CHAPTER TEN
THE Chemical Potential

Introduction

The first law of thermodynamics is simply a statement of the conservation of energy for systems in which
energy can be exchanged: 1) thermally, 2) mechanically, or 3) through the gain or loss of particles (diffusion, or
mixing). We treated the first two cases earlier in our brief review of thermodynamic concepts. In this chapter we
will look at changes to the first law which arise from the interaction of particles with one another in a system, and
in particular when we allow different particles to be added to our system (a diffusive interaction). We will then
use what we have learned thus far to rewrite the first law in terms of state variables only.

The Internal Energy of Gas with Intermolecular Forces

The classical equipartition theorem states that, for a system in equilibrium, the average energy per particle,
\( \langle E \rangle \), is given by

\[
\langle E \rangle = \frac{1}{2} kT \times \text{# of degrees of freedom for the particle}
\]

where a “degree of freedom” is defined as a quadratic term in the total energy expression for the particle. As an
example, consider a diatomic molecule which can move in three-dimensions, can rotate about three different axes
of rotation, and can vibrate along the internuclear axis of the molecule. The total energy of this molecule is given
by

\[
E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}}
\]

\[
E = \left\{ \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \right\} + \left\{ \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z} \right\} + \left\{ \frac{1}{2} \mu \ddot{r}^2 + \frac{1}{2} \kappa r^2 \right\}
\]

where \( m \) is the mass of the molecule and \( \mu \) is the reduced mass of the molecule. This molecule has 8 degrees of
freedom. Thus the classical equipartition theorem would imply that the average internal energy of a single non-
interacting molecule would be \( \frac{5}{2} kT \). This is actually incorrect, however, because the “turn-on” temperature for
one of the degrees of freedom (rotation about the internuclear axis) is much too high for this degree of freedom
ever to be activated (the molecule would dissociate before this temperature is ever reached). The existence of a
“turn-on” temperature is a purely quantum mechanical effect which we will discuss later. If we take this
“quantum” effect into consideration, the average energy for a single diatomic molecule must be \( \frac{7}{2} kT \). For an
“ideal” diatomic system the individual molecules do not interact with each other (i.e., there is no potential energy
of interaction, or the intermolecular distances are so large that the interaction is essentially negligible). Thus the
average total internal energy of the system is just the sum of the energy for each individual molecule. The total
internal energy of \( N \) such diatomic molecules in a volume \( V \) is, therefore,

\[
E = \frac{7}{2} N kT
\]

Notice that this discussion of the internal energy of a system suggests that the total energy is distributed equally
among all the possible degrees of freedom. This is consistent with our a priori assumption that all the possible
states of the system are equally likely.

Now if the individual molecules actually do interact with one another (i.e., if the gas is not “ideal”), the
internal energy of the system is complicated by the fact that the potential energy of interaction will depend
somewhat on the density of the gas (i.e., the closer together the particles are, on average, the greater the
interaction and the larger the average contribution of the potential energy term). To illustrate this, consider Fig.
10.1 which is a schematic of the potential energy of interaction of a particle and its nearest neighbor. In this
illustration we assume an attractive potential similar to a Leonard-Jones 6-12 potential (i.e., where
\[ V(r) = \frac{1}{r^6} - \frac{1}{r^3} \] which appears to be approximately correct for induced dipole - dipole attractions. The potential energy is plotted on the vertical axis, and the average intermolecular separation is plotted on the horizontal axis.

Now if the molecules are very far apart on average, the potential energy of interaction is approximately zero, so that the gas is essentially an “ideal” gas. If the number of particles in a given volume, however, were to increase, or if the available volume were to decrease, the average separation of the particles would change (decreasing in this case) and the average potential energy of interaction would also change. Thus, we would expect there to be a particular value for the average potential energy of interaction between all the particles of the system for a particular temperature, pressure and volume of the system, i.e., for a given state of the system. But when the state of the system changes, the average interaction potential may also change. This change in average interaction potential is a change in the internal energy of the gas.

