

## Chapter 1: The First Law

### *Introduction*

A discussion of thermodynamics typically begins with the first law of thermodynamics. In very simple terms, the first law is a conservation law. That is, the first law states that the energy of the universe is constant. In a thermodynamics context, energy, also referred to as internal energy, is symbolized by  $U$  or  $E$ . The quantity symbolized by  $U$  represents the sum of all kinetic and potential energy for a set of particles. As such, if we knew the current state (positions and momenta) of this set of particles, we could determine the internal energy of that collection of particles. This means that internal energy is a state function rather than a path function. A state function does not depend on the history of the system but only on the current configuration of a set of particles. Most, but not all, thermodynamic properties which we will discuss are state functions.

Another way of stating the first law is that any change in the energy of a system is balanced by an equal and opposite change in the energy of the surroundings. The system is that (small) portion of the universe under study while the remainder of the universe is defined to be the surroundings.

$$\Delta U_{\text{sys}} = -\Delta U_{\text{sur}} \quad (1)$$

This formulation of the first law is the most useful formulation in a laboratory setting. This is because, in the laboratory, we are typically interested in what is happening in only a very small portion of the universe (the system) rather than what is happening to the entire universe. Furthermore, it is often easier to measure an effect in the surroundings and then use the first law to deduce what is occurring in the system.

### *Heat and Work*

In addition to defining internal energy, the first law also defines the two mechanisms for transferring energy between the system and the surroundings; heat and work. At a macroscopic level, work is defined as the application of a force through a distance or the displacement of matter through a potential. Thus we can speak of gravitational work as the displacement of mass through a gravitational potential difference or electrical work as the movement of charge through an electrical potential difference, or chemical work as the movement of molecules through a chemical potential difference. Mathematically, the differential work can be represented as the dot product of two vector quantities (force and displacement).

$$dw = \vec{F} \cdot d\vec{l} \quad (2)$$

Since work is defined as a dot product, it will be a scalar rather than vector quantity. Thus work does not have a direction associated with it but is a signed quantity. The sign associated with an amount of work done is always determined in thermodynamics from the perspective of the system. If the internal energy of the system increases, then we say the surroundings did work on the system and  $w$  is positive. If the internal energy of the system decreases, we say that the system did work on the surroundings and  $w$  is negative.

An interesting feature of the common types of work is that in each case, differential work is calculated by multiplying an intensive quantity times the differential of an extensive quantity. An intensive quantity is a property of a system that is independent of the number of moles in the system while an extensive property is one which depends linearly on the number of moles. For instance, consider a system composed of liquid water. If we double the number of moles of water in a system, we will double the volume as well so that volume is an extensive property of the system. However, we can double the number of moles of water without changing the temperature at all thus temperature is an intensive quantity. Likewise, if we double the moles of water, we do not change the density of water; so density is intensive even though it is a ratio of two extensive quantities (mass and volume). The example of density illustrates a general principal. Any extensive property can be made intensive by reporting it on a per mole basis. So mass is extensive but molecular weight is intensive; volume is extensive but molar volume is intensive and kinetic energy is extensive but energy per mole is intensive.

The total work done is the path integral of equation 2. It is a path integral because the value of  $w$  depends not only on the state of the system at the beginning and end of the process but also on the path by which the system moves from the initial to final state. A common type of work is the work involved in expanding or compression a system containing a gas. The amount of work will be different if the volume is changed at constant pressure than if the volume is changed at constant temperature. Also the amount of work will depend on the whether the volume is changed from its initial value to its final value in one step or a series of smaller steps. Thus unlike internal energy for which we need to know only the initial and final states in order to calculate the change in energy, in order to calculate work, we must have knowledge of the path or process which connects the initial and final states.

The second mechanism of energy transfer between the system and surroundings is called heat and is given the symbol  $q$ . Heat is often correlated at a macroscopic level with a change in temperature of the system. However, it is important to recognize that there can be a transfer of heat between system and surroundings without a temperature change and that the same temperature change may represent different amounts of heat transfer depending on the path used. As with work, heat is a scalar quantity and the sign associated with heat identifies the direction of the energy transfer. If  $q$  is positive, the heat flow is into the system and the internal energy of the system increases. If  $q$  is negative, the heat flow is out of the system and the internal energy of the system decreases. Like work, heat is also a path function. We must specify the path taken to get from the initial to the final state in order to calculate the heat for a particular process. Thus if we change the temperature of the system while keeping the volume constant, the heat will be different than if we change the temperature by the same amount while keeping the pressure constant.

We can write the first law of thermodynamics for any process in terms of heat and work as

$$\Delta U = q + w \quad (3)$$

Note that we define the change in  $U$  (internal energy) but that  $q$  and  $w$  are never written with  $\Delta$  in

front of them. There is no such thing as a change in heat or a change in work since they are path functions. However, since  $U$  is a state function,  $\Delta U$  is a well defined concept;  $U$  of the final state minus  $U$  of the initial state. An odd feature of this formulation of the first law is that a change in a state function ( $U$ ) can be represented as a sum of path functions ( $q$  and  $w$ ). This tells us that for different paths, heat and work will be different but must change in complementary ways so that  $\Delta U$  always has the same value for the same initial and final states.

