentially the conservation of energy for thermodynamic systems. However, the energy of a system is *not* constant; since work can be done upon the system and heat can be transferred to it, the energy can be changed. Specifically, the change in energy of a system is equal to the sum of work performed upon it and the heat delivered to it.

We know that heat can be delivered to a system by increasing its temperature, but it is still unclear on how work is to be performed on a thermodynamic system, or how a system can do work on its surroundings. We can see an example of this by considering a piston filled with gas. The pressure of the gas,

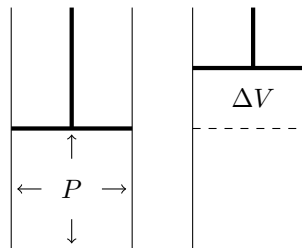
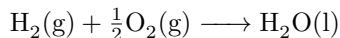


Figure 1: A gas expanding by a volume ΔV at a constant pressure P does work $W = P\Delta V$ on its environment.

or the force it exerts on the walls of the container per area, is taken to be P . Then the force acting on the area A of the piston is PA . When the piston moves a distance ℓ , the work done (equal to the force times the distance it acts) is $PA\ell$. However, the area times the displacement is simply the change in volume. Hence, we write $W = P\Delta V$.

However, the sort of work just described, known as *pressure-volume work*, is not the only way for the energy of a chemical system to change. When the contents of a system change through chemical reaction, there is a change in its intrinsic energy. We symbolize this energy by U and call it the *internal energy* of a system. For example, consider the reaction for the formation of water:



This reaction is accompanied by an energy change of $\Delta U = -282.123 \text{ kJ mol}^{-1}$, which expresses the inherent difference in energy between water and its elemental components. However, this reaction which transforms gases into a liquid clearly also results in a change in a volume, leading to pressure-volume work. We can compute this change in volume at standard conditions of 1 atm and 25 °C. According to the ideal gas law, the molar volume of $\text{H}_2(\text{g})$ is $\frac{RT}{P}$, and that of $\frac{1}{2}\text{O}_2(\text{g})$ is $\frac{RT}{2P}$ (half of the value for $\text{H}_2(\text{g})$). Water has a molar volume of 18 mL mol^{-1} . Therefore:

$$P\Delta V = P(18 \text{ mL mol}^{-1}) - P\left(\frac{RT}{P} + \frac{RT}{2P}\right) = -3.717 \text{ kJ mol}^{-1}$$

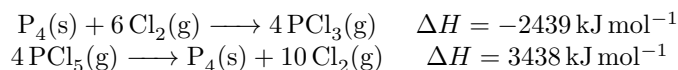
We are primarily interested in the total change in energy associated with a reaction, rather than the parts due to change in internal energy and pressure-volume work. We thus define the *enthalpy* of a system $H = U + PV$. Then the enthalpy of a reaction is $\Delta H = \Delta U + P\Delta V$. For the formation of water, this is $-282.123 - 3.717 = -285.840 \text{ kJ mol}^{-1}$.

2.1 Hess's Law

Hess's Law states that *the energy of a system is a function only of its state*. That is to say, enthalpy is not dependent upon the path taken to arrive at some state, but only the state itself. This can be shown from the conservation of energy by considering reversible transformations, although the argument will not be given here. Hess's Law is evident from our definition of enthalpy as $U + PV$; this is a function only of the state. The primary consequence of this law is that the change in enthalpy between two states, such as the beginning and the end of a chemical reaction, is the same irrespective of the path taken. For example, consider the following reaction, with unknown enthalpy change:



And the following two reactions with known enthalpy change:



If we perform the two reactions in sequence, which corresponds to algebraically adding their chemical equations, Hess's law guarantees that we can also simply add the values of ΔH . Therefore, we have:

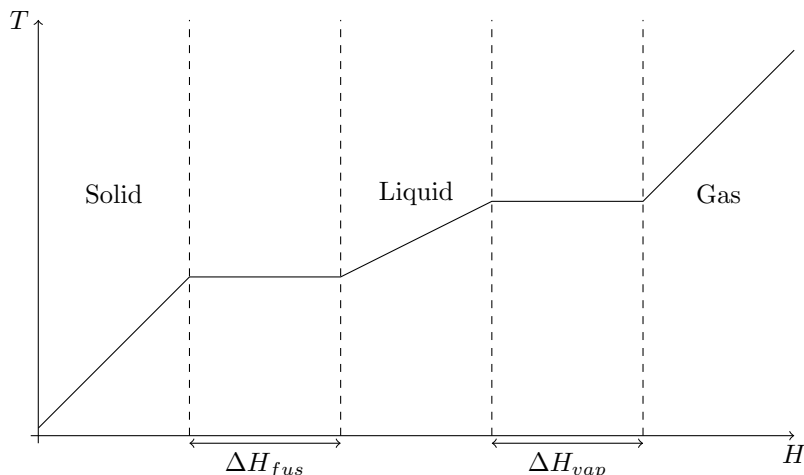
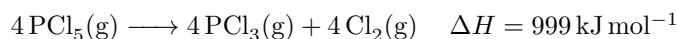
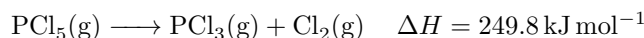