We have already shown that the first law of thermodynamics expressed in the equation

\[ dE = dQ - \delta W \tag{10.5} \]

is simply a “bookkeeping” tool for keeping up with the energy of the system. This equation reflects our conviction that energy is neither created or destroyed, but simply transferred from one form to another. The significance of this equation is the fact that heat energy and mechanical energy are considered on an equal footing. The question we are now faced with, however, is this: How do we keep up with the fact that the average potential energy of interaction between the various molecules of the system explicitly depends upon the state of the system?

For the ideal gas, we took the total internal energy of the system to be just the kinetic energy of monatomic molecules, since we assumed that there was no interaction between the particles of the system. This is the same thing as taking the internal energy of the system to be the kinetic energy of the system plus zero potential energy. Thus, the first law equation expresses the average total energy of the system relative to some arbitrary reference point to which we assigned zero potential energy.

As an example of this consider our typical assumption when working mechanics problems. The floor of the room is quite often chosen as our reference point and assigned a gravitational potential energy of zero. In this case, we might write the total energy, \( \mathcal{E} \), of a rubber ball a distance \( h \) above the floor using the equation

\[ \mathcal{E}_1 = \frac{1}{2}mv_1^2 + mgh \tag{10.6} \]

where the potential energy \( U = mgh \). However, if the floor of the room is on the second floor of the building (a distance \( D \) above the ground), and there is an open window (or a hole in the floor), it may be easier to measure the potential energy relative to the ground, rather than relative to the floor. For, if the ball were to pass out of the room (through the window, or through the hole in the floor), the total energy of the ball when it strikes the ground would be given by

\[ \mathcal{E}_2 = \frac{1}{2}mv_2^2 + mg(-D) \tag{10.7} \]

If the total energy of the system is conserved, so that \( \mathcal{E}_1 = \mathcal{E}_2 \), we can determine the kinetic energy of the particle just before hitting the ground using the equation:

\[ \mathcal{E}_1 = \mathcal{E}_2 \tag{10.8} \]

or, rearranging terms,

\[ \frac{1}{2}mv_1^2 = \frac{1}{2}mv_2^2 + mg(h + D) \tag{10.9} \]

We could just as easily have called the potential energy zero at ground level, and we would have obtained the same result! Defining the potential energy to be zero at either point will do, since only changes in the potential energy are important.

But what if you were in an elevator, where your “floor” level might change in time and be sometimes higher than ground level, and sometimes lower than ground level? You would obviously just pick the ground level to be your reference point, since this point is always “fixed”. The only time a problem arises is when there is no simple “fixed” point to choose as the reference point. This is just what happens when we try to define an appropriate zero potential energy point for a system of interacting particles. Since the particles do interact with each other,
the potential energy of the system changes as the system parameters change. The problem is finding an appropriate zero point for our potential energy.

The potential energy arising from the interaction of one molecule with another is shown below for the case where the force between two particles is attractive (Fig. 10.1) and for the case where the force between the two particles is repulsive (Fig. 10.2).

![Fig. 10.1. The potential energy of interaction for two molecules as a function of the molecular separation \( r \) is shown for the case of an attractive force. In a volume of gas, there will be some average separation of the molecules, which has been denoted as \( \langle r \rangle \). The average interaction potential energy is therefore negative. The average energy \( E \) and the average kinetic energy are also labeled.]

To define a zero point for the potential energy of a system, we generally measure the average total energy of a system of particles relative to the average ground state energy (rather than measuring relative to the zero energy point for the single particle interaction energy). This effectively means that the average total energy is set equal to the average kinetic energy of the molecules (the average potential energy is taken to be zero). Now, for the case of an attractive force acting between the particles, if more and more particles are added to the system, the average intermolecular distance between the particles \( \langle r \rangle \) decreases, so that the average ground state energy per particle is lowered. This means that the average kinetic energy per particle must increase! If we are measuring the average total energy relative to the ground state energy, the average kinetic energy and the average total energy must be the same so we write this as an increase in the total energy of the system. This means that the total energy of the system must increase with number of particles according to the equation

\[
dE = \mu \, dN
\]

where \( \mu \) is called the chemical potential and is positive for attractive systems.