We can also describe heat and work from a microscopic perspective. We know that at a microscopic level, we can use quantum mechanics to describe a system of atoms or molecules. In quantum mechanics, particles are required to exist in allowed energy levels. Thus we would define a system by describing the number of particles in each of the allowed energy levels of the system. For this point of view, work occurs during any process which changes the allowed energy levels. A simple example of this would be a set of protons in an nmr tube which can be spin up or spin down (two allowed energy levels). When the nmr tube is placed in a magnetic field, the spacing between the two allowed energy levels changes and so from a thermodynamic point of view work was done during the act of placing the tube in the magnetic field. In contrast, at a microscopic level, heat occurs in any process which redistributes a set of particles among a set of allowed energy levels. So in our nmr example, if we use a radio pulse to excite a set of protons from the lower energy level to the higher energy level, this would be considered heat since, we are not changing the spacing between allowed energy levels, we are only changing the number of particles in each allowed level. In the general case, we can change both the allowed energy levels and the distribution of particles among the allowed levels and so from a thermodynamic perspective both heat and work can occur in a particular process.

### *Calculations of thermodynamic quantities for ideal gases*

We will now consider example calculations for the determination of heat, work and  $\Delta U$  for various processes. First we will consider a constant temperature (isothermal) expansion of a gas. The differential work is given by  $-PdV$ . In order to calculate the work, we merely need to integrate this differential from the initial to final volumes. The difficulty is that in the general case, pressure will be a function of volume and in order to evaluate the integral we must know how pressure changes with volume. In order to express this relationship, we will use an equation of state. An equation of state is a mathematical relationship between the intensive lab variables which describe the state of the system. The most well known equation of state is the ideal gas law. To proceed with our calculation, we will use the ideal gas law to substitute for pressure.

$$w = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1} \quad (4)$$

In evaluating this integral, we used the fact that we have a closed system ( $n$  is constant) and that the path is isothermal ( $T$  is constant). Based on this formula, if we double the volume of one mole of an ideal gas at 300 K, the work will be -1730 J. The negative sign reminds us that the system did work on the surroundings and that energy was leaving the system in the form of work. Now we have one of the three quantities defined by the first law. In order to evaluate  $\Delta U$  and  $q$ , we need additional information. In our example, we have used the ideal gas law. We can take

advantage of one additional characteristic of an ideal gas to further our calculations. An ideal gas possesses only kinetic energy and not potential energy. The kinetic energy depends on temperature since average velocity is higher at higher temperatures but does not depend on volume. Therefore, since we are considering an isothermal expansion,  $\Delta U$  will be zero and from the first law,  $q$  will equal  $+1730$  J in our example. That is heat will flow into the system to compensate for the energy leaving the system as work. A calculation of the thermodynamic properties for the compression of an ideal gas would work the same way except that the signs on  $w$  and  $q$  would be reversed.

Next we will consider a constant volume heating. If the volume is constant during the process there can be no expansion/compression work. If we are limiting ourselves to considering only PV work, then  $w$  is zero and by the first law  $q = \Delta U$ . In the general case, there will be non-PV work and so  $w$  is not automatically zero for every constant volume process. In order to calculate  $q$  and  $\Delta U$ , we need to know how internal energy changes with temperature and volume. We can express this dependence in terms of a total differential as shown in equation 5.

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (5)$$

A total differential is the sum of partial derivatives multiplied by the differential of an independent variable. There will be as many terms in the total differential as there are independent variables needed to describe the system. If we have a pure homogeneous system, we only need two independent variables to completely describe the state of the system. We have some flexibility in choosing which variables will be our independent variables. Because of the path we are examining, temperature and volume make a convenient set of independent variables. For a constant volume heating of an ideal gas, the second term drops out and the change in internal energy can be calculated by integrating equation 5.

$$\Delta U = \int_{T_1}^{T_2} \left( \frac{\partial U}{\partial T} \right)_V dT = \int_{T_1}^{T_2} C_V dT \quad (6)$$

Because the derivative of internal energy with respect to temperature occurs in so many different contexts in thermodynamics, it is given its own symbol ( $C_V$ ) and is referred to as the constant volume heat capacity of a substance. As a first derivative,  $C_V$  may be a constant, but is more often itself a function of temperature. As such, in order to evaluate the integral in equation 6, we will need to know how  $C_V$  for a particular system varies with temperature. As a simple example, we will consider the constant volume heating of an ideal noble gas with a constant heat capacity ( $C_V$ ) of  $12.5$  J/mol K. If 1 mole is heated from  $273$  K to  $373$  K,  $\Delta U$  is equal to  $1250$  J as is  $q$ .

