

11.5: Vaporization and Vapor Pressure

Key Concept Video Vaporization and Vapor Pressure

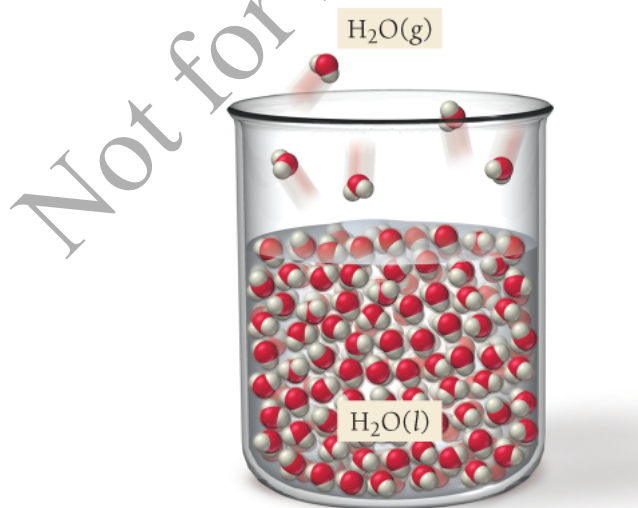
We now turn our attention to vaporization, the process by *which thermal energy can overcome intermolecular forces and produce a state change from liquid to gas*. We first introduce the process of vaporization itself, then we discuss the energetics of vaporization, and finally the concepts of vapor pressure, dynamic equilibrium, and critical point. Vaporization is a common occurrence that we experience every day and even depend on to maintain proper body temperature.

The Process of Vaporization

Imagine water molecules at room temperature in a beaker that is open to the atmosphere (Figure 11.20). The molecules are in constant motion due to thermal energy. If we could actually see the molecules at the surface, we would witness what Roald Hoffmann described as a “wild dance floor” (see the chapter-opening quote) because of all the vibrating, jostling, and molecular movement. *The higher the temperature, the greater the average energy of the collection of molecules*. However, at any one time, some molecules have more thermal energy than the average and some have less.

Figure 11.20 Vaporization of Water

Some molecules in an open beaker have enough kinetic energy to vaporize from the surface of the liquid.

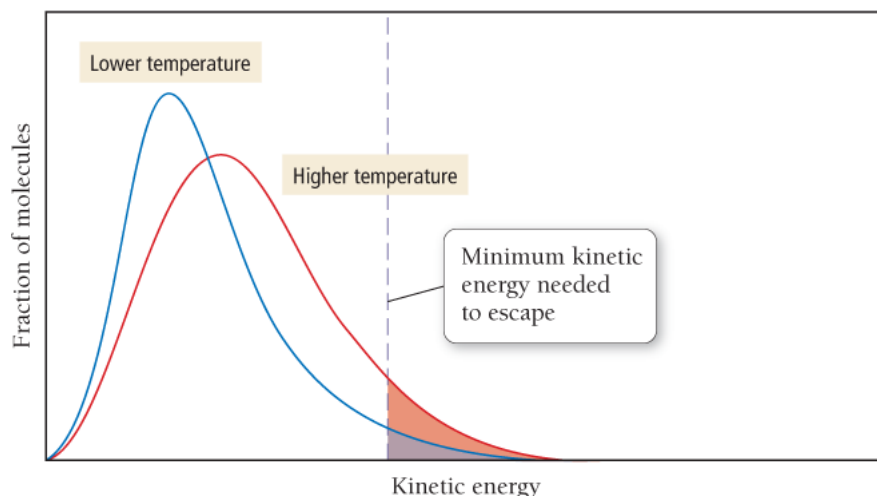


The distributions of thermal energies for the molecules in a sample of water at two different temperatures are shown in Figure 11.21. The molecules at the high end of the distribution curve have enough energy to break free from the surface—where molecules are held less tightly than in the interior due to fewer neighbor–neighbor hydrogen bonds—and into the gas state. This transition, from liquid to gas, is called **vaporization**. Some of the water molecules in the gas state, at the low end of the energy distribution

curve for the gaseous molecules, plunge back into the water and are captured by intermolecular forces. This transition, from gas to liquid, is the opposite of vaporization and is called **condensation**.

Figure 11.21 Distribution of Thermal Energy

The thermal energies of the molecules in a liquid are distributed over a range. The peak energy increases with increasing temperature.



Although both evaporation and condensation occur in a beaker open to the atmosphere, under normal conditions, evaporation takes place at a greater rate because most of the newly evaporated molecules escape into the surrounding atmosphere and never come back. The result is a noticeable decrease in the water level within the beaker over time (usually several days).