For the case where the molecules experience a net repulsive force, an increase in the number of molecules would again decrease the average distance between the molecules, but the average kinetic energy would decrease. Again, if we measure the average total energy of our system relative to the average ground state energy, we can still represent the change in the energy of the system by the expression

\[
dE = \mu \, dN
\]

provided we now take \( \mu \) to be negative for repulsive potentials.
Fig. 8.2. The potential energy of interaction for two molecules as a function of the molecular separation \( r \) is shown for the case of a repulsive force. In a volume of gas, there will be some average separation of the molecules, which has been denoted as \( \langle r \rangle \). The average interaction potential energy is therefore positive. The average energy \( E \) and the average kinetic energy are also labeled.

From what we have just discussed, it should be obvious that the average ground state energy (which we will designate as \( U \)) is a function of the average intermolecular spacing (or the number of particles, the volume, the temperature, etc.) and the intermolecular potential energy. For an ideal gas, we assume that there are no intermolecular forces, except when the particles actually collide. In that case the potential energy of interaction is zero and the internal energy is a function only of the temperature (the average kinetic energy) of the molecules, and not of the intermolecular spacing. You might expect that the chemical potential in this case must be zero. This is not the case, however. The total energy of the system depends upon the total number of particles making up the system, even if the particles are non-interactive. In fact, the chemical potential is a function of the number of particles, the temperature, and the volume of an ideal gas, as we will demonstrate later in this chapter.

The average ground state energy for a non-ideal gas, however, depends upon the average intermolecular spacing of the molecules. This average spacing can be changed by changing such system parameters as the volume or the number of molecules in the enclosed volume. Our task in this chapter is to modify the first law to take into account the change in the total energy of the system as a function of the number of particles present.

The First Law of Thermodynamics and the Chemical Potential

Thermal Interactions: When two systems are allowed to interact thermally, we actually mean that the molecules in one system are allowed to transfer some of their thermal energy (e.g., kinetic, vibrational, or rotational energy of motion) to molecules of the other system without the molecules actually going from one system into the other. This takes place at the interface of the two systems as the molecules collide with one another. This process we call heat conduction: the transfer of heat energy from one point to another without the actual transport of material.

We know that heat will flow from a hotter object into a colder object, so that the hotter object cools down, while the colder object is heated, and we have shown how this is related to the change in entropy of the system. This means that when molecules collide, the faster (hotter) ones lose some of their energy to the slower (colder) ones, so that, on average, the faster molecules slow down, and the slower molecules speed up. Now this may not be true of an individual collision, but this must be true for the majority of the collisions.

Since heat is a form of energy, the internal energy of the system must increase if heat is added to the system. This is explicitly expressed by the equation

\[
dE = \delta Q
\]  

(10.12)

where \( \delta Q \) is taken to be positive if heat is added to the system and negative if heat is taken from the system. Now from our discussion above, the total energy of the system is given by
where the translational energy is measured relative to the average ground state energy. If the transfer of energy from one system to another effectively changes the average ground state energy we treat this as an increase (or decrease) in the average translational energy of the molecules (and thus as an increase in the thermal energy of the system). We define heat transfer as the transfer of energy which occurs when the macroscopic parameters of the system, such as volume, remain constant. We, therefore, exclude mechanical interactions and/or any change in the number of particles in the system which would alter the intermolecular distances.

**Mechanical Interactions:** In this case the wall separating our two systems is considered to be adiabatic and impermeable, but movable (i.e., no thermal transfer of energy is allowed, nor any particle transfer). When a molecule strikes the moving wall it will gain or lose kinetic energy depending upon whether the wall is moving toward the molecule, or away from the molecule. Consider a baseball thrown at the back of a truck. We will assume that the collision is elastic. If the truck is moving toward you, the baseball will rebound off the truck with a larger velocity than it had before it struck the truck. If the truck moves away from you, the rebound velocity will be smaller. Thus, if molecules collide with a wall moving inward (compressing the gas) the kinetic energy of the molecules would increase, even if there were no intermolecular forces. However, as the walls are moving inward, the average intermolecular distance will decrease, causing a change in the average ground state energy of the system. In the case of attractive forces, the average ground state energy will decrease giving an increase in the average translational kinetic energy of the system. This means that work done on the system to compress the system will tend to increase the average energy of the system for ideal gases, and for real gases with attractive intermolecular forces.