Consider now, how the thermodynamic quantities will change if the heating is done at constant pressure rather than constant volume. In this case, there will be expansion work since the volume of the system will be changing.

$$w = - \int_{V_1}^{V_2} PdV = -P\Delta V \quad (7)$$

We will again consider heating 1 mol of an ideal gas from 273 to 373 K. This time the pressure will be fixed at 1.00 bar. From the ideal gas law, the initial volume is 22.7 L and the final volume is 31.0 Liters. Thus  $w$  for this process is  $-(1.00 \text{ bar}) \cdot (31.0 - 22.7 \text{ L}) = -830 \text{ J}$ . Notice that work is again negative because the system is expanding. How can we determine  $q$  and  $\Delta U$  in this example? One approach is to recognize that the initial state of the system was one mole of gas at 273 K and the final state was one mole at 373 K. These are the same initial and final conditions as in our previous example. Since  $U$  is a state function,  $\Delta U$  must be the same as in the previous example, because the initial and final temperatures are the same and  $U$  depends only on temperature for an ideal gas. Thus  $\Delta U$  is 1250 J and the heat transfer from the first law is  $1250 \text{ J} + 830 \text{ J} = 2080 \text{ J}$ .

There is a second approach we can use to calculate  $q$  in this example. We can use a mathematical tool called a Legendre transform to define a new thermodynamic function. We will start by considering a closed system with a single component and limit ourselves to PV work. Then the first law in differential format can be written as

$$dU = dq - PdV \quad (8)$$

Mathematically, from the definition of a total differential, equation 8 tells us that  $P$  is a first derivative of  $U$  and  $V$  is an independent variable. We can define a new function, enthalpy ( $H$ ) as

$$H = U + PV \quad (9)$$

We are using this transformation to convert from  $V$  as the independent variable to  $P$  as the independent variable. The transformation in independent variables will be more obvious if we consider the total differential of  $H$

$$dH = dU + PdV + VdP = dq - PdV + VdP + PdV = dq + VdP \quad (10)$$

Equation 10, leads to two immediate conclusions. First that while  $V$  is a “natural” independent variable for  $U$ ,  $P$  is a natural variable for  $H$ . Therefore,  $H$  will be the more useful and convenient thermodynamic function for any constant pressure path. Second, for a constant pressure path in which expansion or compression is the only type of work,  $dH$  will equal  $dq$  and  $\Delta H$  will equal  $q$ . We can also write the total differential for  $H$  in terms of lab variables. As before we have some flexibility in choosing our independent variables. Since we are examining a constant pressure process and using enthalpy it will be convenient to choose  $T$  and  $P$  as the independent variables

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP = C_p dT + \left( \frac{\partial H}{\partial P} \right)_T dP \quad (11)$$

The derivative of  $H$  with respect to  $T$  is seen in a wide variety of situations and so is given its own symbol ( $C_p$ ) and is referred to as the constant pressure heat capacity. For the constant pressure heating of an ideal gas, the second term in equation 11 drops out and we can evaluate  $H$  and thus  $q$  by integrating the first part of equation 11

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad (12)$$

As with the constant volume heat capacity,  $C_p$  is often a function of temperature itself in which case, we would need to know how  $C_p$  varies with temperature in order to evaluate the integral. The simplest case is if  $C_p$  is a constant. In all cases,  $C_p$  will be greater than  $C_v$ . This is because in a constant pressure heating, some of the energy entering the system as heat is leaving the system as expansion work and so more heat will have to be added in order to raise the temperature of the same system by one degree which is the practical definition of a heat capacity. Likewise in a constant pressure cooling, some of the energy leaving the system in the form of heat is being replaced by the work the surroundings are doing on the system by compressing the system. Thus more heat needs to leave the system to drop the temperature by one degree than in a constant volume cooling.

We have described how to calculate thermodynamic quantities for three common types of paths so far. There is one additional category of path to consider. This is an adiabatic path. Adiabatic means that there is no heat transfer between system and surroundings. In other words, we would describe the system as perfectly insulated. In this case,  $q$  is zero so  $\Delta U = w$ . We will focus on an adiabatic expansion or compression of an ideal gas. For an expansion, the system is doing work on the surroundings so energy is leaving the system in the form of work and is not being replaced by a heat flow since the path is adiabatic. Thus the temperature of the system must be decreasing. For an ideal gas, knowing the amount of temperature decrease is sufficient to determine,  $\Delta H$  and  $\Delta U$  and thus  $w$ . Consider the following example, one mole of an ideal gas is expanded adiabatically from 20.0 L to 40.0 L with a starting temperature of 373 K. If we can determine the final temperature it will be possible to evaluate all the thermodynamic functions. We start with the total differential of  $U$ .

$$d\bar{U} = dq - Pd\bar{V} \quad (13)$$

As before, we are restricting ourselves to PV work. The over-bar indicates that all quantities are defined on a per mole basis. That is they are intensive rather than extensive properties. We now apply the adiabatic constraint and the definition of an ideal gas to obtain

$$\bar{C}_v dT + \frac{RT}{\bar{V}} d\bar{V} = 0 \quad (14)$$

which can be rearranged and integrated to give the following relationship

$$\int_{T_1}^{T_2} \bar{C}_v \frac{dT}{T} = -R \int_{\bar{V}_1}^{\bar{V}_2} \frac{d\bar{V}}{\bar{V}} \quad \text{or} \quad \ln \frac{T_2}{T_1} = -\frac{R}{\bar{C}_v} \ln \frac{\bar{V}_2}{\bar{V}_1} \quad \text{or} \quad \frac{P_2 \bar{V}_2}{P_1 \bar{V}_1} = \left( \frac{\bar{V}_1}{\bar{V}_2} \right)^{R/\bar{C}_v} \quad (15)$$

We can make use of one last definition to simplify equation 15. We can define the ratio of  $C_p/C_v$  as  $\gamma$ . This will allow us to calculate the final pressure and from that the final temperature.

$$P_2 = P_1 \left( \frac{\bar{V}_1}{\bar{V}_2} \right)^\gamma \quad (16)$$

Once the final temperature is known,  $\Delta U$  and  $\Delta H$  can be determined using equations 6 and 12.

