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# THERMODYNAMICS, SEPARATIONS, AND EQUILIBRIUM

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Thermodynamics is the branch of science that deals with the movement of energy between materials, very frequently fluids (liquids and gases). There are two essential elements: (1) the state of the material, in other words, its physical characteristics such as temperature or specific volume; and (2) the processes that the materials that make up the system may undergo as energy is exchanged.

A critical component of thermodynamics is the definition of the system. The system is usually the materials contained within a physical space, such as a unit of equipment. However, it can also be a subset of the materials within that physical space. The system will exchange energy with the surroundings, all of the material located outside the system.

## 7.1 IDEAL GASES

In 1662, Robert Boyle discovered that if he placed an ideal gas into a container, as shown in Figure 7.1, and was very careful to maintain a constant temperature on the system, the pressure on the gas ( $p$ ) would increase inversely to the volume of the cylinder ( $V$ ). In other words, moving the piston such that the volume would be

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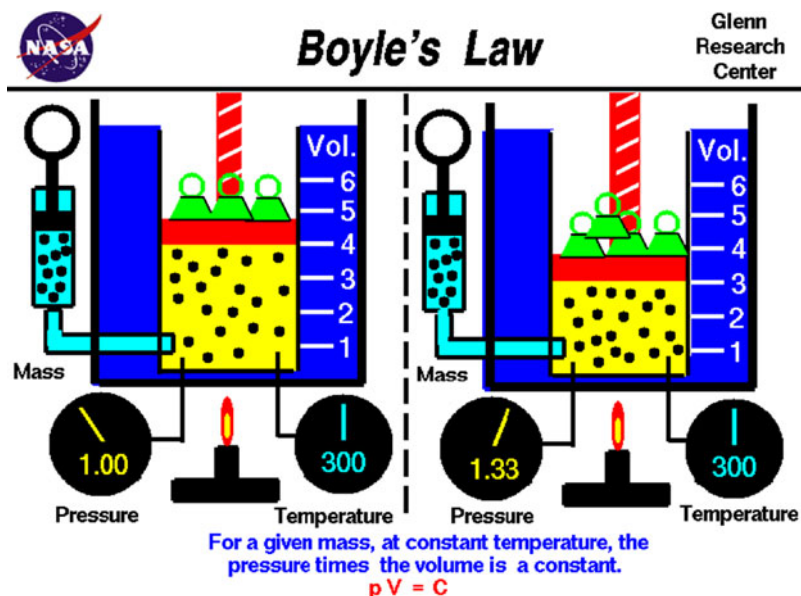


Figure 7.1. A pictorial description of Boyle's law [1].

reduced to half of the original volume would result in a doubling of the pressure. One can envision that the molecules of the ideal gas, which are constantly moving within the cylinder, would strike the wall of the cylinder more frequently. The number of strikes of the molecules on the wall of the cylinder corresponds to the pressure of the gas. The operation described in Figure 7.1, and making up the experiment that leads to Boyle's law, would be termed an isothermal compression.

Mathematically, Boyle's law is best described as

$$p_1V_1 = p_2V_2 \quad (7.1)$$

A similar relationship was found by Jacques Charles in the 1780s, when he determined that the volume of a gas ( $V$ ) increased as the temperature of the gas ( $T$ ) also increased. When evaluated using an appropriate thermodynamic temperature scale (which did not exist at the time of Charles' discovery), it was determined that the temperature and volume increased proportionally, as shown in Figure 7.2.

We can write Charles' law as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (7.2)$$

By combining Boyle's law with Charles' law, we can develop a relationship that describes the properties of the ideal gas through changes in the pressure ( $p$ ), volume ( $V$ ), and temperature ( $T$ ):

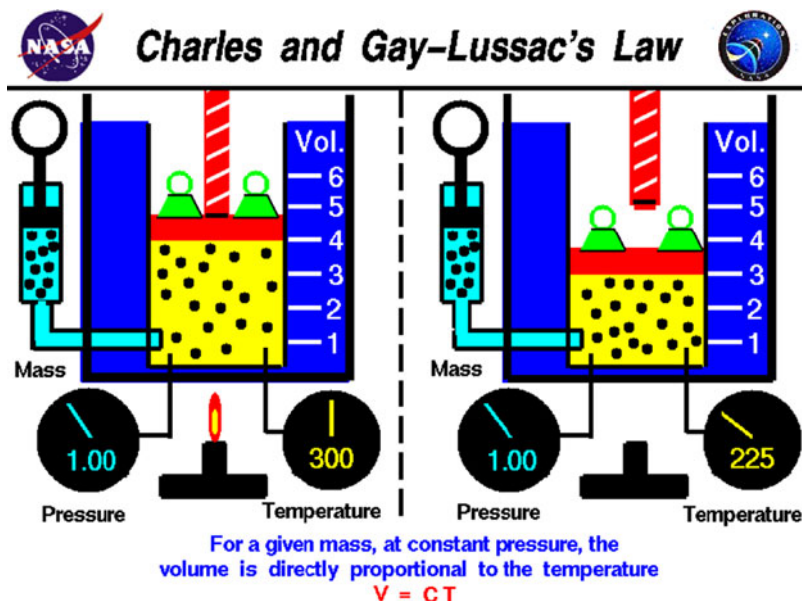


Figure 7.2. A pictorial description of Charles' law [2].

$$p_1 \frac{V_1}{T_1} = p_2 \frac{V_2}{T_2} \tag{7.3}$$

This combined relationship serves to relate the properties of a fluid in a closed system, but does not permit the absolute calculation of any specific property, since the amount of the substance present is not known. For that, we require Avogadro's law, developed in 1811 by Amedeo Avogadro, which states that the number of molecules ( $n$ ) in a specific volume of fluid ( $V$ ) at a given pressure ( $P$ ) and temperature ( $T$ ) is always the same. Together, this provides the ideal gas law, which can be used to relate the properties of the ideal gas under any conditions.

$$PV = nRT \tag{7.4}$$

The ideal gas law holds under conditions in which the molecules behave as independent, randomly moving particles—that is, there are no molecular interactions. Many gases can be modeled as an ideal gas, particularly at high temperature and low pressure.  $R$  is the universal gas constant, which identifies the internal kinetic energy of a mole of an ideal gas at the indicated temperature, and is given in a variety of units in Table 7.1 (J=joules; K=kelvin; Pa=pascal; atm=atmosphere; cal=calorie; lbmol=the number of moles on an English scale; °R=absolute temperature scale in English units; BTU=British thermal unit; psia=pounds per square inches, absolute).

One place where the ideal gas law is found to be useful in processes is in the definition of flow rates identified at *standard conditions* (or sometimes, standard

TABLE 7.1. Values of  $R$  Constants

7.314 J/mol K	
7.314 m <sup>3</sup> Pa/mol K	0.7302 ft <sup>3</sup> atm/lbmol °R
82.05 cm <sup>3</sup> atm/mol K	10.73 ft <sup>3</sup> psia/lbmol °R
1.987 cal/mol K	1.987 BTU/lbmol °R

### Highlight 7.1 Calculation of Flow Rate

Air enters a pipe at a rate of 10 ft<sup>3</sup>/min, at 200 °F and 2 atm. The air leaves the pipe at standard conditions (60 °F and 1 atm). Determine the flow rate of the exiting air.

**Solution:**

We apply the ideal gas law twice—first to determine the molar flow rate of the entering air, and then a second time to calculate the volumetric flow rate at standard conditions.

$$\text{Molar flow rate: } n = \frac{PV}{RT} = \frac{(2\text{ atm})(10\text{ ft}^3/\text{min})}{(0.7302\text{ ft}^3\text{ atm} / \text{lbmol } ^\circ\text{R})(660\text{ } ^\circ\text{R})} = 0.04\text{ lbmol} / \text{min}$$

Volumetric flow rate at standard conditions (1 atm, 60 °F) is calculated as

$$V = \frac{nRT}{P} = \frac{(0.7302\text{ ft}^3\text{ atm} / \text{lbmol } ^\circ\text{R})(520\text{ } ^\circ\text{R})(0.04\text{ lbmol} / \text{min})}{(1\text{ atm})} = 15.6\text{ scfm}$$

temperature and pressure, STP). These are defined as 273 K (or 492 °R) and 1 atm. There is also an “industry standard” referred to as normal temperature at 60 °F (F=Fahrenheit). With this definition, we can define volumetric flow rates as standard liters per minute or standard cubic feet per minute (scfm) or standard cubic centimeters per minute (sccm). A slpm is a liter per minute at STP. The ideal gas law provides a mechanism for converting actual flow rates to standard flow rates, as described in Highlight 7.1.

The ideal gas law applies to both pure gases and gas mixtures. In order to apply the ideal gas law to a particular species in a gas mixture, we need to multiply both sides of the equation by the mole fraction ( $y_i$ ) of the particular component, which provides

$$(y_i P)V = (y_i n)RT \quad (7.5)$$

Using this equation, we can define the partial pressure ( $p_i$ ) as

$$p_i = y_i P \quad (7.6)$$

and see that the ideal gas law provides, for an individual species in a gas mixture,

$$p_i V = n_i RT \tag{7.7}$$

If we sum over all of the species in the mixture, we obtain

$$\sum p_i = \sum \frac{n_i RT}{V} = \sum n_i \frac{RT}{V} = \frac{nRT}{V} = P \tag{7.8}$$

Thus, we see that the sum of all of the species partial pressures provides the total pressure of the gas. This is often termed Dalton’s law.

