

Thermodynamics

The First Law of Thermodynamics

A system can be described by its total **internal energy**, U , which is the sum of the kinetic and potential energies of all the particles in the system. A process can then be described by the **change in internal energy**, ΔU . There are two ways a system can change the amount of internal energy. It can transfer heat (q) in or out, or it can do work (w) or have work done on it. The first law of thermodynamics states that the change in internal energy is the sum of the heat and the work.

$$\Delta U = q + w$$

Heats of reaction and Internal Energy

When a reaction takes place there may be heat exchanged with the surroundings. This heat can be measured using calorimetric techniques some of which we explored in Chemistry 101. But what about the work? How can we define work in terms of a chemical process? IF we think about a process that takes place inside of a cylinder fitted with a piston, we can see that the piston may move in or out depending on how the number of moles of gas changes during the process. If the piston moves out, because the number of moles of gas increases, the system is doing work on the surroundings. If the piston moves in, because of a decrease in the number of moles of gas, the surroundings do work on the system. Work is defined as a force moving through a distance:

$$w = F \times d$$

The force applied to the piston is the pressure (external) times the area of the piston:

$$w = P \times A \times d$$

The area of the piston times the distance it moves is the change in volume of the system:

$$w = P \times \Delta V$$

Now, we must consider what the signs are here. Remember that everything is from the system's point of view. If the system does work, that is a negative energy. Above, we saw that if the system does work the piston moves out, which increases the volume of the container. That means the ΔV is a positive quantity. In order for the work to be negative, there must be a negative sign present in the above formula:

$$w = -P\Delta V$$

Because we are looking at a system that is under a constant pressure, we can rewrite the formula for the change in internal energy as:

$$\Delta U = q_p - P\Delta V$$

In Chapter 6 we defined the heat at constant pressure as the change in enthalpy, ΔH . Now we can define the enthalpy more precisely as:

$$H = U + PV.$$

Note that this is not a change in enthalpy but an “absolute enthalpy.” We can find an expression for the change in enthalpy:

$$\Delta H = H_f - H_i = (U_f + PV_f) - (U_i + PV_i) = (U_f - U_i) + P(V_f - V_i) = \Delta U + P\Delta V$$

Substituting in for ΔU , we get:

$$\Delta H = q_p - P\Delta V + P\Delta V = q_p$$

which is the result we had in chapter 6. We can calculate the enthalpies of reaction as we did in chapter 6:

$$\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

From this and the balanced chemical equation we can calculate ΔU .

$$\Delta U = \Delta H - P\Delta V = \Delta H - \Delta nRT$$

The last step here is an application of the Ideal Gas Law. Δn is the change in the number of moles of gas in the balanced chemical equation. R is the ideal gas constant $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

The change in internal energy can also be directly measured. Remember that the heat transferred at constant pressure is the change in enthalpy of the reaction. If we measure the heat transferred at constant *volume* that is also the change in internal energy. This can be measured in a device called a bomb calorimeter. This is setup so that the reaction takes place in a steel bomb. The bomb is rigid so the volume does not change. The pressure in the bomb may change, however, depending on the stoichiometry of the reaction. Bomb calorimetry is useful for measuring the heats of combustion. Coffee-cup calorimetry and Hess' Law cannot generally determine the heat transferred by these reactions. From the change in internal energy we can determine the value of the change in enthalpy using the above equations.

$$\Delta H = \Delta U + \Delta nRT$$

where, again, Δn is the change in the number of moles of gas in the balanced chemical equation.

Entropy and the Second Law of Thermodynamics

Entropy is a measure of the amount of disorder in a system. More disorder means more entropy. If a process creates more disorder the entropy change of the process is positive. The **second law of thermodynamics** states: for any spontaneous process, the total entropy of the universe must increase. Entropy is different from energy. Energy can neither be created nor destroyed. But any spontaneous process creates entropy.

If heat flows into or out of a system, that will change the amount of entropy in the system. More heat involves more entropy. It can be shown that the amount of entropy associated with the heat flow is equal to the heat divided by the absolute temperature so the total entropy change is the entropy from the heat flow plus that created by the process:

$$\Delta S = \frac{q}{T} + \text{entropy created by the process}$$

The amount of entropy created cannot be directly measured but it is always positive. Therefore, we can show that:

$$\Delta S > \frac{q}{T}$$

for any spontaneous process.

This also gives us the units for entropy, J K^{-1} .