What happens if we increase the temperature of the water within the beaker? Because of the shift in the energy distribution to higher energies (see Figure 11.21), more molecules now have enough energy to break free and evaporate, so vaporization occurs more quickly. What happens if we spill the water on the table or floor? The same amount of water is now spread over a wider area, resulting in more molecules at the surface of the liquid. Molecules at the surface have the greatest tendency to evaporate—because they are held less tightly—so vaporization also occurs more quickly in this case. You probably know from experience that water in a beaker or glass may take many days to evaporate completely, while the same amount of water spilled on a table or floor typically evaporates within a few hours (depending on the conditions).

What happens if the liquid in the beaker is not water, but some other substance with weaker intermolecular forces, such as acetone (the main component in nail polish remover)? The weaker intermolecular forces allow more molecules to evaporate at a given temperature, increasing the rate of vaporization. We call liquids that vaporize easily **volatile**, and those that do not vaporize easily **nonvolatile**. Acetone is more volatile than water. Motor oil is virtually nonvolatile at room temperature.

Summarizing the Process of Vaporization:

- The rate of vaporization increases with increasing temperature.
- The rate of vaporization increases with increasing surface area.
- The rate of vaporization increases with decreasing strength of intermolecular forces.

The Energetics of Vaporization

To understand the energetics of vaporization, consider again a beaker of water from the molecular point of view. Now imagine that the beaker is thermally insulated so that heat from the surroundings

or heat, except when imagine that the beaker is extremely insulated so that heat from the surroundings cannot enter the beaker. What happens to the temperature of the water left in the beaker as molecules evaporate? To answer this question, think about the energy distribution curve again (see Figure 11.21). The molecules that leave the beaker are the ones at the high end of the energy curve—the most energetic. If no additional heat enters the beaker, the average energy of the entire collection of molecules decreases—much as the class average on an exam goes down if we eliminate the highest scores. Vaporization is an *endothermic* process; it takes energy to vaporize the molecules in a liquid. Another way to understand the endothermicity of vaporization is to remember that vaporization requires overcoming the intermolecular forces that hold liquids together. Because energy is needed to pull the molecules away from one another, the process is endothermic.

See Chapter 9 to review endothermic and exothermic processes.

Our bodies rely on the endothermic nature of vaporization for cooling. When we overheat, we sweat and our skin becomes covered with liquid water. As this water evaporates, it absorbs heat from the body, cooling the skin. A fan makes us feel cooler because it blows newly vaporized water away from our skin, allowing more sweat to vaporize and causing even more cooling. High humidity, on the other hand, slows down the net rate of evaporation, preventing cooling. When the air already contains large amounts of water vapor, our sweat evaporates more slowly, making the body's cooling system less efficient.



When we sweat, water evaporates from the skin. Since evaporation is endothermic, the result is a cooling effect.

Condensation, the opposite of vaporization, is exothermic—heat is released when a gas condenses to a liquid. If you have ever accidentally put your hand above a steaming kettle or opened a bag of microwaved popcorn too soon, you may have experienced a *steam burn*. As the steam condenses to a liquid on your skin, it releases a lot of heat, causing the burn. The condensation of water vapor is also the reason that winter overnight temperatures in coastal regions, which tend to have water vapor in the air, do not get as low as in deserts, which tend to have dry air. As the air temperature in a coastal area drops, water condenses out of the air, releasing heat and preventing the temperature from dropping further. In deserts, the air contains almost no moisture to condense, so the temperature drop is more extreme.

The amount of heat required to vaporize one mole of a liquid to gas is its heat (or enthalpy) of vaporization (ΔH_{vap}). The heat of vaporization of water at its normal boiling point of 100 °C is +40.7 kJ/mol.



The heat of vaporization is always positive because the process is endothermic—energy must be absorbed to vaporize a substance. The heat of vaporization is somewhat temperature-dependent. For example, at 25 °C the heat of vaporization of water is +44 kJ/mol, slightly more than it is at 100 °C because the water contains less thermal energy at 25 °C. Table 11.7 lists the heats of vaporization of several liquids at their boiling points and at 25 °C.

Table 11.7 Heats of Vaporization of Several Liquids at Their Boiling Points and at 25 °C

Liquid	Chemical Formula	Normal Boiling Point (°C)	ΔH_{vap} (kJ/mol) at Boiling Point	ΔH_{vap} (kJ/mol) at 25 (°C)
Water	H ₂ O	100.0	40.7	44.0
Rubbing alcohol (isopropyl alcohol)	C ₃ H ₈ O	82.3	39.9	45.4
Acetone	C ₃ H ₆ O	56.1	29.1	31.0
Diethyl ether	C ₄ H ₁₀ O	34.6	26.5	27.1

The sign conventions of ΔH were introduced in [Chapter 9](#).

When a substance condenses from a gas to a liquid, the same amount of heat is involved, but the heat is emitted rather than absorbed.



When 1.00 mol of water condenses, it releases 40.7 kJ of heat. The sign of ΔH in this case is negative because the process is exothermic.