If the wall is moving outward, however, the kinetic energy of an ideal gas would decrease. In addition, since the intermolecular spacing would also increase, the average ground state energy of an attractive system would rise, decreasing the translational kinetic energy. Thus, as a system is expanding, doing work on its surroundings, the average energy of the system is decreasing. We express this situation by the equation

$$ dE = -\delta W $$

where we let $dE$ be the change in the total average energy of the system, and where $\delta W$ is the work done by the system. The minus sign is there since the average energy decreases when the work done by the system is positive, since we define positive work as being associated with an increase in the system's volume.

**Particle Transfer:** If we add H$_2$SO$_4$ to water, the system heats up significantly due to a release of chemical energy. This chemical energy is the energy of interaction between the two chemically different species H$_2$O and H$_2$SO$_4$. To get an idea of where this energy comes from, we again consider the interaction potential between two particles which are separated by a long distance. The potential energy curve associated with the interaction of the two particles indicates that when the two particles are far apart, the potential energy of interaction is approximately zero. However, as we bring the two particles together, the potential energy of the system becomes more and more negative. This corresponds to an increase in the kinetic energy of the system as the different particles approach. Thus, as the two particles approach, the potential energy of interaction is converted to kinetic energy of the approaching particle.

This same thing happens as a molecule of H$_2$SO$_4$ is added to water. When the two are separated, the potential energy of interaction is zero. When the H$_2$SO$_4$ is added to the water, the acid molecule gains kinetic energy (thermal energy) as it falls into the potential well. Some of this energy will then be imparted to other particles in the system by collisions. Thus, the energy stored in the potential energy of interaction (the chemical potential) is imparted to other particles in the system so that the system as a whole is “heated up”.

As we add each new H$_2$SO$_4$ molecule to the system, each one “falls down” a potential well to impart additional energy to the system, so that the energy added to the system by adding $dN$ particles to the system is
given by
\[ dE_{\text{chem}} = \mu \, dN \] (10.15)
where \( \mu \) is the chemical potential and is positive for attractive potentials. The chemical potential, then, is the amount by which each individual particle decreases the potential energy of the system as it is added to the system. Thus, the addition of \( dN \) particles decreases the internal potential energy by an amount \( \mu \, dN \), and this means a net increase in the average kinetic energy of the system.

We can, therefore, indicate a change in the internal energy of the system by the general equation,
\[ dE = \delta Q - \delta W + \mu \, dN \] (10.16)
This is the first law of thermodynamics in which we allow for a variation in the number of particles of the system. We should point out here that the chemical potential will in general be a function of the average separation of the particles, and therefore, of the temperature, density, etc., so that we will write \( \mu = \mu(N,V,T) \). Similarly, if more than one species of particle is present, we must modify the first law to give
\[ dE = \delta Q - \delta W + \sum_{i} \mu_i \, dN_i \] (10.17)
where each species of particle has its own chemical potential \( \mu_i \).

**The First Law in Terms of a Complete Set of State Variables**

We now have a general expression for the first law of thermodynamics in which we allow a system to gain or lose energy in the form of heat, in mechanical interactions, and in the addition of particles. We write this general expression in the form
\[ dE = \delta Q - \delta W + \mu \, dN \] (10.18)
where the heat added to the system and the work done by the system are inexact differentials because heat and work are not state variables. However, the differential work can be expressed in terms of the pressure and the differential change in volume of a system undergoing a reversible (quasi-static) change
\[ \delta W = P \, dV \] (10.19)
Likewise, we have found that the heat added to a system during a reversible (quasi-static) process can be written as
\[ \delta Q = T \, dS \] (10.20)
where \( T \) is the equilibrium temperature of the system and where \( dS \) is the change in entropy of the system. We can therefore write the first law in terms of state variables to obtain
\[ dE = T \, dS - P \, dV + \mu \, dN \] (10.21)
As we have pointed out previously, the fact that the first law can be written in terms of exact differentials means that we can find unambiguous relationships between the various state parameters that we have defined. For example, consider the case where \( N \) and \( V \) are constants. The first law gives
\[ dE_{V,N} = T \, dS_{V,N} \] (10.22)
which is equivalent to the familiar equation
\[ \left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T} \] (10.23)
since the partial derivative is just the derivative with respect to one variable when all others are being held constant.