When a phase transition (equilibrium) occurs the changes are spontaneous, but they are also **reversible**. Reversible means just what it says. Any small change to a system at equilibrium can cause it to go in either direction. In this case the amount of entropy created by the process is very close to zero. This then gives:

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

for a process at equilibrium (reversible). For a phase change, q is equal to the heat of the phase change. ΔH_{fus} for melting and ΔH_{vap} for vaporization.

This gives us some insight into being able to calculate whether or not a process is spontaneous. For a spontaneous process we have:

$$\Delta S > \frac{q}{T} = \frac{\Delta H}{T}$$

$$\frac{\Delta H}{T} - \Delta S < 0$$

$$\Delta H - T\Delta S < 0$$

If the quantity $\Delta H - T\Delta S$ is negative then the process is spontaneous.

The Third Law of Thermodynamics

The **third law of thermodynamics** states that for a perfect crystalline substance at 0 K, there is no entropy. In other words, there is no disorder. We can then calculate an “absolute” entropy from this crystalline state. These entropies are tabulated in your book for substances at 298.15 K. These are the **standard entropies, S°** . These are for the standard states of the substances, 1 atm partial pressure and 1 M concentration. We can use these standard entropies to calculate the entropy change for a reaction:

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

We can also guess at the sign of the entropy change for a reaction. If more disorder is created, there will be a positive sign. Entropy increases are usually involved in:

- A reaction where one molecule is broken up
- A reaction where there is an increase in the number of moles of gas
- A process where a solid is changed into a gas or liquid, or a liquid changes into a gas.

Gibbs' Free Energy

The quantity used to determine spontaneity, $\Delta H - T\Delta S$, is called the **Gibbs' Free Energy change, ΔG** . The free energy change must be negative for a spontaneous process. The standard Gibbs' free energy change is given by:

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

where everything is in the standard state (1 atm partial pressure, 1 M concentration and 298.15 K). **Standard free energies of formation, ΔG_f°** , are tabulated in your book. The free energy change for a reaction can be calculate from the ΔG_f° 's by a similar equation to the other two:

$$\Delta G^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants})$$

To determine if a reaction is spontaneous, we need to calculate the change in the free energy at the conditions of the reaction. If this is under standard conditions then we can calculate ΔG° . If it isn't, we calculate ΔG , which can be calculated from ΔH° and ΔS° :

$$\Delta G = \Delta H^\circ - T\Delta S^\circ \quad \text{at a non-standard temperature}$$

If the pressures and concentrations are not standard this calculation is a little more complicated.

If we calculate ΔG and get a negative value, the reaction is spontaneous. If we get a positive value, the reaction is not spontaneous. If ΔG is zero the reaction is at equilibrium.

Interpretation of Free Energy

What do we mean by "Free Energy?" The simplest explanation is that the free energy is the amount of energy we can use to do useful work if there is no change in entropy. This gives us the relationship

$$w_{\max} = \Delta G$$

In reality, there is never a process that occurs without an entropy change. So there is never the maximum amount of work produced.

During the course of a reaction, the free energy for the reaction drops to some minimum value. How early this minimum value occurs determines the size and sign of the overall free energy change and, therefore, the equilibrium constant. If the minimum occurs early the free energy change is positive (a "non-spontaneous" reaction) and the equilibrium constant is small (less than one). If the minimum occurs later in the reaction the free energy change is negative (a "spontaneous" reaction) and the equilibrium constant is large (greater than one).

Free Energy Change and the Equilibrium Constant

We just saw that the change in free energy is related to the equilibrium constant. We can determine the mathematical relationship between these two by looking at the expression for ΔG under non-standard conditions:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the thermodynamic reaction quotient. In the thermodynamic reaction quotient, gases are expressed as their pressures in atmospheres and aqueous species are expressed as their molar concentrations. If we consider a reaction at equilibrium, ΔG is zero (see above) and Q is equal to K . This gives:

$$0 = \Delta G^\circ + RT \ln K$$

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

$$K = e^{-\Delta G^\circ / RT}$$

From an equilibrium constant we can determine free energy change and vice-versa.

Change in free energy with temperature

In order to calculate the change in free energy at a different temperature, we must make some approximations. The main one is that the enthalpy change and the entropy change do not change much with temperature. With this approximation we can show that:

$$\Delta G_T^\circ = \Delta H^\circ - T\Delta S^\circ$$

In this equation the ΔH° and ΔS° are the values at 25°C. This equation will give us a value for ΔG° at the *specified temperature*.

We can now explore the situations where the free energy change is always negative, always positive, or changes depending on temperature.

ΔH°	ΔS°	spontaneity
+	+	not at low T, spont at high T
+	-	never spontaneous
-	+	always spontaneous
-	-	spont at low T, not at high T