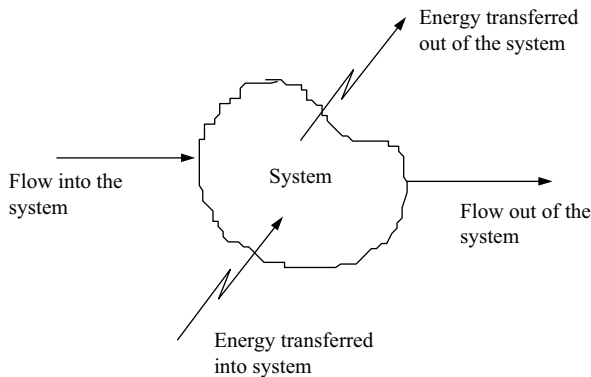
### 7.2 THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics derives from the fundamental physical principle that energy can be neither created nor destroyed. We can move energy around in a system, but we must always be able to account for where it is and where it goes. Thus, if we are looking at any system, we can do an energy balance to relate the energy flows entering and leaving the system. The general energy balance equation is

$$\text{Energy entering the system} - \text{Energy leaving the system} = \text{Accumulation in the system}$$

Figure 7.3 gives a general view of energy flows entering and leaving a system.

Notice that energy can enter a system either through a flowing stream, or through work being done on the system, or heat being added to the system. Let’s look at each of the energy terms in more detail.



**Figure 7.3.** General view of energy flows.

1. **Flow into or out of the system.** This is the energy that is brought into the system by the flow of material, or that leaves the system by the flow of material out of the system. This consists of three separate parts:

- *Kinetic energy* is the energy associated with motion and is given by

$$E_k = \frac{mv^2}{2g_c} \quad (7.9)$$

where  $v$  is the velocity of the material and  $m$  is its mass. The constant  $g_c$  is included in this equation to allow for the conversion between the mass unit pounds ( $\text{lb}_m$ ) and the use of pounds as a unit of force ( $\text{lb}_f$ ). In English units  $g_c = 32.2 \text{ (lb}_m \text{ ft/s}^2\text{)}/\text{lb}_f$ . In metric units,  $g_c = 1 \text{ (N m/s}^2\text{)}/\text{J}$ .

- *Potential energy* is the energy associated with the system not being in a state of mechanical equilibrium (e.g., a ball sitting at the top of a hill will tend to roll down the hill). The potential energy is given by

$$E_p = m \frac{g}{g_c} z \quad (7.10)$$

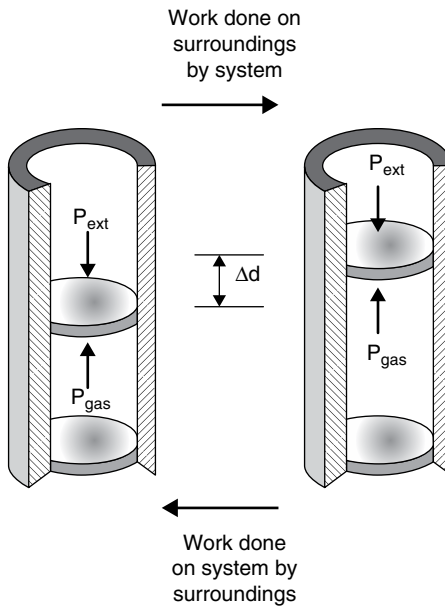
where  $z$  is the height of the system above some defined reference point. Here,  $g$  is the acceleration due to gravity, which is  $32.2 \text{ ft/s}^2$  or  $9.81 \text{ m/s}^2$  in metric units. Note that  $g$  and  $g_c$  are very different and need to be used carefully to account for units.

- *Internal energy* is the latent energy of the species and is due to molecular motion. Internal energy is given the symbol  $U$  and is calculated relative to a defined standard state.

For most of the systems that a chemist is concerned with, the changes in internal energy will far exceed those of kinetic or potential energy. While those terms can be important under special circumstances, we'll restrict further discussion to the internal energy and neglect the contributions of kinetic and potential energy components.

2. **Heat.** Heat is the flow of energy resulting from a temperature difference. Energy always transfers from a system at high temperature to a system at lower temperature. Heat is given the symbol  $Q$  and is defined as positive when heat is transferred into the system.
3. **Work.** Work is energy transferred through some physical process, such as mechanical agitation. Work is given the symbol  $W$  and is defined as positive when work is done on the system. The fundamental definition of work (from solid mechanics) being done on an object is the force on the object multiplied by the distance over which the force acts. In thermodynamics, we are interested in pressure (force per unit area) and volume (distance times area) so the work done by the system becomes

$$W = -\int P dV \quad (7.11)$$



**Figure 7.4.** Description of work as evaluated through changes in pressure and volume [3]. (Courtesy of Carl Hepburn.)

Figure 7.4 describes the relationship of work to the pressure and volume of the fluid.

Now that we have identified all of the possible energy terms, we can write the energy balance equation appropriate for the chosen system.

### 7.2.1 Closed System

Let’s start with the closed system, which is defined as one in which there is no movement of fluid. Heat can transfer into the system from the surroundings, and it’s possible to do work on the system, but energy cannot enter or leave the system with the fluid, since there is no movement of fluid. Thus, any energy entering or leaving the system must be related to heat ( $Q$ ) or work ( $W$ ), and the energy balance is written as

$$U_{\text{final}} - U_{\text{initial}} = Q + W \tag{7.12}$$

In other words, the change in the internal energy of the system is strictly related to the amount of energy that is added to the system by heat transfer or mechanical work. Often, one will use the symbol  $\Delta$  to describe the difference between two points, in which case the first law of thermodynamics for a closed system is written as

$$\Delta U = Q + W \tag{7.13}$$

### 7.2.2 Open System

In working with an open system, the problem is somewhat more complex. First, let's assume that the system is operating at steady state. Then, we can derive an equation nearly identical to the above equation for a closed system, except that we need to account for all of the flowing streams. This gives

$$\sum_{\substack{\text{output} \\ \text{streams}}} m_j \hat{U}_j - \sum_{\substack{\text{input} \\ \text{streams}}} m_j \hat{U}_j = Q + W \quad (7.14)$$

where  $\hat{U}_j$  is the internal energy per unit mass of the flowing stream. One difficulty in solving the balance for an open system is that the fluid entering the system is doing work on the system, while the fluid leaving the system is having work done on it by the system. Thus, we need to account for these flow work terms. Following our previous definition for work, we will now define two different types of work—shaft work ( $W_s$ ) and flow work ( $W_f$ ). Then the total work is

$$W = W_f + W_s \quad (7.15)$$

According to the previous definition of work as being associated with the force exerted on an object, we see that the flow work term is given by

$$W_f = P_{\text{in}} V_{\text{in}} - P_{\text{out}} V_{\text{out}} \quad (7.16)$$

which accounts for the net work done on the system. Substitution into the energy balance provides

$$\sum_{\substack{\text{output} \\ \text{streams}}} m_j (\hat{U}_j + P_j V_j) - \sum_{\substack{\text{input} \\ \text{streams}}} m_j (\hat{U}_j + P_j V_j) = Q + W_s \quad (7.17)$$

Now, in thermodynamics, we define the *enthalpy* as

$$H = U + PV \quad (7.18)$$

which is substituted into the energy balance to provide

$$\sum_{\substack{\text{output} \\ \text{streams}}} m_j \hat{H}_j - \sum_{\substack{\text{input} \\ \text{streams}}} m_j \hat{H}_j = Q + W_s \quad (7.19)$$

Finally, if we use the symbol  $\Delta$  to stand for the difference between total output and total input, we have

$$\Delta H = Q + W_s \quad (7.20)$$

which is the first law of thermodynamics for open systems.



### 7.3 IDEAL GAS CALCULATIONS

While the energy balance (or first law) is required to evaluate the energy changes of the system, the ideal gas law describes the relationship between the gas properties. For a closed system, the energy balance was written as

$$\Delta U = \delta q + \delta W \quad (7.21)$$

where  $\delta$  is used to indicate a small change in the property. If we know the conditions under which the process change is implemented, we can calculate the amount of work required, or the heat added, to complete the change. We take advantage of the fact that the properties of the gas are independent of the process used to get this gas to the indicated conditions. In other words, the properties of the gas depend only on the state of the gas. However, the amount of energy required to accomplish the change (or the work) depends on the process used. We can calculate the energy requirements if we know the process, by substituting appropriate forms for work, heat, and internal energy, into our energy balance.

Let's suppose we are interested in evaluating the work associated with an isothermal compression. Since an ideal gas has no molecular interactions, the internal energy is a function of temperature only, and thus the energy balance reduces to

$$\Delta U = 0$$

or

$$\delta q = -\delta W \quad (7.22)$$

Next, we substitute our known definition for the work associated with the change in volume:

$$W = -\int P dV \quad (7.23)$$

For 1 mole of an ideal gas,  $PV = RT$ , and substitution of this relationship into the definition of work provides a relationship that can be integrated. We find

$$W = -\int P dV = -RT \int \frac{dv}{v} = -RT \ln \frac{V_2}{V_1} \quad (7.24)$$

Substituting the ideal gas relationship into this last expression, we can also obtain the work requirement in terms of the pressure change:

$$W = RT \ln \frac{P_2}{P_1} \quad (7.25)$$

We can complete similar calculations to determine the work required for processes that occur under other conditions. The following example helps to illustrate this behavior.