This more complete version of the first law is expressed in terms of seven state variables. But since there are only three types of interaction that we have considered — thermal, mechanical, and chemical — there can be only three independent variables. Thus, we can write any one of the seven state variables as a function of any of the other three.
Now, consider the first law in the form
\[ dE = TdS - pdV + \mu dN \]  
(10.24)

If we take the internal energy to be a function of the entropy, the volume, and the number of particles in the system, i.e., \( E = E(S, V, N) \), we can write the differential of \( E \) as
\[ dE = \frac{\partial E}{\partial S} dS + \frac{\partial E}{\partial V} dV + \frac{\partial E}{\partial N} dN \]  
(10.25)

using the chain rule. Now, if we compare this with the first law, we can relate the partial derivatives in the equation above with parameters in the first law, and obtain:
\[ \left( \frac{\partial E}{\partial S} \right)_{V,N} = T \quad \left( \frac{\partial E}{\partial V} \right)_{S,N} = -p \quad \left( \frac{\partial E}{\partial N} \right)_{V,S} = \mu \]  
(10.26)

So we see that the chemical potential can be determined if we can measure the change in energy of the system as particles are added to the system (provided, of course, that the volume entropy remain constant, which may not be easily accomplished). [Notice that if the internal energy (the thermal energy) increases as the number of particles increase, the chemical potential is positive; otherwise, the chemical potential is negative!] Similarly, the pressure is a measure of how the energy of the system changes with volume (provided, of course, that the number of particles and entropy remain constant), and the temperature is a measure of how the energy of the system changes with entropy (provided the number of molecules and the volume remain constant – which is usually fairly simple).

Alternately, we can rearrange the first law, and write
\[ TdS = dE + pdV - \mu dN \]  
(10.27)

or
\[ dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN \]  
(10.28)

This last equation expresses the fact that the entropy of the system is a function of the total internal energy (the thermal energy), the volume, and the number of particles in the system, i.e., \( S = S(E, V, N) \). This means that
\[ dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial N} dN \]  
(10.29)

Comparing these last two equations we see that
\[ \left( \frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T} \quad \left( \frac{\partial S}{\partial V} \right)_{N,E} = \frac{p}{T} \quad \left( \frac{\partial S}{\partial N} \right)_{E,V} = -\frac{\mu}{T} \]  
(10.30)

We can continue this process to come up with additional relationships, some of which we will consider later. (Notice that each of these partials requires that the volume, number of particles and/or the total energy of the system be fixed, and that this is relatively easy to do in practice.)

Let’s work a simple example to illustrate the power of the ideas we have just introduced. Consider the case of an ideal gas. In the last chapter, we found an expression for the entropy of a three-dimensional ideal gas, the Sakur-Tetrode equation
\[ S(E) = Nk \left\{ \ln \left( \frac{V}{N} \right) \left( \frac{4\pi mE}{3Nh_0^2} \right)^{3/2} \right\} + \frac{5}{2} \]  
(10.31)

We can now use this equation to obtain expressions for the temperature, pressure, and chemical potential for an ideal gas. The pressure is given by
\[ \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{N,E} = \frac{Nk}{V} \quad \Rightarrow \quad PV = NkT \]  
(10.32)
which is the equation of state for an ideal gas. The temperature of the ideal gas is given by

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} = \frac{3Nk}{2E}$$

(10.33)

from which we get a simple expression for the average total energy of an ideal gas:

$$E = \frac{3}{2} NkT$$

(10.34)

The chemical potential can be found from the equation

$$-\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right)_{E,V}$$

(10.35)

To make this somewhat easier to evaluate, let’s write the Sakur-Tetrode equation in the form

$$W(I) = R5 \left( \frac{5}{2} \right) R5 \left( \frac{5}{2} \right) R5 \left( \frac{5}{2} \right)$$

(10.36)