Figure 2: The heating curve shows the latent heats of fusion and vaporization.



To obtain the desired reaction, we can divide both the equation and the enthalpy change by four:



2.2 Heat Capacity, Heat of Fusion, and Heat of Vaporization

Physical changes as well chemical changes are accompanied by a change in enthalpy. An obvious example is a substance changing temperature, which requires either the addition or subtraction of heat. It has already been noted that a gram of water must absorb one calorie, or 4.184 J, to increase its temperature by 1 °C. We say that the *heat capacity* (or *specific heat*) of water is 1 cal/g K or 4.184 J/g K. For example, to bring a kilogram of water from 15 to 25 °C, we must deliver (4.184 J/g K)(1000 g)(10 K) = 41.84 kJ of energy. The specific heat is denoted by C_p , to signify that it is measured at constant pressure. The specific heat at constant volume, which is less often used, is C_v .

Changes of state also have associated changes of enthalpy. For the process of melting, it is called the *enthalpy of fusion*, and for boiling, it is the *enthalpy of vaporization*. The enthalpy of fusion for water is approximately $\Delta H_{fus} = 79.8 \text{ cal g}^{-1}$, and its enthalpy of vaporization is approximately $\Delta H_{vap} = 536.9 \text{ cal g}^{-1}$. These are known as latent heats; they must be added to the substance while it remains at a constant temperature (either its melting or boiling point. This may be shown in a heating curve, such as the one in Figure 2. The temperature plateaus at the melting and boiling points while the latent heat of fusion or vaporization is added, and only then continues to rise.

3 Entropy and the Second Law of Thermodynamics

In addition to enthalpy, we can define a quantity called *entropy* to describe a thermodynamic system. Although quantum theory allows us to determine an absolute entropy for a system, we most often deal with relative entropies. Even so, the change in entropy due to a transformation must be defined with calculus:

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

However, at constant temperatures, we can simplify this expression:

$$\Delta S = \frac{\Delta Q}{T}$$

where ΔQ is the amount of heat transferred to the system by a source at a constant temperature T . Entropy represents the multiplicity of the system, or intuitively, the number of degrees of freedom of the system. The second law of thermodynamics states that the entropy of an isolated system never decreases; in effect, an isolated system will always tend towards a state with maximal degrees of freedom. Thus, only transformations for with $\Delta S = 0$ are reversible.

Entropy, like enthalpy, is a state function, so that we can make calculations similar to those made with Hess's Law.

4 Free Energy and Spontaneity

In chemistry, we have many cases in which two states A and B can coexist, with no tendency for one to transform into the other. We call this a state of *equilibrium*. We now have the tools to define the thermodynamic condition for equilibrium. Consider a reversible transformation (that is, a transformation for with $\Delta S = 0$) from A to B, with no net change in pressure or temperature. Let the heat transferred to the system in the transformation be q_{rev} and the work performed upon it (not including pressure-volume work) be w_{rev} . The first law of thermodynamics states:

$$\Delta H = H_B - H_A = q_{\text{rev}} + w_{\text{rev}}$$

The entropy change of the surroundings is $-\frac{q_{\text{rev}}}{T}$, and that of the system is $S_B - S_A$. For the transformation to be reversible, the sum of these must be zero, allowing us to solve for q_{rev} :

$$\begin{aligned} -\frac{q_{\text{rev}}}{T} + S_B - S_A &= 0 \\ q_{\text{rev}} &= T(S_B - S_A) \end{aligned}$$

We can substitute this in our first equation to obtain:

$$w_{\text{rev}} = H_B - H_A - T(S_B - S_A)$$

We define a new quantity $G = H - TS$, so that:

$$w_{\text{rev}} = G_B - G_A$$

This new quantity G is called the *Gibbs free energy*. We see immediately that for $G_B = G_A$, no work accompanies the transformation from A to B, and so the two states can exist in equilibrium. If $G_A > G_B$, then the work is negative, which represents the system performing work on or releasing energy to the environment. In this scenario, A spontaneously transforms to B. Alternatively, if $G_B > G_A$, then B spontaneously transforms to A. In addition, the value of ΔG represents the amount of work necessary to cause a transformation (or, if it is negative, the maximum work that may be obtained by performing a transformation).