We can use the heat of vaporization of a liquid to calculate the amount of energy required to vaporize a given mass of the liquid (or the amount of heat given off by the condensation of a given mass of liquid), using concepts similar to those covered in [Section 9.6](#). The heat of vaporization is like a conversion factor between the number of moles of a liquid and the amount of heat required to vaporize it (or the amount of heat emitted when it condenses), as demonstrated in [Example 11.3](#).

Example 11.3 Using the Heat of Vaporization in Calculations

Calculate the mass of water (in g) that can be vaporized at its boiling point with 155 kJ of heat.

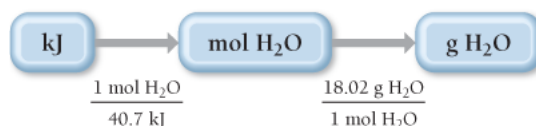
SORT You are given a certain amount of heat in kilojoules and asked to find the mass of water that can be vaporized.

GIVEN: 155 kJ

FIND: g H₂O

STRATEGIZE The heat of vaporization gives the relationship between heat absorbed and moles of water vaporized. Begin with the given amount of heat (in kJ) and convert to moles of water that can be vaporized. Use the molar mass as a conversion factor to convert from moles of water to mass of water.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$$\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol (at } 100^\circ\text{C)}$$

$$18.02 \text{ gH}_2\text{O} = 1 \text{ mol H}_2\text{O}$$

SOLVE Follow the conceptual plan to solve the problem.

SOLUTION

$$155 \text{ kJ} \times \frac{1 \text{ mol H}_2\text{O}}{40.7 \text{ kJ}} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 68.6 \text{ g H}_2\text{O}$$

FOR PRACTICE 11.3 Calculate the amount of heat (in kJ) required to vaporize 2.58 kg of water at its boiling point.

FOR MORE PRACTICE 11.3 Suppose that 0.48 g of water at 25 °C condenses on the surface of a 55 g block of aluminum that is initially at 25 °C. If the heat released during condensation goes only toward heating the metal, what is the final temperature (in °C) of the metal block? (The specific heat capacity of aluminum is 0.903 J/g °C).

Interactive Worked Example 11.3 Using the Heat of Vaporization in Calculations

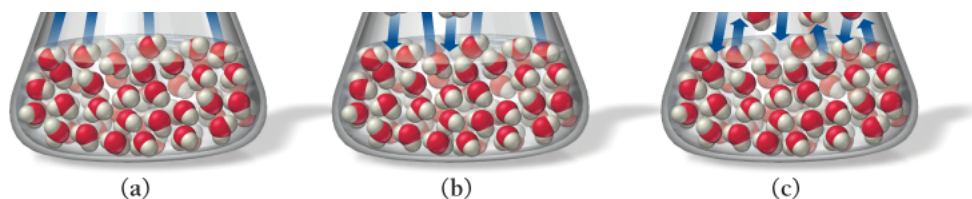
Vapor Pressure and Dynamic Equilibrium

We have already seen that if a container of water is left uncovered at room temperature, the water slowly evaporates away. But what happens if the container is sealed? Imagine a sealed evacuated flask—one from which the air has been removed—containing liquid water, as shown in Figure 11.22. Initially, the water molecules evaporate, as they did in the open beaker. However, because of the seal, the evaporated molecules cannot escape into the atmosphere. As water molecules enter the gas state, some start condensing back into the liquid. As the concentration (or partial pressure) of gaseous water molecules increases, the rate of condensation also increases. However, as long as the water remains at a constant temperature, the rate of evaporation remains constant. Eventually, the rate of condensation and the rate of vaporization become equal—in other words, **dynamic equilibrium** is reached (Figure 11.23). Condensation and vaporization continue at equal rates, and the concentration of water vapor above the liquid is constant.

Figure 11.22 Vaporization in a Sealed Flask

(a) When water is in a sealed container, water molecules begin to vaporize. (b) As water molecules build up in the gas state, they begin to recondense into the liquid. (c) When the rate of evaporation equals the rate of condensation, dynamic equilibrium is reached.

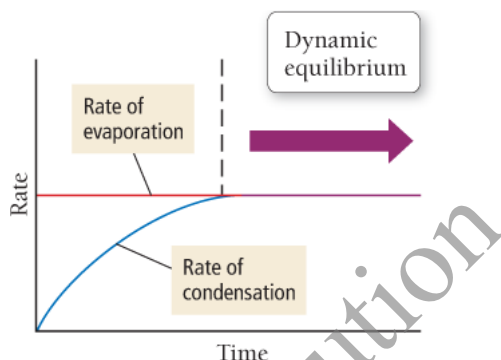




The pressure of a gas in dynamic equilibrium with its liquid is its **vapor pressure**. The vapor pressure of a particular liquid depends on the intermolecular forces present in the liquid and the temperature. Weak intermolecular forces result in volatile substances with high vapor pressures because the intermolecular forces are easily overcome by thermal energy. Strong intermolecular forces result in nonvolatile substances with low vapor pressures.