What happens if the temperature is not constant? Our first law equation doesn't include the temperature explicitly, but we've said several times that the energy of the fluid is related to its temperature. What is that relationship? We define another property of the material, termed the heat capacity ( $C$ ), which describes the change in the temperature ( $\Delta T$ ) of the fluid when it is heated. In mathematical terms, this provides

$$C = \frac{Q}{\Delta T} \quad (7.26)$$

The units of the heat capacity are  $J/^\circ C$ . The heat capacity is normally described based on the amount of the material. For example, chemists would use the specific heat capacity defined as

$$C = \frac{Q}{\Delta T \times m} \quad (7.27)$$

In this case the units of the specific heat capacity are  $J^\circ C^{-1} g^{-1}$ .

The molar heat capacity ( $C_m$ ) is defined similarly by using

$$C_m = C \times M \quad (\text{with } M = \text{molecular weight}) \quad (7.28)$$

The units of the molar heat capacity are  $J^\circ C^{-1} mol^{-1}$ .

At the beginning of this section, we stated that the energy change depended on the process used to effect the change. As a result, there are two different types of heat capacity that can be defined. One assumes that the heating of the fluid occurs in a constant volume system, such as a closed vessel. Recall the first law for a closed system (Equation 7.13):

$$\Delta U = Q + W$$

If there is no work being done, then

$$\Delta U = Q \quad (7.29)$$

From the definition of the heat capacity above, substitution provides the definition of the heat capacity at constant volume:

$$\Delta U = C_v \Delta T \quad (7.30)$$

We can complete a similar analysis for an open system, one in which the pressure remains constant. For an open system, the first law is written as

$$\Delta H = Q + W \quad (7.20)$$

which upon substitution provides the definition for the heat capacity at constant pressure:

$$\Delta H = C_p \Delta T \quad (7.31)$$

Thermodynamic relationships reveal that the heat capacities at constant volume and constant pressure must be related, and it turns out that

$$C_p = C_v + R \quad (7.32)$$

where  $R$  is once again the gas constant, usually expressed in units of J/mol K.

Using these relationships for an ideal gas and the first law of thermodynamics expressed for the correct type of system, it is possible to determine changes in pressure, temperature, and volume for a range of important processes (Highlight 7.2).

### **Highlight 7.2 Calculating the Energy Effects of Processes for Ideal Gases**

Under many conditions, air can be considered as an ideal gas, with a heat capacity  $C_p = \frac{7}{2}R$  (where  $R$  is again the universal gas constant, in this case, 1.986 BTU/lbmol °R). A compression operation is used to compress 100 lb of air from an initial condition of 1 atm and 70 °F to a final state of 3 atm and 70 °F through a reversible process in a closed system. Determine the work required and the heat transferred for each case:

- Isothermal compression.
- Heating at constant volume followed by cooling at constant pressure.
- Adiabatic compression followed by cooling at constant pressure.

#### **Solution:**

We will convert the mass quantity to a molar value (since the ideal gas law is in molar units):

$$n = \frac{100 \text{ lb}}{29 \text{ lb/lbmol}} = 3.45 \text{ lbmol}$$

The value of the gas constant, 1.986 BTU/lbmol °R, is used to determine

$$C_p = 3.5(1.986 \text{ BTU/lbmol } ^\circ\text{R}) = 6.95 \text{ BTU/lbmol } ^\circ\text{R}$$

(a) We derived the equations describing the work associated with isothermal compression previously, so we can simply plug in the data into the formula to calculate the work required.

$$\begin{aligned} W &= nRT \ln \frac{P_2}{P_1} \\ &= (3.45 \text{ lbmol})(1.986 \text{ BTU/lbmol } ^\circ\text{R})(530 ^\circ\text{R}) \ln \left( \frac{3 \text{ atm}}{1 \text{ atm}} \right) \\ &= 4000 \text{ BTU} \end{aligned}$$

(b) We consider the steps independently. For the first process (heating at constant volume), we find the final temperature using the ideal gas law:

$$\begin{aligned} \frac{T_2}{T_1} &= \frac{P_2}{P_1} \\ T_2 &= (530 ^\circ\text{R})(3 \text{ atm} / 1 \text{ atm}) = 1590 ^\circ\text{R} \end{aligned}$$

For a constant volume process,  $\Delta V=0$ ; therefore,  $W=0$ , so  $\Delta U=Q$ .

$$\begin{aligned} Q &= \Delta U \\ &= nC_v \Delta T = (3.45 \text{ lbmol})(4.97 \text{ BTU} / \text{lbmol } ^\circ\text{R})(1590 ^\circ\text{R} - 530 ^\circ\text{R}) \\ &= 18,150 \text{ BTU} \end{aligned}$$

The second step involves cooling at constant pressure. In this case,

$$\begin{aligned} Q &= \Delta H \\ &= nC_p \Delta T = (3.45 \text{ lbmol})(6.95 \text{ BTU} / \text{lbmol } ^\circ\text{R})(530 ^\circ\text{R} - 1590 ^\circ\text{R}) \\ &= -25,420 \text{ BTU} \end{aligned}$$

For the two-step process,

$$Q = Q_1 + Q_2 = 18,150 \text{ BTU} - 25,420 \text{ BTU} = -7270 \text{ BTU}$$

Since  $\Delta U=0$  (for the process),  $W=-Q=7270 \text{ BTU}$ .

(d) For adiabatic compression,  $Q=0$ , so the energy balance provides

$$dU = \delta W$$

which after substitution provides

$$C_V dT = -P dV$$

Now we substitute the ideal gas law and rearrange the expression to provide a solution that allows calculation of  $T_2$  as a function of  $V_2$ :

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{R/C_V}$$

And then substitute the pressure ratio in place of the volume ratio,

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\gamma-1/\gamma}$$

where we have made use of a shorthand to describe the ratio of the gas constants:

$$\gamma = C_P / C_V$$

This allows us to insert the pressure ratio, from which we can calculate the temperature obtained by the adiabatic compression:

$$\begin{aligned} \frac{T_2}{T_1} &= \left( \frac{P_2}{P_1} \right)^{\gamma-1/\gamma} \\ T_2 &= (590 \text{ }^\circ\text{R}) \left( \frac{3 \text{ atm}}{1 \text{ atm}} \right)^{1.4-1/1.4} = 807.6 \text{ }^\circ\text{R} \end{aligned}$$

To calculate the work, we return to the energy balance for a closed system

$$dU = Q + W$$

and with  $Q=0$ , we see that the work of this process is simply the change in internal energy. Recall that  $dU = C_V dT$  and evaluate the integral

$$\Delta U = C_V (T_2 - T_1)$$

from which we find

$$\begin{aligned}
 W &= \Delta U \\
 &= nC_V \Delta T = (3.452 \text{ lbmol})(4.97 \text{ BTU/lbmol } ^\circ\text{R})(807.6 \text{ } ^\circ\text{R} - 530 \text{ } ^\circ\text{R}) \\
 &= 4760 \text{ BTU}
 \end{aligned}$$

In order to determine the work on cooling, we will need to know the volume at both high and low temperature conditions. The ideal gas law provides

$$V = \frac{nRT}{P} = \frac{3.45 \text{ lbmol}(0.7302 \text{ ft}^3 \text{ atm/lbmol } ^\circ\text{R})(807.6 \text{ } ^\circ\text{R})}{3 \text{ atm}} = 678.2 \text{ ft}^3$$

and

$$V = \frac{nRT}{P} = \frac{3.45 \text{ lbmol}(0.7302 \text{ ft}^3 \text{ atm/lbmol } ^\circ\text{R})(590 \text{ } ^\circ\text{R})}{3 \text{ atm}} = 495.4 \text{ ft}^3$$

Finally, we calculate the work of cooling

$$\begin{aligned}
 W &= -P \Delta V \\
 &= -(3 \text{ atm})(495.4 \text{ ft}^3 - 678.2 \text{ ft}^3) \left( \frac{1 \text{ BTU}}{0.3676 \text{ ft}^3 \text{ atm}} \right) = -1491.6 \text{ BTU}
 \end{aligned}$$

So that

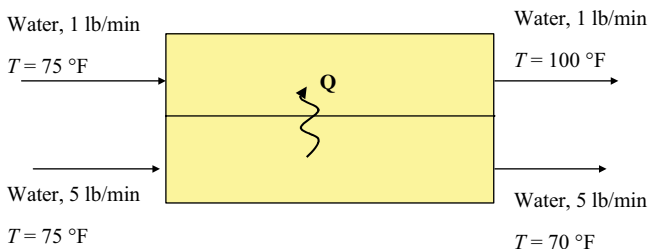
$$W = W_1 + W_2 = 4760 \text{ BTU} - 1492 \text{ BTU} = 3268 \text{ BTU}$$

It is helpful to summarize these results through the following table. Recall that, in all cases,  $\Delta U=0$  for the process, so  $W=-Q$ .

Process	Work (BTU)
(a) Isothermal compression	4000
(b) Heating ( $\Delta V=0$ ), cooling ( $\Delta P=0$ )	7270
(c) Adiabatic compression, cooling ( $\Delta P=0$ )	3268

## 7.4 ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

The energy balance, also termed the first law of thermodynamics, describes how energy can be exchanged within or between processes, but it makes no statement about whether an exchange of energy is possible. For example, consider the heat exchange operation in Figure 7.5. The energy balance for this system provides



**Figure 7.5.** An impossible heat exchange operation.

$$\Delta H = (mC_p\Delta T)_1 + (mC_p\Delta T)_2 = 0 \tag{7.33}$$

Substituting numbers, we find

$$\begin{aligned} \Delta H &= (1\text{lb / min}) (1\text{cal / lb } ^\circ\text{F}) (25 ^\circ\text{F}) + (5\text{lb / min}) (1\text{cal / lb } ^\circ\text{F}) (-5 ^\circ\text{F}) \\ &= 0 \end{aligned}$$

So the energy balance is satisfied. But we know that the situation drawn in Figure 7.5 is impossible. What have we missed?