In our example, using the ideal gas law, the initial pressure is 1.55 bar. We will assume that  $\gamma$  is 5/3 which is appropriate for a noble gas. Using equation 16, the final pressure is 0.488 bar. The final temperature using the ideal gas law is 235 K. If the constant volume heat capacity is 12.47 J/mol K, then  $\Delta U$  is -1720 J and  $\Delta H$  is -2870 J. Since  $q$  is zero by definition for an adiabatic process,  $w$  is equal to  $-\Delta U$  by the first law and is -1720 J. The sign indicates that the system is doing work on the surroundings and energy is leaving the system which is consistent with the expansion and the temperature drop.

How can we extend these calculations to systems other than ideal gases? For each of the paths previously described, the starting point is the same as for the ideal gas. Thus to calculate work for an isothermal expansion, we would still integrate  $-PdV$ . The difference is that we would use an some other equation of state rather than the ideal gas law. As an example, consider the isothermal expansion of a van der Waals gas. In this case

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \quad \text{and thus}$$

$$w = -n \int_{\bar{V}_1}^{\bar{V}_2} \left( \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \right) d\bar{V} = -n \left( RT \ln \left( \frac{\bar{V}_2 - b}{\bar{V}_1 - b} \right) + a \left( \frac{1}{\bar{V}_2} - \frac{1}{\bar{V}_1} \right) \right) \quad (17)$$

Recall that in the van der Waals equation of state,  $a$  and  $b$  are molecule specific parameters. Unlike an ideal gas, the internal energy of a real gas depends on both temperature and volume. Thus, we would need to integrate both terms in equation 5. Likewise the enthalpy of a real gas depends on both temperature and pressure and so we would need to integrate both terms in equation 11. Once we have values for  $w$  and  $\Delta U$ , we can determine  $q$  by difference.

## Chapter 2: The Second Law

### *Entropy and Spontaneity*

In addition to calculating heat, work, and changes in internal energy, we would like to predict whether a particular process will be spontaneous. By spontaneous, we mean that it will occur without outside interference on the system. This suggests that we might be able to use  $\Delta U$  to determine if a process is spontaneous. Clearly, doing work on the system or having heat flow into the system from the surroundings would be considered to be outside interference. Therefore, we might think that any process for which  $\Delta U$  or  $\Delta H$  of the system is positive will be non-spontaneous while any process for which  $\Delta U$  or  $\Delta H$  of the system is negative will be spontaneous. Unfortunately, this hypothesis is not born out by experience. Many processes for which  $\Delta U$  and  $\Delta H$  of the system are positive are spontaneous and likewise many examples exist of processes for which  $\Delta U$  and  $\Delta H$  of the system are negative but the process is non-spontaneous. The most familiar examples of this are phase transitions. Freezing of water is exothermic yet at room temperature it is not spontaneous. Likewise vaporization of water is endothermic and yet at 400 K it is spontaneous. Thus if we want a general criterion for spontaneity, we must look to some other thermodynamic state function and not rely on internal energy or enthalpy as our guide.

In the course of the 19<sup>th</sup> century, the study of steam engines from a thermodynamic perspective was a very hot topic. Engineers and scientists were trying to understand what factors influence the efficiency of an engine. In other words, how could you get the most work out from the combustion of a fixed amount of fuel? The work of Carnot and Clapeyron and others led to the definition of a new thermodynamic function; entropy (S). As a differential quantity, entropy is defined as

$$dS = \frac{dq_{rev}}{T} \quad (1)$$

Notice that entropy change is defined in terms of heat. The subscript *rev* stands for reversible. Since heat is a path function, the amount of heat flow will depend on the path chosen. We can calculate entropy changes from heat only for a specific category of paths. In the thermodynamic sense, reversible means that the system is in equilibrium with the surroundings all throughout the process. For example in the reversible compression of a gas, the pressure of the gas in the system is always equal to the external pressure in the surroundings. We can also define a reversible process as one which occurs infinitely slowly or requires an infinite number of steps to complete. From this definition, we can see that a reversible process is an ideal limit to any real process since a real process can not take an infinite amount of time to complete.