Figure 11.23 Dynamic Equilibrium

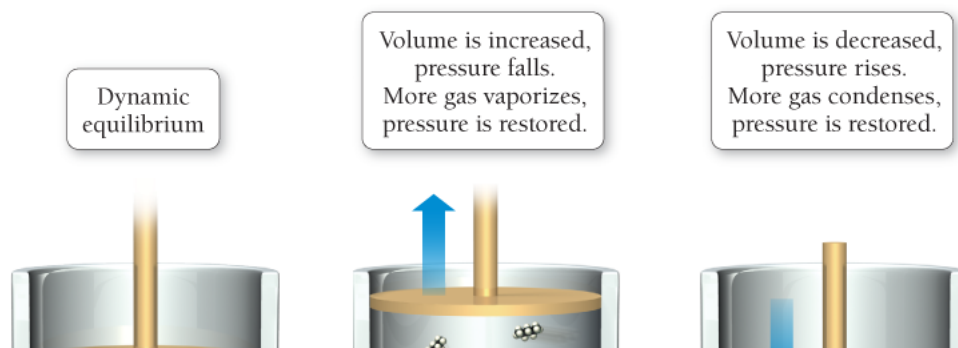
Dynamic equilibrium occurs when the rate of condensation is equal to the rate of evaporation.

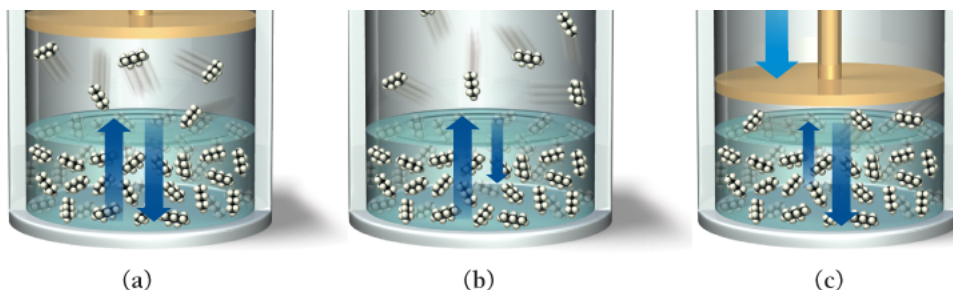


A liquid in dynamic equilibrium with its vapor is a balanced system that tends to return to equilibrium if disturbed. For example, consider a sample of *n*-pentane (a component of gasoline) at 25 °C in a cylinder equipped with a moveable piston (Figure 11.24a). The cylinder contains no other gases except *n*-pentane vapor in dynamic equilibrium with the liquid. Because the vapor pressure of *n*-pentane at 25 °C is 510 mmHg, the pressure in the cylinder is 510 mmHg. What happens when we move the piston upward to expand the volume within the cylinder? Initially, the pressure in the cylinder drops below 510 mmHg, in accordance with Boyle's law. Then, however, more liquid vaporizes until equilibrium is reached once again (Figure 11.24b). If we expand the volume of the cylinder again, the same thing happens—the pressure initially drops and more *n*-pentane vaporizes to bring the system back into equilibrium. Further expansion causes the same result as long as any liquid *n*-pentane remains in the cylinder.

Figure 11.24 Dynamic Equilibrium in *n*-Pentane

(a) Liquid *n*-pentane is in dynamic equilibrium with its vapor. (b) When the volume is increased, the pressure drops and some liquid converts to gas to bring the pressure back up. (c) When the volume is decreased, the pressure increases and some gas converts to liquid to bring the pressure back down.





Boyle's law is discussed in [Section 10.4](#).

Conversely, what happens if we lower the piston, decreasing the volume in the cylinder? Initially, the pressure in the cylinder rises above 510 mmHg, but then some of the gas condenses into liquid until equilibrium is reached again ([Figure 11.24c](#)).

We describe the tendency of a system in dynamic equilibrium to return to equilibrium with the following general statement:

When a system in dynamic equilibrium is disturbed, the system responds to minimize the disturbance and return to a state of equilibrium.

If the pressure above a liquid–vapor system in equilibrium decreases, some of the liquid evaporates, restoring the equilibrium pressure. If the pressure increases, some of the vapor condenses, bringing the pressure back down to the equilibrium pressure. This basic principle—*Le Châtelier's principle*—is applicable to any chemical system in equilibrium, as we shall see in [Chapter 15](#).