The second law of thermodynamics describes whether a particular energy exchange is possible. Specifically, recall that we previously indicated energy always flows from a higher energy state to a lower energy state. An alternate description would be that energy must always act in a way to increase the microscopic randomness of the system. We use this concept to define a new thermodynamic property called *entropy*:

There exists a property called entropy,  $S$ , which is an intrinsic property of the system, functionally related to the measurable conditions of the system.

Now, noting that energy must always flow from higher states to lower states, we define the second law of thermodynamics in terms of our definition of entropy:

The entropy change of any system, and its surroundings, considered together, is positive and approaches zero as the process more closely approximates a reversible process.

This form of the second law can be translated into a mathematical expression describing the entropy change of a process:

$$\Delta S \geq 0 \tag{7.34}$$

What is meant by a reversible process? Let's look at a simple example. Suppose we heat a 1 lb block of copper ( $C_p = 94 \text{ kcal/lb } ^\circ\text{F}$ ) from  $50^\circ\text{F}$  to  $100^\circ\text{F}$ . In order to raise the temperature of the copper, the energy input, according to the first law, is

$$\Delta H = mC_p\Delta T = (1\text{lb})(94 \text{ kcal/lb } ^\circ\text{F})(50^\circ\text{F}) = 4700 \text{ kcal}$$

If we were to cool that same block of copper from  $100^\circ\text{F}$  to  $50^\circ\text{F}$ , the first law would then provide

$$\Delta H = mC_p\Delta T = (1\text{lb})(94 \text{ kcal/lb } ^\circ\text{F})(-50^\circ\text{F}) = -4700 \text{ kcal}$$

So the first law indicates that the energy change of heating is the same as the energy change of cooling. However, for each of these processes individually, the entropy must either increase or (if the process is reversible) remain the same. So, in order to recover the full 4700 kcal that was stored in the copper block when it was heated, the heat exchange processes must be reversible. A *reversible process* implies a situation in which the process can be run either forward or backward with the same energy effects.

In a real system with dissipative losses, it requires more than 4700 kcal of energy to increase the temperature of this copper block by  $50^\circ\text{F}$ . Likewise, we cannot recover the full 4700 kcal of energy when the block is cooled back to  $50^\circ\text{F}$ . This irreversibility results in energy losses that cannot be recovered.

For a reversible process, changes in entropy may be calculated as

$$dS = \frac{\delta Q_{\text{rev}}}{T} \quad (7.35)$$

The use of entropy in solving problems requires a mathematical relationship for entropy as a function of temperature and pressure. We return to the first law,

$$dU = Q + W \quad (7.13)$$

and substitute for  $Q = T dS$  and  $W = -P dV$  to provide

$$dU = T dS - P dV \quad (7.36)$$

which is solved for  $dS$ :

$$dS = \frac{dU}{T} + \frac{P}{T} dV \quad (7.37)$$

Finally, noting that  $dU = C_v dT$ , and for an ideal gas,  $P/T = R/V$  provides

$$dS = C_v \frac{dT}{T} + R \frac{dV}{V} \quad (7.38)$$



For an *isentropic process* (i.e., a process in which there is no change in entropy), direct integration of this expression provides

$$\frac{T}{T_0} = \left( \frac{V_0}{V} \right)^{\gamma-1} \quad (7.39)$$

We can develop a similar expression relating the temperature change to a known pressure change. We again start with the energy balance

$$dU = Q + W \quad (7.13)$$

This time, we note that  $dU = dH - d(PV)$ , and again we use  $Q = T dS$  and  $W = -P dV$ . This provides

$$dH - P dV - V dP = T dS - P dV \quad (7.40)$$

Dividing by  $T$ , simplifying, and rearranging provides

$$dS = C_p \frac{dT}{T} - R \frac{dP}{P} \quad (7.41)$$

When  $dS=0$ , integration provides

$$\frac{T}{T_0} = \left( \frac{P}{P_0} \right)^{\gamma-1/\gamma} \quad (7.42)$$

Note that this result is the same as we obtained for adiabatic compression.

We will also need to obtain a relationship for the work of an isentropic compression (Highlight 7.3). Using the prior result from adiabatic compression, we obtain

$$W = \frac{RT_1}{\gamma-1} \left[ \left( \frac{P_2}{P_1} \right)^{\gamma-1/\gamma} - 1 \right] \quad (7.43)$$

### Highlight 7.3 Operation of an Air Compressor

Air is compressed isentropically from 11.5 bar and 30 °C to 18 bar. What is the temperature for the air at the end of this process? What is the required work of compression? Assume that  $\gamma_{\text{air}} = 1.4$ .

#### **Solution:**

First, we calculate the compression ratio

$$R = \frac{18 \text{ bar}}{11.5 \text{ bar}} = 1.57$$

We will assume that air is an ideal gas, so we can calculate the exit temperature using the isentropic compression relationship

$$\frac{T}{T_0} = \left( \frac{P}{P_0} \right)^{\gamma-1/\gamma}$$

$$T = (303\text{K}) \left( \frac{18\text{ bar}}{11.5\text{ bar}} \right)^{1.4-1/1.4} = 344.4\text{K}$$

Next, we can calculate the work of compression

$$W = \frac{RT_1}{\gamma-1} \left[ \left( \frac{P_2}{P_1} \right)^{\gamma-1/\gamma} - 1 \right]$$

$$W = \frac{(8.314\text{ J/mol K})(303\text{ K})}{1.4-1} \left[ \left( \frac{18\text{ bar}}{11.5\text{ bar}} \right)^{1.4-1/1.4} - 1 \right]$$

$$= 860\text{ J/mol}$$

## 7.5 REAL GAS PROPERTIES

We know from experience that a rapid decrease in pressure will lead to a decrease in the temperature of the fluid. This is why frost is formed on the exhaust from a gas relief pipe.

Can we describe this process using our knowledge of thermodynamics? We rewrite the first law of thermodynamics for an open system and, recognizing that there is no work being done on the fluid and no heat being added to the system, we find that

$$\begin{aligned} \Delta H &= Q + W \\ &= 0 \end{aligned}$$

Recall that the change in the temperature is simply a function of the change in the enthalpy, and for an ideal gas,  $dH = C_p dT$ . Thus, there will be no temperature change when an ideal gas is throttled. But we know from experience that there is a significant temperature change when a gas passes through a valve and into the surroundings. Clearly, there must be more to the properties of gases than can be described through the ideal gas law.

For real fluids, the enthalpy can also be a function of pressure. Under these circumstances, we need a new method of evaluating the thermodynamic properties of the fluid. There are several alternatives:

1. Assume ideal gas behavior (not very helpful in many cases).
2. Use an alternate equation of state that adequately models the real gas properties. One choice is the virial expansion,

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \quad (7.44)$$

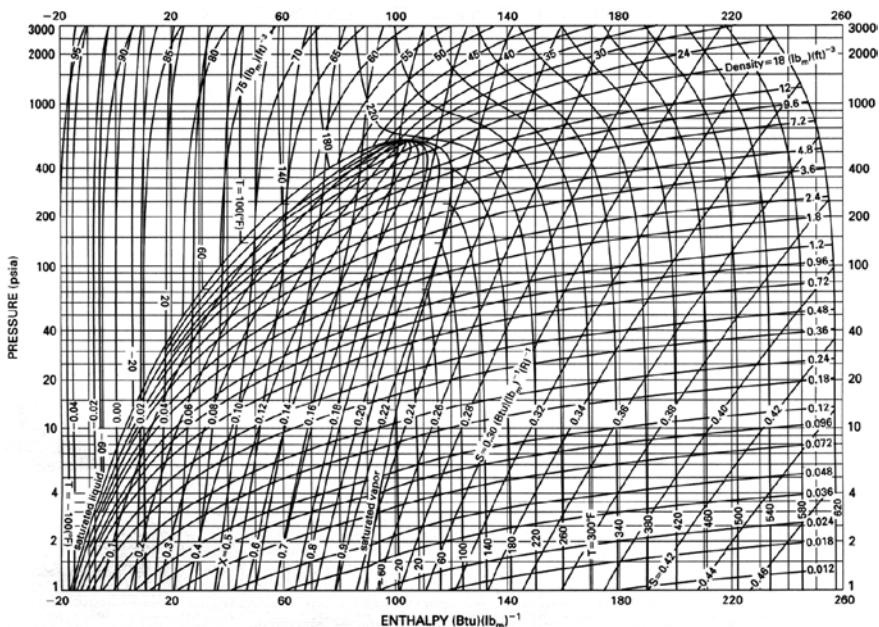


Figure 7.6. The thermodynamic properties of R134a [4]. (Courtesy of M. Huber and M. McLinden.)

An alternative is to use a cubic equation of state, such as the van der Waals equation (this and similar cubic equations of state are often used by chemists)

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{7.45}$$

3. Finally, we can make use of tabulated data (where available). One example is the steam tables. For other common thermodynamic fluids, such as refrigerants, data is provided in graphical form. Figure 7.6 thermodynamic data for Refrigerant 134a (1,1,1,2-tetrafluoroethane) in pressure–enthalpy coordinates.

This thermodynamic diagram provides descriptions of fluid properties as a function of pressure and enthalpy. One can follow lines of constant temperature, density, or entropy. The (mostly) horizontal curves represent constant density, and the (mostly) vertical curves are lines of constant entropy.

The large region in the middle of the diagram (shaded) is the two-phase region, the region in which the fluid can coexist as both a liquid and a vapor. Note that, in this region, the lines of constant temperature (isotherms) are horizontal, indicating that a pure substance boils at a constant pressure and temperature.