We can also define a reversible path by the amount of work done on the path. Consider the expansion of an ideal gas at 300 K from 1.0 liters to 11.0 liters in a single step against an opposing pressure of 1.00 bar. Then the work done in this irreversible process is  $-(11-1 \text{ liter}) \cdot 1.00 \text{ bar}$  or  $-10 \text{ Liter} \cdot \text{bar}$  which is equivalent to  $-1000 \text{ Joules}$ . Notice the negative sign which tells us that the system is doing work on the surroundings. Now assume that we do the expansion in two steps. In the first step, the opposing pressure is 2.0 bar and the ending volume is 5.5 liters. In the second step, the opposing pressure is 1.0 bar and the final volume is again 11.0 liters. The work is given by  $-(5.5 - 1 \text{ liters}) \cdot 2.00 \text{ bar} + -(11 - 5.5 \text{ liters}) \cdot 1.00 \text{ bar}$  which equals  $-14.5 \text{ liter} \cdot \text{bar}$  or  $-1450 \text{ J}$ . Notice that with more steps, the system can do more on the surroundings. This suggests that the maximum work that the system can do on the surroundings is obtained from a process that takes an infinite number of steps. In other words, the maximum amount of work is obtained from a reversible process. To calculate the reversible work, we replace our sum of steps with an integral.

$$w_{rev} = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \left( \frac{V_2}{V_1} \right) \quad (2)$$

In our example this would be equal to  $-2640 \text{ J}$ . Since by all the paths we have described in the preceding paragraph, we have moved from the same initial state to the same final state,  $U$  would be the same for all the different paths. Thus if for this expansion,  $w$  has its most negative value for the reversible path, then  $q$  will have its largest possible positive value. By a similar line of reasoning, we can show that for a compression of a gas, the reversible path will require the minimum amount of work into the system. This means that the reversible compression will have the smallest magnitude of heat transfer to the surroundings.

We know that heat is a path function, but what about entropy? Since it is calculated using heat it might be reasonable to assume that entropy is also a path function. However, the first law indicates that changes in state functions can be calculated using path functions. It turns out that this is also the case for entropy which is a state function. In mathematical terms, we can say that the reciprocal of temperature is an integrating factor which converts an inexact differential ( $dq$ ) into an exact differential  $dS$ . All thermodynamic state functions have exact differentials while path functions have inexact differentials. A necessary characteristic of an exact differential is that the mixed second derivatives are equal. As an example consider the total differential for  $P$  in terms of  $T$  and  $V$ .

$$dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV \quad (3)$$

If  $P$  is a state function then

$$\frac{\partial}{\partial V} \left( \frac{\partial P}{\partial T} \right)_V = \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial V} \right)_T \quad (4)$$

If we evaluate these derivatives using the ideal gas law, we find that both mixed second derivatives are equal to  $-nR/V^2$ . Likewise if we use the van der Waals equation, we find that both mixed second derivatives are equal to  $-R/(V-b)^2$ . This example demonstrates that pressure is a state function. Likewise as we will see the mixed second derivatives of entropy are also equal.

A second necessary condition for any state function is that the cyclic integral be equal to zero. A cyclic path is a path that takes the system in a series of steps back to the starting state. Consider what is referred to as the Carnot cycle. This is a reversible four step process consisting of an isothermal expansion at high temperature, an adiabatic expansion, an isothermal compression at low temperature and an adiabatic compression. Since steps two and four are adiabatic, they do not contribute to  $q$ . Since they are reversible, they do not contribute to  $S$ . The total heat for the cycle is

$$q = nRT_{hot} \ln \left( \frac{V_2}{V_1} \right) + nRT_{cold} \ln \left( \frac{V_4}{V_3} \right) \quad \text{Or} \quad q = nR(T_{hot} - T_{cold}) \ln \left( \frac{V_2}{V_1} \right) \quad (5)$$

To obtain the second equality in equation 5, we used the relationship between temperature and volume for an adiabatic expansion or compression. Notice for this cycle,  $q$  is positive meaning that the net heat flow is into the system. Notice also that  $q$  for the cycle is not zero which again demonstrates the  $q$  is a path function. What about  $S$ . From equation 1, we can say that

$$\Delta S = \frac{q_{hot}}{T_{hot}} + \frac{q_{cold}}{T_{cold}} = nR \ln \left( \frac{V_2}{V_1} \right) + nR \ln \left( \frac{V_4}{V_3} \right) = 0 \quad (6)$$

Although our derivation used an ideal gas, the conclusion that for any cycle  $S$  must be zero is actually valid no matter what substance the system is composed of. Clausius and others used proofs related to the efficiency of engines to demonstrate that for any reversible (equilibrium) process occurring in an isolated system,  $S$  must be zero and that for any irreversible (spontaneous) process in an isolated  $S$  must be positive. These statements form the basis of the

2<sup>nd</sup> law of thermodynamics. Since the universe can be considered an isolated system. The second law is often phrased as “The entropy of the universe increases in any spontaneous process”.