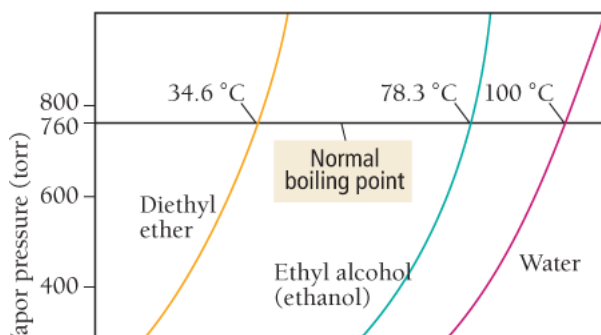
Conceptual Connection 11.5 Vapor Pressure

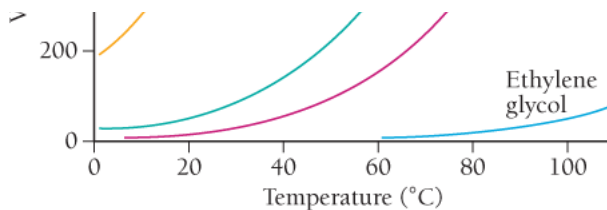
Temperature Dependence of Vapor Pressure and Boiling Point

When the temperature of a liquid increases, its vapor pressure rises because the higher thermal energy increases the number of molecules that have enough energy to vaporize (see [Figure 11.21](#)). Because of the shape of the thermal energy distribution curve, a small change in temperature makes a large difference in the number of molecules that have enough energy to vaporize, which results in a large increase in vapor pressure. For example, the vapor pressure of water at 25 °C is 23.3 torr, while at 60 °C the vapor pressure is 149.4 torr. [Figure 11.25](#) shows the vapor pressure of water and several other liquids as a function of temperature.

Figure 11.25 Vapor Pressure of Several Liquids at Different Temperatures

At higher temperatures, more molecules have enough thermal energy to escape into the gas state, so vapor pressure increases with increasing temperature.





The **boiling point** of a liquid is the temperature at which the liquid's vapor pressure equals the external pressure. When a liquid reaches its boiling point, the thermal energy is enough for molecules in the interior of the liquid (not just those at the surface) to break free of their neighbors and enter the gas state (Figure 11.26). The bubbles in boiling water are pockets of gaseous water that have formed within the liquid water. The bubbles float to the surface and leave as gaseous water or steam.

The **normal boiling point** of a liquid is the temperature at which its vapor pressure equals 1 atm. The normal boiling point of pure water is 100 °C. However, at a lower pressure, water boils at a lower temperature. In Denver, Colorado, where the altitude is around 1600 m (5200 ft) above sea level, for example, the average atmospheric pressure is about 83% of what it is at sea level, and water boils at approximately 94 °C. For this reason, it takes slightly longer to cook food in boiling water in Denver than in San Francisco, California (which is at sea level). Table 11.8 shows the boiling point of water at several locations of varied altitudes.

Table 11.8 Boiling Points of Water at Several Locations of Varied Altitudes

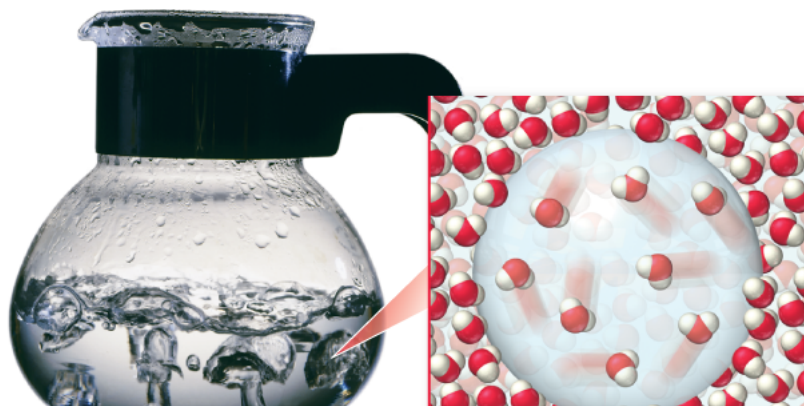
Location	Elevation (ft)	Approximate Pressure (atm)*	Approximate Boiling Point of Water (°C)
Mount Everest, Tibet (highest mountain peak on Earth)	29,035	0.32	78
Mount McKinley (Denali), Alaska (highest mountain peak in North America)	20,320	0.46	83
Mount Whitney, California (highest mountain peak in 48 contiguous United States)	14,495	0.60	87
Denver, Colorado (mile high city)	5,280	0.83	94
Boston, Massachusetts (sea level)	20	1.0	100

*The atmospheric pressure in each of these locations is subject to weather conditions and can vary significantly from the

Figure 11.26 Boiling

A liquid boils when thermal energy is high enough to cause molecules in the interior of the liquid to become gaseous, forming bubbles that rise to the surface. Sometimes you see bubbles begin to form in hot water below 100 °C. These bubbles are dissolved air—not gaseous water—leaving the liquid.

When a liquid boils, molecules in the interior of the liquid become gaseous.