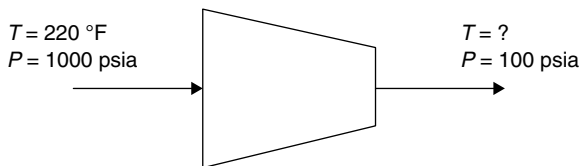
In order to see how to use the data presented in the diagram, we consider a throttling process using a real gas in Highlight 7.4.

### Highlight 7.4 Expansion Through a Valve

One particularly important function of throttling is in cooling operations, such as in an air conditioner or refrigerator. A working fluid is expanded through a valve to create cooling, and then later in the cycle, that fluid is used to absorb heat from inside the refrigerator to keep it cool, and transfer that heat to the environment (i.e., your kitchen). In this specific example, R134a is expanded, at constant enthalpy, through a valve (this is termed a Joule–Thompson expansion) from 1000 psia and 220 °F to 100 psia. Determine the exit temperature and the quality of the fluid (percent liquid). Incidentally, R134a is termed a hydrofluorocarbon and was the first generation replacement for fluorocarbons that were used in refrigeration systems prior to being taken out of service per compliance with the Kyoto Protocol.

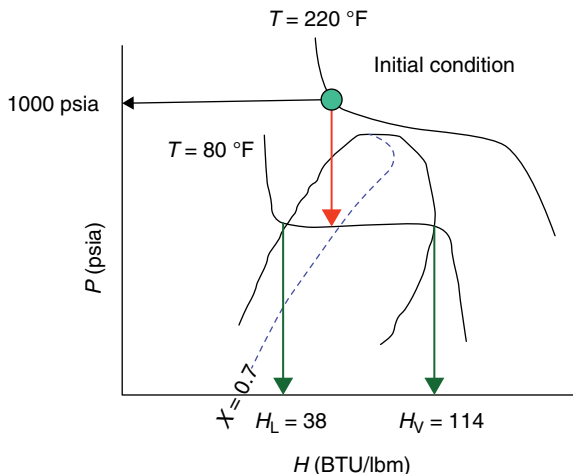
#### Solution:

We can begin by drawing a flowchart of the process:



Based on the data, we can identify the thermodynamic condition of the fluid at the inlet condition using the thermodynamic diagram. This provides  $H = 90\text{ BTU/lbm}$ .

The expansion takes place at constant enthalpy. On the thermodynamic diagram, this means that we draw a vertical line, until we reach the point at 100 psia and  $H = 90\text{ BTU/lbm}$ . We can read the temperature from the chart as 80 °F, as indicated by the figure below.



Quality refers to the percentage of the mixture that is a liquid. In order to determine the quality, we can read this value from the chart, following the curve marked  $x$ . This is the fraction that is vapor, so the quality is  $1-x$ , or 0.3. Alternatively, the overall enthalpy is equal to the fraction liquid times the liquid enthalpy plus the fraction vapor times its enthalpy. In other words,

$$H = xH_L + (1-x)H_V$$

From the graph, we find the liquid enthalpy is 38 BTU/lbm, and the vapor enthalpy is 114 BTU/lbm. We require the overall enthalpy to be 90 BTU/lbm. Substituting and solving provides

$$x = \frac{H - H_V}{H_L - H_V} = \frac{90 - 114}{38 - 114} = 0.32$$

We see that the two solutions are the same, within the limits of our ability to read the chart.

### 7.6 THE PHASE DIAGRAM

In order to understand how thermodynamic data is tabulated, it is helpful to look at a phase diagram. A simple one-component diagram is shown in Figure 7.7. Here, you can see the curves marking the phase boundaries, or two-phase lines, where, for

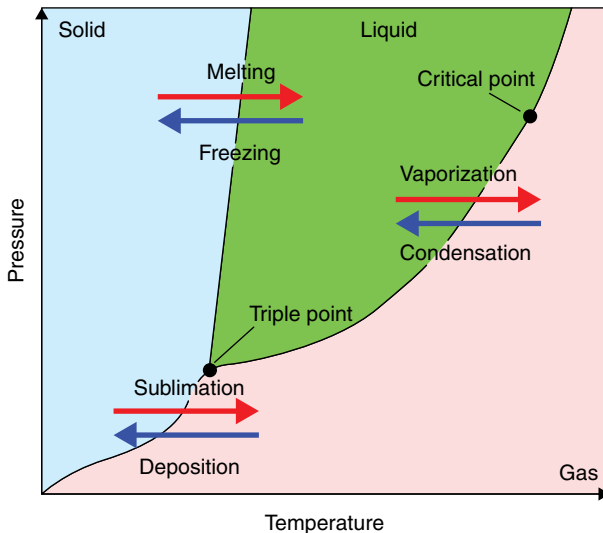


Figure 7.7. Phase diagram for a pure species [5]. (Courtesy of Carl Hepburn.)

example, a liquid is in equilibrium with a vapor. We will consider the specific case of steam and water, but for now, just consider the generic diagram shown here. The phase boundary is defined by a curve; thus, knowing the pressure defines the temperature at equilibrium and thus all of the thermodynamic properties of the fluid. However, each phase is defined by a region, and thus you need to specify both the temperature and pressure to know precisely where you are on the diagram.

We begin by looking at the phase diagram for a pure component. Pure fluids may be present in any one of three phases: solid, liquid, or gas. The phase boundaries occur along well-defined equilibrium curves, which determine where two phases can exist simultaneously. Figure 7.7 is a typical phase diagram (*PVT* diagram), which describes the phase behavior of some arbitrary fluid.

There are three distinct lines shown on this diagram.

1. The *sublimation curve*, which separates the solid phase from the vapor phase. At low temperature and low pressure a material can go directly from the solid to the vapor phase. A good example of this is  $\text{CO}_2$ , which is sold as dry ice (a solid at low temperature and atmospheric pressure).
2. The *melting or fusion or freezing curve* separates the solid from the liquid. As you are aware, water freezes at  $0^\circ\text{C}$  and 1 atm. However, if we increase the pressure, the freezing point temperature goes down (water is a unique case, in most cases, as we increase the pressure, the freezing point temperature will also increase, as indicated in Figure 7.7).
3. The *boiling or vapor pressure or condensation curve*, which separated the liquid and vapor phases. As the pressure is increased, the boiling point temperature of the fluid increases. As a practical example, water boils at a temperature below  $100^\circ\text{C}$  at high elevations (for example, in Denver, Colorado), requiring one to boil water for a longer period of time to cook spaghetti noodles in Denver than in Toledo, Ohio.

There are two additional important points plotted on the phase diagram.

1. *Triple Point*: This is the one point for which a single pure species may coexist as three separate phases.
2. *Critical Point*: This marks the end of the vapor–liquid equilibrium line. Above this temperature and pressure, the fluid will pass from properties that are liquid-like to properties that are gas-like without undergoing a phase change. A fluid above its critical point is said to be supercritical.

A phase change typically experienced in chemical processing occurs when we adjust the conditions of the fluid to cross a phase boundary. For example, consider heating a liquid at constant pressure, a horizontal line on the diagram. We will eventually cross the vapor pressure curve, at which point the liquid will start boiling and a vapor will be produced. As we continue to add more energy into the system, more of the liquid will be converted to the vapor phase. Eventually, all of the fluid

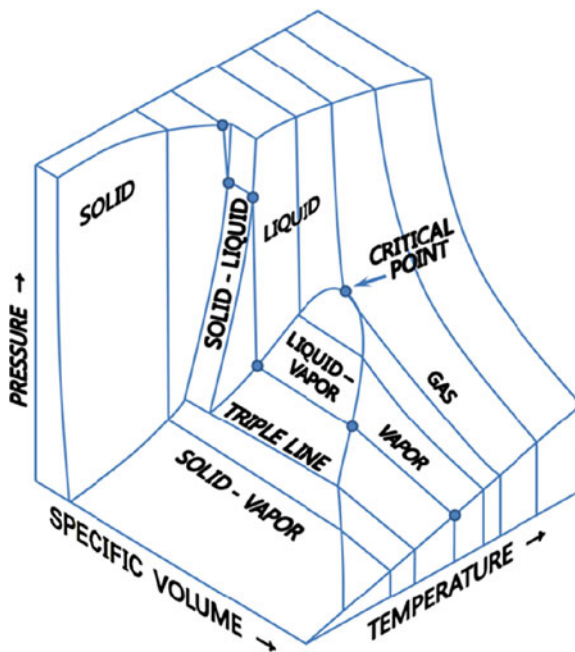


Figure 7.8. A full PVT projection showing the two-phase regions [6].

will exist as a vapor, and if we continue to add energy, the temperature of the vapor will increase.

A more complete phase diagram is provided by Figure 7.8, in which the pressure is plotted as a function of volume and temperature. Here we see that depending on the temperature, we may either pass through the two-phase region or, if the fluid is above its critical temperature, we avoid a phase separation. The point at the top of the liquid–vapor region is the critical point of the fluid. The region marked “LIQUID–VAPOR” depicts the two-phase envelope—below this curve two phases exist in equilibrium.

Figure 7.8 shows clearly that the vapor and liquid phases have a different specific volume (density), although the pressure and temperature of the system is the same. Here we see that the molar volume of the liquid and the vapor are connected in the phase diagram by a *tie-line*. The tie-line graphically reveals the properties of the two phases that are in equilibrium. The pressure at which the two phases coexist is termed the *saturation pressure*.

The system is said to be in phase equilibrium when it can exist simultaneously as both a gas and a liquid. The pressure at which a fluid is in equilibrium is said to be the saturation pressure and is a function of the temperature of the system. The data in the steam tables includes the saturation pressure for water, as a function of temperature. Likewise, the saturation pressure for other species can sometimes be found in graphical form, as in the PVT diagram shown in Figure 7.8.