We will use the vaporization of water to demonstrate the second law in action. First we will consider the vaporization of water at 373 K, the normal boiling point. Normal boiling is defined as taking place at constant pressure of one atmosphere and so heat for the system is equal to  $H$ . The enthalpy of vaporization for one mole of water is 40.656 kJ. Notice that the process is endothermic since interactions between molecules are being disrupted. The path is isothermal and so  $S_{\text{system}}$  is equal to  $H/T$  or 0.1089 kJ/K. What about  $S$  for the surroundings? For the surroundings,  $q$  is equal to -40.656 K. Since the surroundings are also at 373 K,  $S_{\text{surr}}$  is equal to -0.1089 kJ/mol and the entropy change for the universe is zero which is required for a reversible process. What if the water is vaporized at 383 K. This is clearly a spontaneous process according to our everyday experience.  $S$  for the surroundings is now -40.656/383 or -0.1061 kJ/K. For the system, we must construct an equivalent reversible path so that reversible heat can be determined and used to calculate  $S$ . We first reversibly cool the water to 373 K. Then the water is vaporized reversible, and finally the vapor is heated reversibly to 383 K. We add the entropy change for each of the three steps and obtain an  $S$  of 0.1077 kJ/K. Thus the entropy change for the universe is 1.6 J/K and is positive as required. What if we consider vaporization at 363 K where it should be non-spontaneous.  $S$  for the surroundings is now -112.0 J/K. For the system,  $S$  is now 110.0 J/K and the entropy change for the universe is -2.0 J/K as required by the 2<sup>nd</sup> law for a non-spontaneous process.

Although the second law provides an unambiguous, universally applicable method for determining whether any particular process will be spontaneous, it suffers from the limitation that it is a property of the universe rather than of the system that is used to decide spontaneity. It will be convenient to define additional state functions which will provide criteria for spontaneity based just on the system. We will limit ourselves to processes occurring at a fixed temperature and assume that the system and surroundings are in thermal equilibrium. In other words that the temperature of the surroundings is the same as the temperature of the system. From the second law, we can say that

$$dS_{\text{universe}} = dS_{\text{system}} + dS_{\text{surr}} \geq 0 \quad (7)$$

The volume of the surroundings can be considered as essentially constant even if the volume of the system is changing because of the vast size of the surroundings. Therefore,  $dq$  for the surroundings is equal to  $dU$  for the surroundings. Since  $U$  is a state function,  $dU$  must have the same value regardless of path. So we can say that  $dq$  for the surroundings must correspond to a reversible path from the perspective of the surroundings regardless of what is happening in the system. Thus we can replace  $dS_{\text{surr}}$  with  $dq_{\text{surr}}/T$ . From the first law, we know that  $dq_{\text{system}}$  is equal to  $-dq_{\text{surr}}$  and so we obtain the following as a criterion for spontaneity

$$dS - \frac{dq}{T} \geq 0 \quad \text{or} \quad dq - TdS \leq 0 \quad (8)$$

We have dropped the subscripts since all quantities now refer to the system. To proceed further,

we apply additional constraints. There are two possibilities. First the process of interest may be occurring at constant volume. Then  $dq$  is equal to  $dU$  and we obtain

$$dU - TdS \leq 0 \quad \text{or} \quad \Delta U - T\Delta S \leq 0 \quad (9)$$

The second possibility is that the process is occurring at constant pressure then  $dq$  is equal to  $dH$  and we see that

$$dH - TdS \leq 0 \quad \text{or} \quad \Delta H - T\Delta S \leq 0 \quad (10)$$

Notice that our expressions contain only state functions. This means that these combinations must also be state functions. This function based on equation 9 is called the Helmholtz function and is given the symbol  $A$ .

$$A = U - TS \quad \text{or} \quad \Delta A = \Delta U - T\Delta S \quad (11)$$

Notice that  $A$  is another Legendre transform of  $U$  using the terminology previously used when defining  $H$ . According to equation 9,  $A$  must be negative for any spontaneous process occurring under conditions of constant temperature and volume and is zero for any process at equilibrium under those same constraints. Based on equation 10, we can define the Gibbs function as a Legendre transform of enthalpy

$$G = H - TS \quad \text{or} \quad \Delta G = \Delta H - T\Delta S \quad (12)$$

Our criteria for spontaneity for any process occurring at constant temperature and pressure is that  $dG$  or  $G$  for the system must be negative. The criteria for equilibrium is then that  $dG$  or  $G$  must equal zero. Because chemical reactions and phase equilibria are often studied under conditions of fixed temperature and pressure, the Gibbs function will be the most common criteria for spontaneity.

We can also relate the Helmholtz function and Gibbs function to the amount of work available from a particular isothermal path. We begin by noting that  $A = U - TS$ . Then we use the first law to obtain

$$dA = dU - TdS = dq + dw - TdS = TdS + dw - TdS = dw \quad (12a)$$

This derivation required that the path be reversible so that  $dq$  could be substituted by  $TdS$ . If the process is spontaneous  $dA$  is negative as is  $dw$  and so  $A$  represents the amount of reversible work that the system can do on the surroundings for the process under study. Thus the Helmholtz function is often referred to as the work or Arbeit function; hence the symbol  $A$  for the function. Arbeit is the German word for work. We can perform a similar derivation for the Gibbs function as follows

$$dG = dH - TdS = dU + PdV - TdS = dq + dw + PdV - TdS \quad (12c)$$

This differential assumed constant temperature and constant pressure for the path. If we further restrict ourselves to a reversible path,  $dq$  and  $TdS$  will cancel out to leave

$$dG = dw + PdV = dw' - PdV + PdV = dw' \quad (12d)$$

In this expression, we have separated work into two categories PV work and all non-PV work ( $dw'$ ). From our derivation, we see that for an isothermal isobaric reversible process,  $G$  is equal to the amount of non expansion/compression work that the system can do on the surroundings. In other words,  $G$  is the portion of the energy change that is free (available) to do work on the surroundings. This is why  $G$  is often referred to as the free energy change. By non-PV work, we are usually referring to electrical work (batteries) or chemical work (hydrolysis of ATP for

example).