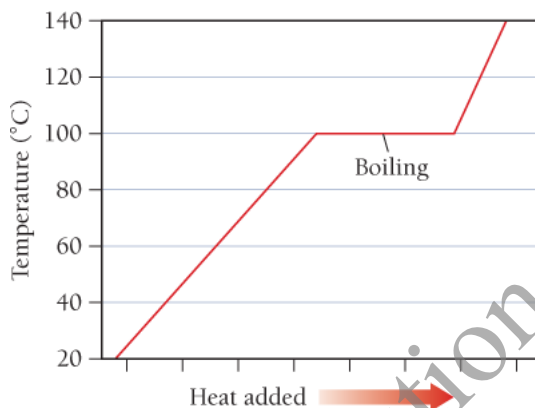




Once the boiling point of a liquid is reached, additional heating only causes more rapid boiling; it does not raise the temperature of the liquid above its boiling point, as shown in the *heating curve* in [Figure 11.27](#). Therefore, at 1 atm, boiling water always has a temperature of 100 °C. *As long as liquid water is present, its temperature cannot rise above its boiling point.* After all the water has been converted to steam, the temperature of the steam can rise beyond 100 °C.

Figure 11.27 The Temperature During Boiling

The temperature of water during boiling remains at 100 °C.



Now, let's return to [Figure 11.25](#). As we can see from the graph, the vapor pressure of a liquid increases with increasing temperature. However, *the relationship is not linear.* In other words, doubling the temperature results in more than a doubling of the vapor pressure. The relationship between vapor pressure and temperature is exponential, and we express it as:

[11.1]

$$P_{\text{vap}} = \beta \exp\left(\frac{-\Delta H_{\text{vap}}}{RT}\right)$$

In this expression P_{vap} is the vapor pressure, β is a constant that depends on the gas, ΔH_{vap} is the heat of vaporization, R is the gas constant (8.314 J/mol · K), and T is the temperature in kelvins. We can rearrange [Equation 11.1](#) by taking the natural logarithm of both sides:

[11.2]

$$\ln P_{\text{vap}} = \ln \left[\beta \exp\left(\frac{-\Delta H_{\text{vap}}}{RT}\right) \right]$$

Because $\ln AB = \ln A + \ln B$ we can rearrange the right side of [Equation 11.2](#):

[11.3]

$$\ln P_{\text{vap}} = \ln \beta + \ln \left[\exp\left(\frac{-\Delta H_{\text{vap}}}{RT}\right) \right]$$

Because $e^x = x$ (see [Appendix IB](#)), we can simplify [Equation 11.3](#):

$$\ln P_{\text{vap}} = \ln \beta + \frac{-\Delta H_{\text{vap}}}{RT}$$

A slight additional rearrangement gives the important result:

$$\ln P_{\text{vap}} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + \ln \beta$$

Clausius–Clapeyron equation

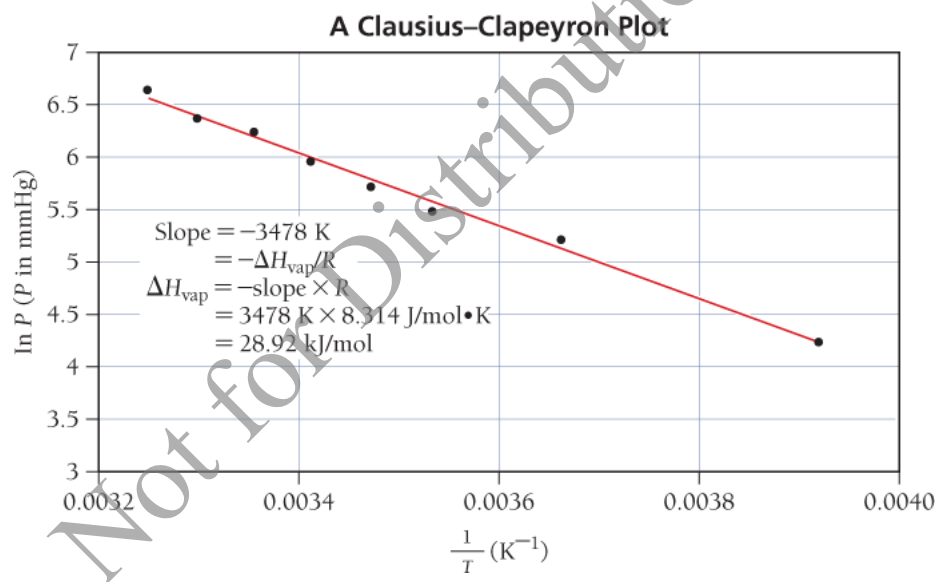
$$y = m(x) + b$$

Equation for a straight line

Notice the parallel relationship between the **Clausius–Clapeyron equation** and the equation for a straight line. Just as a plot of y versus x yields a straight line with slope m and intercept b , so a plot of $\ln P_{\text{vap}}$ (equivalent to y) versus $1/T$ (equivalent to x) gives a straight line with slope $-\Delta H_{\text{vap}}/R$ (equivalent to m) and y -intercept $\ln \beta$ (equivalent to b), as shown in **Figure 11.28**. The Clausius–Clapeyron equation gives a linear relationship—not between the vapor pressure and the temperature (which have an exponential relationship)—but between the *natural log* of the vapor pressure and the *inverse* of temperature. This is a common technique in the analysis of chemical data. If two variables are not linearly related, it is often convenient to find ways to graph *functions of those variables* that are linearly related.