For species in which tabulated data is not available, the most common technique for estimating the vapor (or saturation) pressure is to use Antoine's equation, which is written as

$$\log P^{\text{sat}} = A - \frac{B}{C + t} \quad (7.46)$$

where  $P^{\text{sat}}$  is in mm Hg, and  $t$  is in  $^{\circ}\text{C}$ . The constants are obtained from experimental measurement and are tabulated in tables. Antoine's equation can be used to estimate the vapor (or saturation) pressure if the temperature is known or, conversely, can be used to estimate the saturation temperature if the pressure is known.

Chemists will often be faced with multicomponent mixtures, and thus it is important to be able to extend the discussion from pure species. We have already seen that in a system containing only one component there is only one point at which a pure component can coexist as three phases. Also, we have seen that if we specify the temperature at which two phases coexist then we have fully specified the system. In other words, by stating that water is in equilibrium with water vapor at  $100^{\circ}\text{C}$ , we know the pressure is 1 atm. However, if I have pure liquid water at  $60^{\circ}\text{C}$  completely filling a container, I know nothing about the pressure. Thus, we would need to specify two variables ( $P$  and  $T$ ) to define the system.

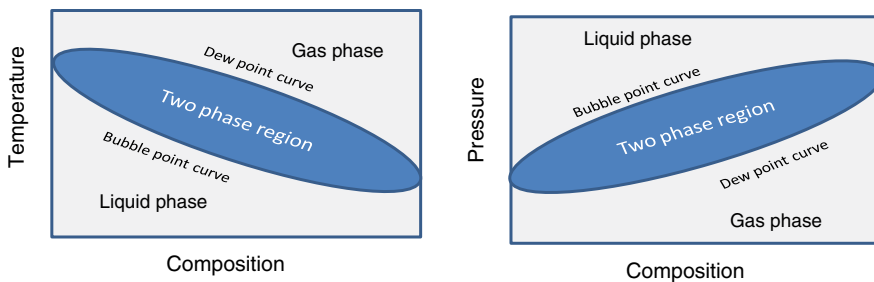
Now, let's suppose that we have two components. In this case, the two-phase line becomes a two-phase region (i.e., we can vary the temperature and pressure independently and remain within the two-phase region). This is because the composition of the system is an additional variable. Within the two-phase region, we need to specify the temperature, the pressure, and the overall composition of the mixture. Figure 7.9 shows two very common ways of describing the equilibrium of a two-component mixture. In the figure on the left, the temperature is plotted on the  $y$ -axis and the composition is plotted across the  $x$ -axis. The region above the two-phase region is the gas phase, and below the two-phase region is the liquid. In the figure on the right, the pressure is plotted on the  $y$ -axis, while both the liquid and vapor compositions are plotted on the  $x$ -axis. In the case, the region above the two-phase region is the liquid phase. Note that two phases can exist over the entire range of compositions. At a specific pressure (or temperature), the composition of the liquid in equilibrium with the vapor is defined by a horizontal line.

Many important chemical processes involve the transition between the single-phase and two-phase regions. Consider the situation in the figure on the right in Figure 7.9. If we start from a pure liquid state and decrease the pressure on the system, then at some point the liquid will begin to boil. This is termed the *bubble point* and is the location where the first drop of vapor is formed. If instead we initially have a vapor phase mixture and we increase the pressure (or decrease the temperature), then liquid will form at the *dew point*. The dew point is defined as the location where the first drop of liquid is formed.

When we generalize this result to many species and many phases we obtain the Gibbs phase rule, which provides

$$F = C + 2 - \pi \quad (7.47)$$





**Figure 7.9.** Illustration of the two-phase region for a two component system.

where the degrees of freedom  $F$  is the number of intensive variables that can be independently specified,  $C$  is the number of components, and  $\pi$  is the number of phases. In the example above, with 2 components and 2 phases we find  $F=2$ . This means that we can independently vary the pressure and the composition and still remain within the two-phase region.

## 7.7 EQUILIBRIUM

In many common chemical operations, the liquid phase is in contact with another vapor, and a portion of the liquid will vaporize and mix with the vapor phase. We frequently want to know how much liquid can be contained in the vapor stream, or the saturation condition for the vapor. We define a gas as being saturated when it contains as much of a liquid substance as possible. For example, water evaporating from a pond increases the moisture content in the air above the pond. During the winter, this creates lake effect snow, as saturated air is carried back across the land, experiences a temperature decrease, and loses excess moisture in the form of snow.

In 1882, French Chemist François-Marie Raoult determined that the pressure generated by a solution was a function of the mole fraction of the species in the solution and the vapor pressure of the species. Starting from a simple solution in which only one species has a significant vapor pressure allows a simple expression of *Raoult's law*

$$p_v = y_v P = p_v^{\text{sat}}(T) \quad (7.48)$$

where  $y_v$  is the mole fraction of the volatile species in the vapor phase. Thus, the saturation condition occurs when the partial pressure ( $p_v$ ) is equivalent to the vapor pressure. Raoult's law assumes that there are no molecular interactions in the liquid or vapor phases, which is the assumption of an ideal solution. Solutions of like fluids (such as a mixture of two alkanes) may often be assumed to be ideal; however, dissimilar fluids may form nonideal mixtures, which will complicate the equilibrium.

If the vapor stream contains as much of the liquid as it can possibly hold, then it is saturated. We also define a percent saturation as

$$\text{Percent saturation} = 100 \frac{Y}{Y_s} = 100 \left( \frac{y_a}{1 - y_a} \right) \left( \frac{1 - y_a^{\text{sat}}}{y_a^{\text{sat}}} \right) = 100 \left( \frac{p_a}{P - p_a} \right) \left( \frac{P - p_a^{\text{sat}}}{p_a^{\text{sat}}} \right) \quad (7.49)$$

where  $Y$  and  $Y_s$  represent the molar ratio of the condensable species to the non-condensable species and the subscript  $s$  represents the saturation conditions. Similarly,  $y_a$  and  $y_a^{\text{sat}}$  are the mole fraction of the condensable species and its mole fraction at saturation, while  $p_a$  and  $p_a^{\text{sat}}$  are the partial pressures.  $P$  is the total pressure of the system.

The percent saturation should be distinguished from the percent relative saturation, which is defined as the partial pressure of the condensable component present divided by the partial pressure present at the saturation condition. Thus,

$$\text{Relative saturation} = 100 \frac{y_a}{y_a^{\text{sat}}} = 100 \frac{p_a}{p_a^{\text{sat}}} \quad (7.50)$$

Water holds a unique place in green chemistry, most notably because it is a benign species. Historically, water is important because it is freely available and easy to manipulate. As a result, we often use the term humidity when describing the saturation condition of water.

For a multicomponent system, Raoult's law applies to all species in a solution, so we need to take into account the mole fraction of the species. In this case, the full expression of Raoult's law provides

$$y_i P = x_i p_i^{\text{sat}} \quad (7.51)$$

where  $x_i$  is the mole fraction of the species in the liquid and  $y_i$  is the mole fraction of the species in the vapor.

One may also define a distribution or equilibrium coefficient as

$$K = \frac{y_i}{x_i} \quad (7.52)$$

When Raoult's law is valid, the distribution coefficient can be equated to the ratio of the vapor pressure to the total pressure

$$K = \frac{p_i^{\text{sat}}}{P} \quad (7.53)$$

For an ideal multicomponent system, Raoult's law must hold for all of the species in the mixture. Thus, if we have a binary system consisting of benzene and toluene, Raoult's law provides two equilibrium relations:

$$\begin{aligned}
 y_{\text{ben}}P &= x_{\text{ben}}P_{\text{ben}}^{\text{sat}} \\
 y_{\text{tol}}P &= x_{\text{tol}}P_{\text{tol}}^{\text{sat}}
 \end{aligned}
 \tag{7.54}$$

Note that the total pressure of the system is the same in both cases. Then, summing over all of the species provides

$$\begin{aligned}
 \sum x_i P_i^{\text{sat}} &= \sum (y_i P) \\
 &= \left( \sum y_i \right) P \\
 &= P
 \end{aligned}
 \tag{7.55}$$

since

$$\sum y_i = 1$$

For a two-component system, there are four variables that can be varied—temperature, pressure, and liquid and vapor compositions. In order to calculate the properties of the system, we must know two of these properties, from which we can calculate the other two. Since these are not completely independent, we end up with five different types of equilibrium problems that can be solved. These are:

Problem Type	Variables Specified	Calculate
1. Bubble point temperature	$P, x_i$	$T, y_i$
2. Bubble point pressure	$T, x_i$	$P, y_i$
3. Dew point temperature	$P, y_i$	$T, x_i$
4. Dew point pressure	$T, y_i$	$P, x_i$
5. Flash calculation	$T, P$	$y_i, x_i$

In order to solve these problems, we need to derive the thermodynamic relationships between the vapor and liquid phase compositions, and then combine this information with the appropriate material balance.

Earlier, it was stated that we could solve problems by combining the equilibrium relationships with the mass balance relationships, and then solve for the unknown variables. For example, in the case of the bubble point pressure problem, the liquid compositions and the system pressure are known. Thus, we combine the equilibrium relations with the mass balance and find

$$\sum x_i P_i^{\text{sat}} = P^{\text{bubl}} \tag{7.56}$$

as described previously. Once the bubble point pressure is known, we can calculate the composition of the vapor phase using Raoult's law:

$$y_i = \frac{x_i P_i^{\text{sat}}}{P^{\text{bubl}}} \tag{7.57}$$

Similar solutions can be obtained for all of the bubble and dew point calculations.