### Chapter 3: Thermodynamics and Calculus

We can summarize our discussion of thermodynamic quantities using what are sometimes referred to as the four fundamental equations of thermodynamics. We will start by focusing on closed systems in which only reversible PV work is occurring. Then we can write the first law as

$$dU = TdS - PdV \quad (13)$$

In this form, volume and entropy appear as natural variables of U. Temperature and pressure can then be recognized as first derivatives of U

$$T = \left( \frac{\partial U}{\partial S} \right)_V \quad \text{and} \quad -P = \left( \frac{\partial U}{\partial V} \right)_S \quad (14)$$

From equations 13 and 14, we can make a general statement about a closed system composed of any substance. Since pressure must be a positive quantity, the derivative of internal energy with respect to volume at constant S is always negative. That is increasing the volume lowers the internal energy for adiabatic paths. Since the system must do work on the surroundings in order to increase the volume, and since we have restricted our consideration to paths with no heat flow (constant S), the internal energy must decrease.

Since internal energy is a state function, we can say that the mixed second derivatives must be equal. In thermodynamics, we refer to this type of relationship as a Maxwell relationship in honor of the British scientist James Clerk Maxwell.

$$\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right) = \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right) \quad \text{or} \quad \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \quad (15)$$

The second of the fundamental relationships is for the enthalpy

$$dH = TdS + VdP \quad (16)$$

For enthalpy we see that entropy and pressure are the natural variables. From equation 16, we can obtain a second Maxwell relationship

$$\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \quad (17)$$

The final two equations are for the Helmholtz function and Gibbs function in closed systems

$$dA = -SdT - PdV \quad \text{and} \quad dG = -SdT + VdP \quad (18)$$

For the Helmholtz function, the natural variables are temperature and volume while for the Gibbs function the natural variables are temperature and pressure. The fact that for these two functions the natural variables are typical lab variables explains the special utility of these two functions. Since much chemistry is performed under conditions of constant temperature and pressure, the Gibbs function is particularly useful. From equations 18, we obtain two additional Maxwell relationships.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{and} \quad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad (19)$$

Based on equation 18, we can make a couple of statements about the Gibbs function for any substance in a closed system. If the pressure increases at constant temperature, the Gibbs function must also increase. This is because the first derivative of the Gibbs function with respect to pressure is volume which must have a positive value. So we can say for any gas that the Gibbs function at 2 bar will be larger than the Gibbs function at 1 bar. Furthermore since volume usually decreases as pressure increases, we can say that the higher the pressure, the smaller the effect on the Gibbs function. By similar reasoning, we can say that for all substances, the Gibbs function decreases as temperature increases. Absolute entropies are always non-negative and so the slope of a plot of Gibbs function versus temperature will always be negative. Furthermore, since absolute entropy always increases with temperature, the slope of a plot of Gibbs function versus temperature will be steeper at higher temperatures.

The Gibbs function like the Helmholtz function is an extensive function. As we noted previously, it is preferable to work with intrinsic functions rather than extensive functions. Thus it will be helpful to define a new quantity, chemical potential ( $\mu$ ), also called the partial molar free energy. For a homogeneous pure system, the chemical potential is simply  $G/n$ . In the more general case of multiple components in an open system the chemical potential is defined as

$$\mu = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}} \quad (20)$$

For a system of multiple components, we can re-write the Maxwell relationships in terms of partial molar quantities

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_{P, n_i} = -\left(\frac{\partial \bar{S}}{\partial P}\right)_{T, n_i} \quad (21)$$

We can also write the total Gibbs function for any mixture as a sum of contribution of the different chemical potentials.

$$G = \sum_i \mu_i n_i \quad (22)$$

We will now derive an expression for the chemical potential of an arbitrary pure substance as a function of either temperature or pressure. First let us consider pressure as the independent variable with temperature being held constant. Based on the total differential of  $G$  or  $\mu$  we can write down an integral relationship

$$\int_{\mu^0}^{\mu} d\mu = \int_{P^0}^P \bar{V} dP \quad (23a)$$

In this expression, the naught superscript indicates a standard state; usually 1 bar. For a solid or liquid, we can often approximate density or molar volume as independent of pressure which makes the integral easy to evaluate

$$\mu - \mu^0 = \bar{V}(P - 1) \quad \text{or} \quad \mu = \mu^0 + \bar{V}(P - 1) \quad (23b)$$

notice that chemical potential is usually tabulated with units of J or kJ per mol while the second term in equation 23b has units of L-bar/mol. Thus in performing any calculations, you must watch the units carefully. Since densities or molar volumes must be positive, equation 23b indicates that chemical potential must increase as pressure increases for all liquids and solids. Furthermore, since the molar volume of a typical liquid or solid is small ( a few mL per mole), the chemical potential will change very slowly with pressure. The evaluation of equation 23a is slightly more complicated for a gas because molar volume will change dramatically with pressure for a gas rather than being nearly constant. To proceed, we must use an equation of state to express volume as a function of pressure. The simplest possibility for an equation of state is the ideal gas law. Then equation 23a becomes

$$\mu = \mu^0 + \int_{P^0}^P \frac{RT}{P} dP \quad \text{or} \quad \mu = \mu^0 + RT \ln \left( \frac{P}{P^0} \right) = \mu^0 + RT \ln \left( \frac{P}{1 \text{ bar}} \right) = \mu^0 + RT \ln P \quad (24)$$

The final version is the most commonly used form. If you see the equation with this form, you want to remember that the denominator of 1 bar is implied even if it is not written out so that P must also have units of bar.