Figure 11.28 A Clausius–Clapeyron Plot for Diethyl Ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$)

A plot of the natural log of the vapor pressure versus the inverse of the temperature in K yields a straight line with slope $-\Delta H_{\text{vap}}/R$.



When we use the Clausius–Clapeyron equation in this way, we ignore the relatively small temperature dependence of ΔH_{vap} .

The Clausius–Clapeyron equation leads to a convenient way to measure the heat of vaporization in the laboratory. We measure the vapor pressure of a liquid as a function of temperature and create a plot of the natural log of the vapor pressure versus the inverse of the temperature. We can then determine the slope of the line to find the heat of vaporization, as demonstrated in **Example 11.4**.

Example 11.4 Using the Clausius–Clapeyron Equation to Determine Heat of Vaporization from Experimental Measurements of Vapor Pressure

The vapor pressure of dichloromethane is measured as a function of temperature, and the following

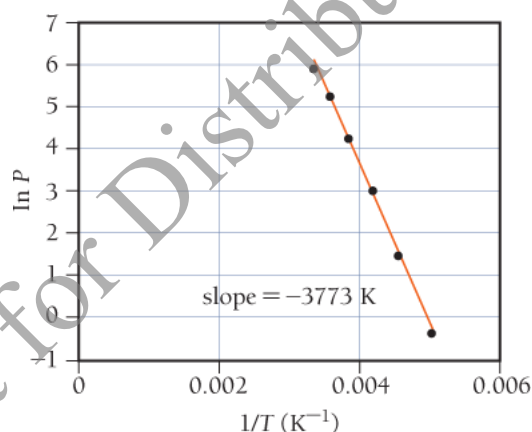
results are obtained:

Temperature (K)	Vapor Pressure (torr)
200	0.8
220	4.5
240	21
260	71
280	197
300	391

Determine the heat of vaporization of dichloromethane.

SOLUTION To find the heat of vaporization, use an Excel™ spreadsheet or a graphing calculator to make a plot of the natural log of vapor pressure ($\ln P$) as a function of the inverse of the temperature in kelvins ($1/T$). Fit the points to a line and determine the slope of the line. The slope of the best-fitting line is -3773 K . Because the slope equals $-\Delta H_{\text{vap}}/R$, we find the heat of vaporization as follows:

$$\begin{aligned}\text{slope} &= -\Delta H_{\text{vap}}/R \\ \Delta H_{\text{vap}} &= -\text{slope} \times R \\ &= -(-3773 \text{ K})(8.314 \text{ J/mol} \cdot \text{K}) \\ &= 31.4 \times 10^4 \text{ J/mol} \\ &= 31.4 \text{ kJ/mol}\end{aligned}$$



FOR PRACTICE 11.4 The vapor pressure of carbon tetrachloride is measured as a function of the temperature, and the following results are obtained:

Temperature (K)	Vapor Pressure (torr)
255	11.3
265	21.0
275	36.8
285	61.5
295	99.0
300	123.8

Determine the heat of vaporization of carbon tetrachloride.

The Clausius–Clapeyron equation can also be expressed in a two-point form that we can use with just two measurements of vapor pressure and temperature to determine the heat of vaporization:

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{Clausius–Clapeyron equation (two-point form)}$$

We can use this two-point form of the equation to predict the vapor pressure of a liquid at any temperature if we know the enthalpy of vaporization and the normal boiling point (or the vapor pressure at some other temperature), as demonstrated in [Example 11.5](#).

The two-point method is generally inferior to plotting multiple points because fewer data points result in more chance for error.

Example 11.5 Using the Two-Point Form of the Clausius–Clapeyron Equation to Predict the Vapor Pressure at a Given Temperature

Methanol has a normal boiling point of 64.6 °C and a heat of vaporization (ΔH_{vap}) of 35.2 kJ/mol. What is the vapor pressure of methanol at 12.0 °C?

SORT You are given the normal boiling point of methanol (the temperature at which the vapor pressure is 760 mmHg) and the heat of vaporization. You are asked to find the vapor pressure at a specified temperature that is also given.

GIVEN:

$$\begin{aligned} T_1 (\text{°C}) &= 64.6 \text{°C} & P_1 &= 760 \text{ torr} \\ \Delta H_{\text{vap}} &= 35.2 \text{ kJ/mol} & T_2 (\text{°C}) &= 12.0 \text{°C} \end{aligned}$$

FIND: P_2

STRATEGIZE The conceptual plan is essentially the Clausius–Clapeyron equation, which relates the given and find quantities.

CONCEPTUAL PLAN

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

(Clausius–Clapeyron equation, two-point form)

SOLVE First, convert T_1 and T_2 from °C to K.