Using the concept of free energy, we can immediately determine whether a given reaction is spontaneous at a given temperature if we know its ΔH and ΔS values. For example, we can find the minimum temperature for which the reaction $\text{H}_2\text{O(s)} \longrightarrow \text{H}_2\text{O(l)}$ is spontaneous, given that the entropy of fusion for water is 22.0 J/mol K (and by converting the enthalpy of fusion for water to 6.0 kJ mol^{-1}). We simply let the change in free energy be less than zero:

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S < 0 \\ 6000 \text{ J mol}^{-1} - (22.0 \text{ J/mol K})T &< 0 \\ T &> 273 \text{ K}\end{aligned}$$

We see that we obtain the expected result: the melting of water is spontaneous only at temperatures above 273 K or 0°C .

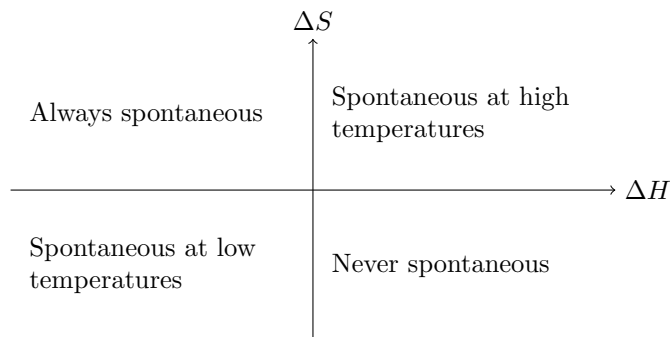
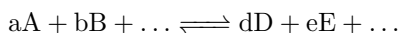


Figure 3: Four different types of reactions have differing relationships between ΔG and temperature.

The melting of water is a process which is spontaneous at higher temperatures, but becomes non-spontaneous at lower temperatures. This is because ΔH is positive, but ΔS is positive as well, so $\Delta G = \Delta H - T\Delta S$ is positive for $T = 0$ but becomes negative for $T > \frac{\Delta H}{\Delta S}$. However, if ΔH and ΔS have different signs, ΔG behaves differently with temperature. Figure 3 shows the behavior of four different classes of reactions based on the signs of their standard enthalpy and entropy changes.

5 The Thermodynamics of Equilibrium

Although we have developed the concept of free energy in relation to equilibrium, we still need a mathematical relationship between the two concepts. Specifically, we seek to determine how ΔG changes with the reaction quotient Q . We will consider the general equilibrium reaction:



We will consider all the reactants and products to be gases, although the derivation is similar for dissolved substances. From the definition of Gibbs free energy, we have that:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$dG = V dP$$

For an ideal gas, we can substitute for the molar volume V and integrate:

$$dG = RT \frac{dP}{P}$$

$$G_2 - G_1 = RT \ln \frac{P_2}{P_1}$$

Taking G_1 to be G° , so that $P_1 = 1$ atm, we have:

$$G = G^\circ + RT \ln P$$

With this relationship describing the variation in G with the pressure of a particular gas, we can derive a similar relationship for an entire reaction. We know that the change in free energy for the reaction is described by the difference of the free energies of the products and the reactants:

$$\Delta G = dG_D + eG_E + \dots - aG_A - bG_B - \dots$$

Substituting $G = G^\circ + RT \ln P$ for each gas, we have:

$$\begin{aligned} \Delta G &= d(G_D^\circ + RT \ln P_D) + e(G_E^\circ + RT \ln P_E) + \dots - a(G_A^\circ + RT \ln P_A) - b(G_B^\circ + RT \ln P_B) - \dots \\ &= (dG_D^\circ + eG_E^\circ + \dots - aG_A^\circ - bG_B^\circ - \dots) + RT \ln \frac{P_D^d P_E^e \dots}{P_A^a P_B^b \dots} \\ &= \Delta G^\circ + RT \ln Q \end{aligned}$$

This is our desired relationship between ΔG and Q . We can also derive a relationship between ΔG° and K by noting that at equilibrium, $\Delta G = 0$:

$$\Delta G^\circ = -RT \ln K$$