Carrying out the differentiation, we obtain

$$-\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right)_{E,V} = kln \left[ V \left( \frac{4\pi m E}{3h_o^2} \right)^{3/2} \right] - klnN^{5/2} - Nk \left[ \frac{5N^{3/2}}{2N^{5/2}} \right] - \frac{5}{2} k$$

(10.37)

The last two terms cancel, leaving an expression for the chemical potential of an ideal gas as

$$\mu = -kT \ln \left[ V \left( \frac{4\pi m E}{3N h_o^2} \right)^{3/2} \right]$$

(10.38)

We can also express the total energy as $E = \frac{3N}{2} kT$, to obtain the chemical potential of an ideal gas in terms of the number of particles, the temperature and the volume of the gas, and we obtain

$$\mu(N, V, T) = -kT \ln \left[ \left( \frac{V}{N} \right) \left( \frac{2\pi m kT}{h_o^2} \right)^{3/2} \right]$$

(10.39)

which can also be written as

$$\mu(v, T) = -kT \ln \left[ \left( \frac{v}{v_{eff}} \right) \left( \frac{2\pi m kT}{h_o^2} \right)^{3/2} \right]$$

(10.40)

where $v$ is the specific volume of the gas. Since the argument of the log must be dimensionless, we can write this last expression as

$$\mu(v, T) = -kT \ln \left[ \frac{v}{v_{eff}} \right]$$

(10.41)

where

$$v_{eff} = \left( \frac{2\pi m kT}{h_o^2} \right)^{-3/2}$$

(10.42)

is some volume that depends upon the temperature, the mass of the particle and $h_o$. If we take $h_o$ to be Planck's constant, this volume is referred to as a quantum volume, associated with the quantum wavelength

$$\lambda_Q = \frac{h_o}{\sqrt{2m\pi kT}}$$

(10.43)
You should consider for a moment the implications of the expression we have derived for the chemical potential of an ideal gas. This expression means that the chemical potential for an ideal gas is not zero even though there is no potential energy of interaction between the various particles. Rather, it depends upon the specific volume (or particle density) and the temperature of the gas. The reason that there is a chemical potential, even for an ideal gas can be understood by examining the process of mixing two gases. When two gases are mixed, the entropy of the gas increases. This can even occur in the situation when the two gases are identical in composition, but not in specific volume and/or temperature. We we look briefly at the process of mixing in the next section.

Note: Now, since the total energy of an ideal monatomic gas is given by

\[ E = \frac{3}{2} NkT \]  

(10.44)

you might be tempted to write

\[ \mu = \frac{\partial E}{\partial N} = \frac{3}{2} kT \]  

(10.45)

But why isn't this correct? The reason that this expression is not correct, can be seen from the expression we derived earlier for the chemical potential in terms of the internal energy

\[ \mu = \left( \frac{\partial E}{\partial N} \right)_{V,S} \]  

(10.46)

To determine the chemical potential, from the last expression, must find the change in energy of the system when we add or remove a particle, but without also changing the entropy or the volume entropy of the system. Although the volume of the system can be held fixed, the entropy is a function of the number of particles present, so that the entropy will generally also change when we add or remove particles! Generally, in order to use the partial derivatives, it is necessary to express the equations in terms of the quantities that must be held constant so that you do not get fooled. The change in the total energy of an ideal gas can be written as

\[ dE = \left( \frac{\partial E}{\partial N} \right)_{T,V} dN + \left( \frac{\partial E}{\partial T} \right)_{N,V} dT \]  

(10.47)

In this equation, we have that

\[ \left( \frac{\partial E}{\partial N} \right)_{T,V} = \frac{3}{2} kT \]  

(10.48)

and

\[ \left( \frac{\partial E}{\partial T} \right)_{N,V} = \frac{3}{2} Nk \]  

(10.49)

but we cannot evaluate the partial derivative of \( E \) with respect to \( N \) while holding \( S \) constant, because \( S \) and \( T \) remaining constant are not the same thing!