Substitute the required values into the Clausius–Clapeyron equation and solve for P_2 . Use the heat of vaporization in J/mol for the correct canceling of units with J in R.

SOLUTION

$$\begin{aligned} T_1 (\text{K}) &= T_1 (\text{°C}) + 273.15 \\ &= 64.6 + 273.15 \\ &= 337.8 \text{ K} \end{aligned}$$

$$T_2 (\text{K}) = T_2 (\text{°C}) + 273.15$$

$$T_2 = 12.0 + 273.15$$

$$= 12.0 + 273.15$$

$$= 285.2 \text{ K}$$

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{P_2}{P_1} = \frac{-35.2 \times 10^3 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{285.2 \text{ K}} - \frac{1}{337.8 \text{ K}} \right)$$

$$= -2.31$$

$$\frac{P_2}{P_1} = e^{-2.31}$$

$$P_2 = P_1(e^{-2.31})$$

$$= 760 \text{ torr} (0.0993) = 75.4 \text{ torr}$$

CHECK The units of the answer are correct. The magnitude of the answer makes sense because vapor pressure should be significantly lower at the lower temperature.

FOR PRACTICE 11.5 Propane has a normal boiling point of -42.0°C and a heat of vaporization (ΔH_{vap}) of 19.04 kJ/mol . What is the vapor pressure of propane at 25.0°C ?

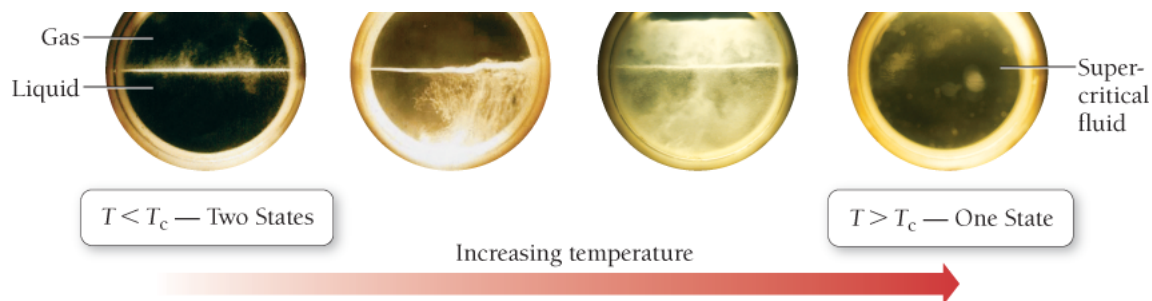
Interactive Worked Example 11.5 Using the Two-Point Form of the Clausius–Clapeyron Equation to Predict the Vapor Pressure at a Given Temperature

The Critical Point: The Transition to an Unusual State of Matter

We have considered the vaporization of a liquid in a container open to the atmosphere with and without heating, and the vaporization of a liquid in a *sealed* container without heating. We now examine the vaporization of a liquid in a *sealed* container *during heating*. Consider liquid *n*-pentane in equilibrium with its vapor in a sealed container initially at 25°C . At this temperature, the vapor pressure of *n*-pentane is 0.67 atm . What happens if we heat the liquid? As the temperature rises, more *n*-pentane vaporizes, and the pressure within the container increases. At 100°C , the pressure is 5.5 atm , and at 190°C the pressure is 29 atm . As the temperature and pressure increase, more and more gaseous *n*-pentane is forced into the same amount of space, and the density of the *gas* gets higher and higher. At the same time, the increasing temperature causes the density of the *liquid* to become lower and lower. At 197°C , the meniscus between the liquid and gaseous *n*-pentane disappears, and the gas and liquid states commingle to form a *supercritical fluid* (Figure 11.29). For any substance, the *temperature* at which this transition to supercritical fluid occurs is the **critical temperature** (T_c). The liquid cannot exist (regardless of pressure) above this temperature. The *pressure* at which this transition occurs is the **critical pressure** (P_c).

Figure 11.29 Critical Point Transition

As *n*-pentane is heated in a sealed container, it undergoes a transition to a supercritical fluid. At the critical point, the meniscus separating the liquid and gas disappears, and the fluid becomes supercritical—neither a liquid nor a gas.



Researchers are interested in supercritical fluids because of their unique properties. A supercritical fluid has properties of both liquids and gases—it is in some sense intermediate between the two. Supercritical fluids can act as good solvents, selectively dissolving a number of compounds. For example, supercritical carbon dioxide is used as a solvent to extract caffeine from coffee beans. The caffeine dissolves in the supercritical carbon dioxide, but other substances—such as those responsible for the flavor of coffee—do not dissolve. Consequently, the caffeine is removed without substantially altering the coffee's flavor. The supercritical carbon dioxide is easily removed from a mixture by lowering the pressure below the critical pressure, at which point the carbon dioxide evaporates, leaving no residue.

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