We are now ready to consider several examples. See Highlight 7.5.

### Highlight 7.5 Composition of Vapor Phase

In 2004, DuPont developed a greener process to produce 1,3-propanediol (PDO) through fermentation of glycerol. Following the reaction, the PDO needs to be recovered from the fermentation broth, and vacuum distillation is used. We want to determine the composition of the vapor phase in equilibrium with a liquid containing 40% PDO and glycerol at 180 °C.

**Solution:**

We start by looking up constants for Antoine's equation for these species, so that we can apply Raoult's law. The NIST Chemical Webbook reports Antoine's data in the following form:

$$\log_{10}(P) = A - (B / (T + C))$$

where  $P$  = vapor pressure (bar) and  $T$  = temperature (K), and provides the appropriate constants:

	A	B	C
1,3-Propanediol	6.29523	3105.018	6.101
Glycerol	3.93737	1411.531	-200.566

We first calculate the vapor pressure for each species in the mixture at the indicated temperature by substituting the appropriate constants into Antoine's equation:

$$\log_{10} P_{\text{PDO}} = 6.29523 - \frac{3105.018}{(180 + 273.15) + 6.101}$$

which provides

$$P_{\text{PDO}} = 0.342 \text{ bar} = 260.0 \text{ mm Hg}$$

Similarly for glycerol, we find

$$\log_{10} P_{\text{G}} = 3.93737 - \frac{1411.531}{(180 + 273.15) - 200.566}$$

which provides

$$P_{\text{G}} = 0.022 \text{ bar} = 17.0 \text{ mm Hg}$$

Once we know the vapor pressure of each species, we can find the equilibrium pressure for the mixture as

$$P = 0.4(260.0 \text{ mm Hg}) + 0.6(17.0 \text{ mm Hg}) = 114.2 \text{ mm Hg}$$

Once we know the equilibrium pressure, we can calculate the amount of each species in the vapor phase:

$$y_i = \frac{x_i p_i^{\text{sat}}}{P}$$

which gives for PDO

$$y_{\text{PDO}} = \frac{0.4(260.0 \text{ mm Hg})}{114.2 \text{ mm Hg}} = 0.911.$$

From the sum of mole fractions equal to 1, we can quickly determine that  $y_{\text{G}} = 0.089$ .

For a dew point problem, it is the vapor phase composition that is known, while the liquid phase composition is unknown. Rearranging the combined equilibrium and material balance equations as before will not provide any benefit in this case. However, let's return to Raoult's law,

$$y_i P = x_i p_i^{\text{sat}} \quad (7.51)$$

and now solve for the liquid phase mole fraction:

$$x_i = \frac{y_i P}{p_i^{\text{sat}}} \quad (7.58)$$

As before, the sum of the mole fractions must equal 1, so we sum the above equation over all the species in the mixture to get

$$1 = \sum \frac{y_i P}{p_i^{\text{sat}}} \quad (7.59)$$

Here,  $P$  is the total pressure that is the same in all cases, so we can rearrange this equation and solve for  $P$  as

$$P = \frac{1}{\sum (y_i / p_i^{\text{sat}})} \quad (7.60)$$

Now we can solve for the dew point pressure directly. See Highlight 7.6.

### Highlight 7.6 Liquid Composition at Dew Point

Styrene is an important monomer of the plastics industry, generally produced from benzene (a known carcinogen) and ethylene (produced from thermal cracking of hydrocarbons). A more desirable process would be to convert toluene to ethylbenzene through a reaction with methane, the primary component of natural gas. In a 2009 BASF patent, they report a new catalyst that allows such a process to occur. Our goal is to identify the temperature at which the unreacted toluene can be recovered as a liquid when the system is operating at 100 psia. The composition of the vapor product contains 80% ethylbenzene and the remainder toluene. What is the liquid composition at the dew point?

#### Solution:

This is the dew point temperature problem, which can most easily be solved through the use of iterative calculations. The process is relatively straightforward and similar to the previous example, except that we don't know the initial temperature. So we complete the following steps:

*Step 1.* Guess a temperature.

*Step 2.* Calculate  $P_i^{sat}$ .

*Step 3.* Calculate the equilibrium pressure for the assumed temperature.

*Step 4.* If  $P_{guess} < P_{actual}$ , choose a higher temperature and repeat from step 2. If  $P_{guess} > P_{actual}$ , choose a lower temperature and repeat from step 2.

*Step 5.* Continue until  $P_{guess} = P_{actual}$ .

We start by looking up Antoine's parameters:

Species	$y_i$	A	B	C
Ethylbenzene	0.8	4.4054	1695.026	-23.7
Toluene	0.2	4.5444	1737.123	0.394

If we assume a temperature of 200 °C, then we can calculate the vapor pressure for ethylbenzene just as we did in the previous example:

$$\log_{10} P_{EB} = 4.4054 - \frac{1695.026}{(200 + 273.15) - 23.7}$$

From which we find  $P_{EB} = 62.29$  psia.

A similar calculation for toluene reveals a vapor pressure of  $P_T = 109.96$  psia.

Since we know the composition of the vapor, we can calculate the dew point pressure for this mixture at 200 °C as

$$P = \frac{1}{0.8 / 62.29 + 0.2 / 109.96} = 69.16 \text{ psia}$$

The operating pressure is 100 psia, so we need to go to a higher temperature. A series of iterations reveals that the actual dew point temperature is 220.13 K.

Once we know that, then we can easily calculate the composition of the liquid at the dew point,

$$x_{EB} = \frac{y_{EB}P}{P_{EB}^{sat}} = \frac{(0.8)(100\text{psia})}{(91.83\text{psia})} = 0.871$$

By difference, the amount of toluene in the liquid is 0.129 mole fraction.

### 7.7.1 The Flash Calculation

A flash operation occurs when a mixture is expanded through a valve from a region of relatively high pressure to a region of relatively low pressure. Because of the change in temperature and pressure, a phase separation can be induced. In this type of process, the temperature and pressure at the final state are known, and while the compositions of the equilibrium vapor and liquid phases are unknown, the composition of the fluid entering the valve is known.

In order to solve this type of problem, we require an overall mass balance to relate the amount of vapor ( $V$ ) and liquid ( $L$ ) to the total amount of material ( $F$ )

$$F = V + L \quad (7.61)$$

Similar equations can be written for each species in the mixture. Defining the mole fraction of the species in the vapor as  $y_i$ , the mole fraction of the species in the liquid as  $x_i$ , and the mole fraction of the species in the original fluid as  $z_i$ , provides the species mass balance

$$z_i F = y_i V + x_i L \quad (7.62)$$

Substituting for  $V = F - L$  in the component mass balance provides

$$z_i F = y_i (F - L) + x_i L \quad (7.63)$$

We incorporate the equilibrium data using the distribution coefficient (which can be obtained from Antoine's equation if necessary)

$$y_i = K_i x_i \quad (7.64)$$

which can be substituted to provide

$$\begin{aligned} z_i F &= K_i x_i (F - L) + x_i L \\ &= x_i [K_i (F - L) + L] \end{aligned} \quad (7.65)$$

This equation contains two unknowns,  $L$  and  $x_i$ . We would like to solve for  $x_i$  and then sum over all of the species, since  $\sum x_i = 1$ . Skipping several steps of mathematics, we find

$$x_i = \frac{z_i}{L / F + K_i (1 - L / F)} \quad (7.66)$$

and after summation, we find

$$\sum x_i = \sum \frac{z_i}{L/F + K_i(1-L/F)} = 1 \quad (7.67)$$

This equation contains only one unknown, the ratio  $L/F$ . An iterative solution is required. Once the ratio is determined, the various liquid compositions can be found using Equation (7.66), and the vapor phase composition can be obtained using the equilibrium relation, expressed by Equation (7.67).

Now let's look at an example in Highlight 7.7.

### Highlight 7.7 The Case of Ethyl Acetate

Ethyl acetate is a green solvent that can be produced from bio-derived ethanol. After the reaction, unreacted ethanol is recovered from the ethyl acetate through pressure swing distillation. Let's assume that we have a product stream leaving the reactor that is cooled to ensure that it is full liquid at 25 °C at 0.1 atm, and containing 50% ethyl acetate and the remainder ethanol. What are the compositions of the vapor and liquid phases at this condition?

#### Solution:

We again start by finding Antoine's constants for these species:

Species	$x_i$	A	B	C
Ethanol	0.7	5.24677	1597.673	-46.424
Ethyl acetate	0.3	4.2281	1245.702	-55.19

From this information, we can calculate the vapor pressure of each species at this temperature.

$$\log_{10} P_{\text{EtOH}} = 4.9253 - \frac{1432.526}{(25 + 273.15) - 61.82}$$

From which we find  $P_{\text{EtOH}} = 0.079$  atm. We want to use a distribution coefficient, and since the total pressure is 0.1 atm, then  $K_{\text{EtOH}} = 0.79$ .

A similar calculation for ethanol reveals a vapor pressure of  $P_{\text{EA}} = 0.126$  atm and a distribution coefficient of  $K_{\text{EA}} = 1.26$ .