How would chemical potential change with temperature under conditions of fixed pressure? Again we start with the total differential in an integral form

$$\int_{\mu^0}^{\mu} d\mu = - \int_{298}^T \bar{S} dT \quad (25a)$$

As before the naught superscript refers to a standard state which is often taken to be 298 K. To evaluate this expression, we need absolute entropy as a function of temperature. If heat capacity is a constant which can be a poor assumption, this expression can be written as

$$\mu = \mu^0 - \bar{S}^0(T - 298) - \bar{C}_p T \ln \frac{T}{298} + \bar{C}_p(T - 298) \quad (25b)$$

Notice that as T increases above 298 K, chemical potential decreases because absolute entropies and heat capacities are always positive. Also since the absolute entropy of a gas is much larger than the corresponding liquid or solid, the drop is most dramatic for gases. For all three phases, the temperature dependence is more pronounced than the pressure dependence because of the magnitude of the absolute entropy at 298 K.

We can generalize equation 24 in the following manner. If the gas under study is non-ideal, then the actual chemical potential will be different than the ideal gas law prediction. The actual chemical potential may be either somewhat larger or smaller than the ideal gas prediction depending on the gas under study and the exact pressure of the gas. We will define a new quantity called the fugacity (f) and then re-cast equation 24 as

$$\mu = \mu^0 + RT \ln f = \mu^0 + RT \ln \gamma P \quad (26)$$

where  $\gamma$  is called the fugacity coefficient and can be slightly greater than or less than one. We

can use the virial equation (or other equations of state) to calculate the fugacity coefficient and thus the fugacity using the following relationship.

$$\ln \gamma = \int_0^P \frac{Z - 1}{P} dP \quad (27)$$

In this expression  $Z$  is the compressibility of a gas as defined in the virial equation. We can see that if  $Z$  is greater than one, the fugacity coefficient will also be greater than one and if  $Z$  is less than one, then the fugacity coefficient will be less than one.

We can extend the concept of non-ideal behavior to the condensed phase by defining a quantity called the activity which will be analogous to fugacity. For a pure solid or liquid, we can define the activity so that

$$\mu = \mu^0 + RT \ln a \quad (28)$$

By definition the activity of any pure liquid or solid is one in the standard state. However, if the substance is at a substantially different pressure or temperature the activity will be different from one. In order to calculate the activity under non-standard conditions, we combine equation 28 with either equation 23 or 25. If we are interested in the pressure dependence, we obtain the following approximate expression

$$\ln a = \frac{\bar{V}}{RT} (P - 1) \quad (29)$$

Consider liquid water at 298 K and 10 bar with a molar volume of 18 mL/mol. Then by equation 29, the activity of water at 10 bar is 1.007 which is barely different from the reference value of 1 at one bar and corresponds to a change in chemical potential on the order of 17 J/mol which is small compared to the value of the chemical potential itself.

#### Chapter 4: Mixtures

Although activity can be used to understand the behavior of pure liquids and solids at high pressure or non-standard temperatures, the real utility of the concept is seen when describing the properties of a mixture of substances. In a solution, we can define the activity of each component as an activity coefficient multiplied by a concentration. The chemical potential of a substance in a mixture is then given by

$$\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln \gamma_i x_i \quad (30)$$

In equation 30, we have used mole fraction ( $x$ ) as the concentration variable. This is the preferred choice of concentration units when mixing two or more liquids and for the solvent when solids are dissolved in liquids. The reference chemical potential is then the pure liquid and the activity coefficient must equal one if the pure liquid is at 298 K and 1 bar. The activity coefficient is represented by the symbol  $\gamma_i$ . The activity coefficient can be either greater or less than one and its value will depend on the identity and concentration of all the various species in solution.

An important point to remember is that the thermodynamic properties of solute and

solvent can not vary independently but must vary in a coordinated way. The mathematical representation of this interrelatedness is called a Gibbs-Duhem relationship.

$$d\mu_2 = -\frac{x_1}{x_2} d\mu_1 \quad \text{Or} \quad d\bar{V}_2 = -\frac{n_1}{n_2} d\bar{V}_1 \quad \text{or} \quad d\ln a_2 = -\frac{x_1}{x_2} d\ln a_1$$

If the chemical potential or molar volume or activity of component one is increasing then the corresponding property for component 2 must be decreasing. We will use this concept when we discuss linkage relationships for receptors that bind more than one ligand.