The Entropy of Mixing

Consider a container of volume \( V \) which can be partitioned into two separate sections of equal volume, \( V/2 \). We now place \( N_A \) atoms in the left side of the container and \( N_B \) atoms in the right side. We assume that these atoms do not interact with one another, so that we have two ideal monatomic gases filling each side of the container. In addition, we assume that the container is isolated and that the two gases are in thermal equilibrium.
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with a temperature $T$. The entropy of the gas on the left side of the container is given by

$$S_A(E) = N_A k \left\{ \ln \left[ \frac{V/2}{N_A} \left( \frac{4\pi m E}{3N_A h^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$$  \hspace{1cm} (10.50)

Expressing the internal energy in terms of the temperature, we can write this as

$$S_A(E) = N_A k \left\{ \ln \left[ \frac{V/2}{N_A} \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$$  \hspace{1cm} (10.51)

Likewise, the entropy of the gas on the right side of the container is given by

$$S_B(E) = N_B k \left\{ \ln \left[ \frac{V/2}{N_B} \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$$  \hspace{1cm} (10.52)

Now, if we remove the partition, so that each gas is allowed to diffuse into the other and so fill the entire volume $V$, the final entropy of each gas is given by

$$S_i(E) = N_i k \left\{ \ln \left[ \frac{V}{N_i} \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$$  \hspace{1cm} (10.53)

Because of the increase in the volume accessible to both gases, the final entropy of each gas is greater than the initial entropy of that gas, and the entropy of the entire system increases. The change in entropy of the gas on the left is given by

$$\Delta S_A(E) = N_A k \left\{ \ln \left[ \frac{V}{N_A} \right] - \ln \left[ \frac{V/2}{N_A} \right] \right\} = N_A k \ln \left[ \frac{\nu_A}{\nu_A/2} \right] = N_A k \ln(2)$$  \hspace{1cm} (10.54)

The change in entropy of the gas on the right would be given by

$$\Delta S_B(E) = N_B k \left\{ \ln \left[ \frac{V}{N_B} \right] - \ln \left[ \frac{V/2}{N_B} \right] \right\} = N_B k \ln \left[ \frac{\nu_B}{\nu_B/2} \right] = N_B k \ln(2)$$  \hspace{1cm} (10.55)

and the total change in entropy of the system would be

$$\Delta S_A(E) = (N_A + N_B) k \ln(2) = N k \ln(2)$$  \hspace{1cm} (10.56)

where $N$ is the total number of particles in the container. This increase in entropy is what we would expect if two different gases are allowed to mix in this way.

But what if the two gases were the same? Would we still get an increase in the entropy? This would seem unreasonable. Notice that the change in entropy of both gases really depends upon the ratio of the specific volumes of the gas before and after expansion, or

$$\Delta S_A(E) = N_A k [\ln(\nu_{A,\text{final}}) - \ln(\nu_{A,\text{initial}})] = N_A k \ln \left[ \frac{\nu_{A,\text{final}}}{\nu_{A,\text{initial}}} \right]$$  \hspace{1cm} (10.57)

If there is really only one type of gas in the container of volume $V$, and if each gas has the same specific volume (i.e., if there are as many particles on one side of the partition as is on the other side before it is removed), the specific volume of each gas is still the same after the partition is removed. Thus, there is no change in the entropy of the gas. However, if the number density is not the same, then there will be an increase in the entropy of the gas, even if the gas on each side of the partition is composed of the same atoms.

Historical Note: The first attempts to calculate the entropy of an ideal gas based upon a simple statistical model did not take into account the indistinguishability of the particles of the gas. Thus, the $1/N!$ term was not initially a part of the formalism, and the entropy was thought to be of
the form

\[ S_A(E) = N_A k \left\{ \ln \left[ V \left( \frac{4\pi m E}{3 N_A h^2} \right)^{3/2} \right] + \frac{5}{2} \right\} \]  

(10.58)

Using this expression for the entropy leads to an increase in the entropy of mixing even when the two gases are identical and have the same specific volume before and after the mixing. This failure of the model forced physicists to re-examine the theoretical basis for deriving the expression for the entropy and led to the addition of the term to compensate for "overcounting." In reality, it was not until the advent of quantum mechanics that physicists really understood that this terms was required because of the indistinguishability of particles at the atomic level.