Application of the formula provides

$$\frac{0.5}{L/F + 0.79(1-L/F)} + \frac{0.5}{L/F + 1.26(1-L/F)} = 1$$

Solving for  $L/F$  by iteration provides a solution when  $L/F = 0.555$ . Then, upon substitution, we can calculate the mole fraction of ethyl acetate in the liquid as



$$x_{\text{EA}} = \frac{0.5}{0.555 + 1.26(1 - 0.555)} = 0.448$$

And finally the mole fraction of ethyl acetate in the vapor is

$$y_{\text{EA}} = (1.26)(0.448) = 0.565$$

## 7.8 SOLUBILITY OF A GAS IN A LIQUID

In many examples of interest, a single component from a gas stream is selectively dissolved into a liquid solvent. This situation was seen previously in Chapter 6, in the case of gas-forming reactions. In that situation, a species that could form a gas was produced by the reaction, and the product would leave the liquid solution to form a separate gas phase. In a similar way, a gas can be dissolved into a liquid and be present as a reactant.

For liquid–vapor equilibrium, we used Raoult’s law to estimate the amount of the liquid that could transfer into the vapor phase. The key parameter was the saturation pressure, which could be estimated from Antoine’s equation. However, for gases that do not normally condense, such as oxygen or  $\text{SO}_2$ , there is no vapor pressure and we need an alternate measure. In addition, the species transferring between the phases is usually very dilute in the liquid phase. Under the conditions of a dilute organic species in a liquid phase, the equilibrium is written using Henry’s law

$$p_i = H_i x_i \quad (7.68)$$

where  $p_i$  is the partial pressure of the organic species in the vapor phase,  $x_i$  is the mole fraction of the organic species in the liquid phase, and  $H_i$  is termed the Henry’s law constant, usually given in units of atm. Values for  $H_i$  are available in many tabulated sources, although the specific form of Henry’s law varies depending on the reference. See Highlight 7.8.

### Highlight 7.8 Concentrations of Oxygen

Estimate the concentration (mol/L) of oxygen in water at atmospheric pressure and 68 °F.

**Solution:**

Air is 21% oxygen, so the partial pressure of oxygen in air at 1 atm is 0.21 atm. Literature reports indicate that  $H = 40,100$  atm/mol fraction at the indicated temperature. Thus, we find

$$\begin{aligned} x &= P_i / H_i = 0.21 \text{ atm} / (40100 \text{ atm/molfrac}) \\ &= 5.24 \times 10^{-6} \text{ mol frac} \end{aligned}$$

Now we need to convert this value from mole fraction to concentration. The concentration of water is 55.6 mol/L, so the concentration of oxygen in water can be calculated as

$$\begin{aligned}C_{O_2} &= (5.24 \times 10^{-6} \text{ mol frac})(55.6 \text{ mol / L}) \\ &= 2.91 \times 10^{-4} \text{ mol / L}\end{aligned}$$

If we wanted to use gaseous oxygen to promote an oxidation reaction in water, this would be the concentration available for the reaction in solution. It is this value that is critical in biological systems, since aerobic microorganisms rely on dissolved oxygen for their metabolism.

## 7.9 SOLUBILITY OF A SOLID IN A LIQUID

Solid liquid equilibrium is observed when a solid is dissolved into a liquid solvent, such as a salt in water. In such cases in the inorganic chemical industry, crystallization is employed as a separation process, particularly where salts are recovered from aqueous media. The feed to a crystallization system consists of a solution from which a solute is crystallized (or precipitated), and the solids are then removed. High recovery of the refined solute is generally the desired design objective.

For an overall process, one must consider three phases of operation—vaporized solvent that contains no solute, liquid solvent containing residual solute, and the produced solid crystals. Solvent is often removed so that the liquid solution is sufficiently concentrated to permit precipitation of solid crystals.

The concentration of solute that remains in the liquid solution is dependent on solid–liquid equilibrium. Phase diagrams can be of many types, depending on the system. The maximum amount of solute that can be dissolved in a given volume of solvent at equilibrium and at a given temperature is called solubility. While it is typical for solubility to increase with increasing temperature, that is not always the case; for example, see  $\text{Ce}_2(\text{SO}_4)_3$ , as seen in Figure 7.10.

The equilibrium diagram is used to determine the amount of solute that can be recovered by cooling a saturated solution from an elevated temperature to a lower temperature. For example, if one has a saturated solution of potassium chloride (KCl) at 80 °C, the solubility diagram indicates that solution contains roughly 51 g of KCl per 100 g of water. If we now decrease the temperature to 40 °C, the solubility is reduced to 40 g KCl per 100 g water. Assuming that we started with 1 kg of water, this means that decreasing the temperature resulted in the production of 110 g of KCl salt crystals on the bottom of the beaker.

The addition of a salt (generally called *solute*) into a liquid (generally called *solvent*) can be used to change the boiling and freezing point properties of that liquid;

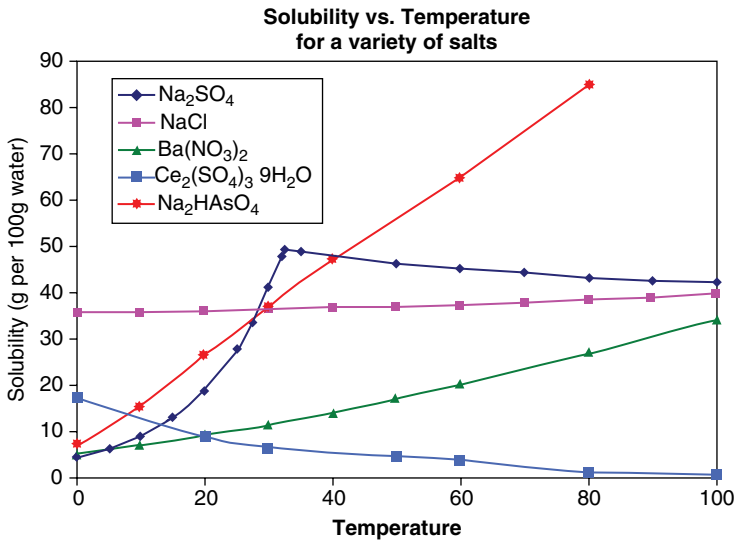


Figure 7.10. Solubility of salts versus temperature [7].

for example, adding a salt into water results in a depression of the freezing point. This is an example of a colligative property (property that depends only on the concentration of the solute in the solution), and the amount of the change in the freezing point depends on the amount of solid added to the solution. It is this chemical phenomenon that we take advantage of when we put salt on the roads in the winter to melt ice (or keep the water from freezing).

When the solution can be considered an ideal solution, then the freezing point depression can be obtained as a simple linear relationship of the molality of the solution, according to

$$\Delta T_f = K_f C_s i \tag{7.69}$$

where  $K_f$  is termed the *cryoscopic constant* and is a function of the solvent only,  $C_s$  is the molality (g of solute per kg of solvent) of the solute (*not to confuse with the concentration or molarity in mol solute/L solution*), and  $i$  is the number of ion molecules generated per molecule of solute. Highlight 7.9 introduces how to calculate freezing point of a solution.

If the system is sufficiently ideal, it is possible to estimate the composition of the solution in equilibrium with the pure solute using thermodynamic data theory. After sufficient simplification, we can use the van't Hoff relationship,

$$\ln x_2 = \frac{\Delta H_f}{RT} \left( \frac{T}{T_m} - 1 \right) \tag{7.70}$$

**Highlight 7.9 Calculation of Freezing Point**

Determine the freezing point (in °C) of a solution containing 1 g of KCl and 100 g of water.

**Solution:**

For water, the cryoscopic constant  $K$  is 1.853 K kg/mol. KCl will dissociate to form 2 ions per mole of salt ( $K^+$  and  $Cl^-$ ), and the concentration is found to be 10 g KCl/kg water, which corresponds to 0.134 mol KCl/kg water. Substituting provides

$$\begin{aligned}\Delta T_f &= (1.853 \text{ K kg/mol})(0.134 \text{ mol KCl/kg water})(2 \text{ ion/mol}) \\ &= 0.497\text{K}\end{aligned}$$

Thus, the freezing point of this solution will be roughly  $-0.5^\circ\text{C}$ .

**Highlight 7.10 Calculation of Solubility**

Ethyl acetate is often considered a cleaner solvent than some harsher organic solvents and may be recovered by extraction with water. Determine the equilibrium solubility of ethyl acetate in water at  $25^\circ\text{C}$ .

**Solution:**

This is a simple application of the van't Hoff equation. We can find the heat of fusion for the solute ethyl acetate as  $\Delta H_{f,EA} = 10.48 \text{ kJ/mol}$  at the melting temperature of  $83.8^\circ\text{C}$ . Converting to absolute temperatures and substituting provides

$$\begin{aligned}\ln x_2 &= \frac{\Delta H_f}{RT} \left( \frac{T}{T_m} - 1 \right) \\ &= \frac{10,480 \text{ J/mol}}{(8.314 \text{ J/molK})(298 \text{ K})} \left( \frac{298 \text{ K}}{356.95 \text{ K}} - 1 \right) \\ &= -0.698 \\ x_2 &= 0.498 \text{ molfrac}\end{aligned}$$

This is the maximum concentration of ethyl acetate that can be found in a solution with water at  $25^\circ\text{C}$ .

where  $\Delta H_f$  is the heat of fusion at the melting temperature,  $T_m$ . The van't Hoff equation provides a simple method for calculating the mole fraction of solute in the liquid at a given temperature using only the properties of the solute, without regard to solvent properties. An example is given in Highlight 7.10.

## 7.10 SUMMARY

Since reactions involve collisions between molecules, reactions can only occur between two species in a common phase. But many systems will have multiple phases. It is important for the chemist to be able to understand the phase behavior of these different types of systems in order to be able to predict the reactions that may occur.

Furthermore, green chemists can use the phase behavior of a system to control the reaction pathways, or to recover a solvent that may be used. By manipulating the temperature and pressure, the phase behavior can be modified and improved reaction performance may be obtained.

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