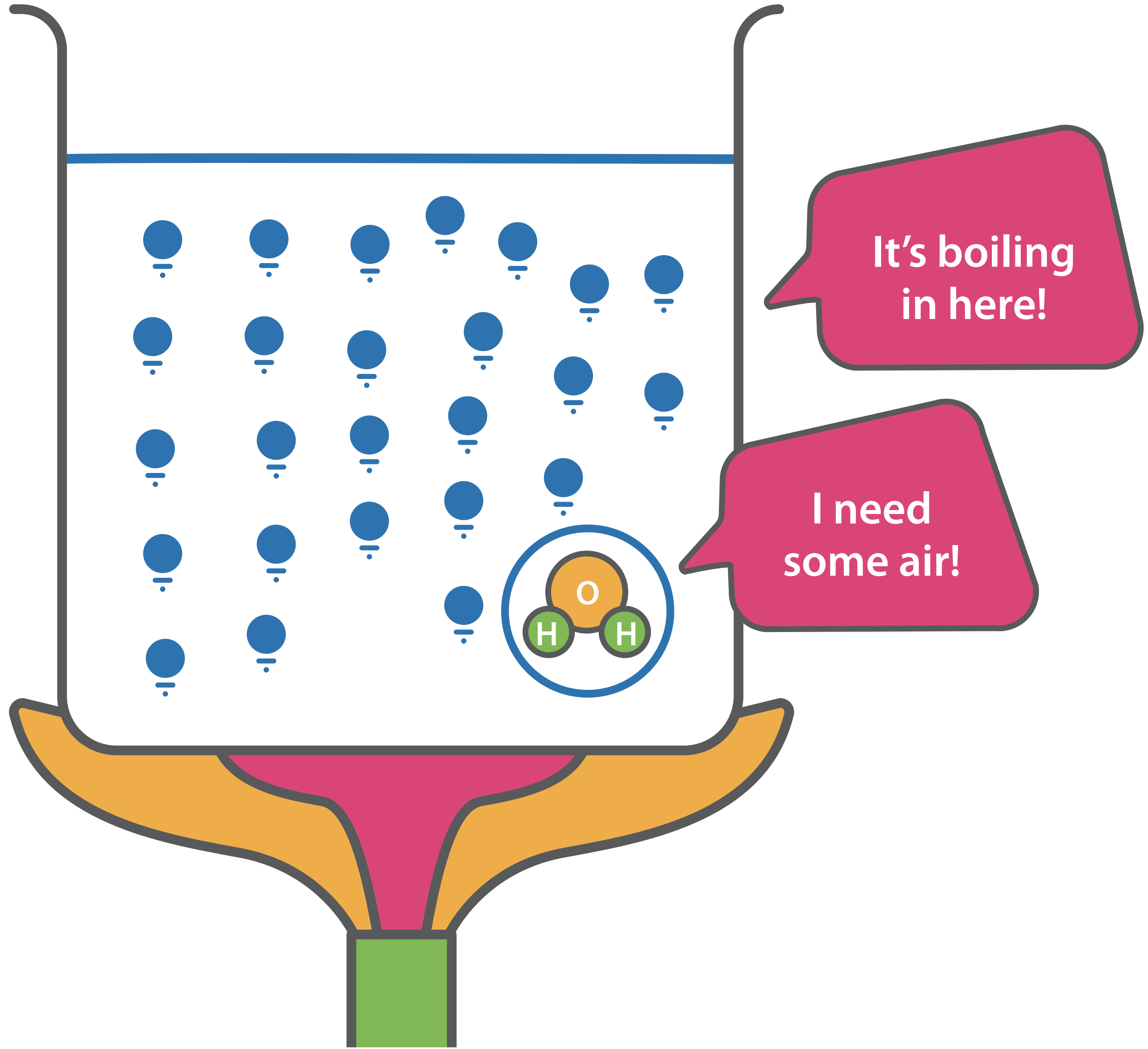
Vapor Pressure



Lesson Objectives

You will be able to

- define and explain vapor pressure,
- describe and explain the effect vapor pressure has on the melting and boiling points of a substance,
- describe and explain how the addition of salts to pure liquids affects the vapor pressure and hence the melting and boiling points,
- identify the relative volatility of a liquid from its vapor pressure,
- outline experimental procedures to measure the vapor pressure of a liquid,
- use experimental data and diagrams to predict the relative temperature or volatility of a liquid,
- calculate the boiling point elevation and freezing point depression when a salt is dissolved in a solvent.

What Is Vapor Pressure?

Imagine a closed container of liquid, such as a sealed jar of water, at room temperature.

If we examine the jar, it may not seem like anything is happening to the water molecules inside.

However, there is a dynamic equilibrium in the jar of water between the process of evaporation and condensation.

Evaporation occurs when molecules escape the liquid phase and become a vapor because those molecules have enough kinetic energy to overcome the intermolecular forces that keep the molecules together in the liquid phase.

At any temperature, even room temperature, some molecules will always be able to evaporate from liquid water.

Definition: Intermolecular Forces

Intermolecular forces are the forces of attraction or repulsion that act between neighboring particles such as atoms, molecules, or ions.

What Is Vapor Pressure? (Continued)

At the same time, some of the water molecules will condense back into the liquid phase as they lose energy and collide with the surface of the liquid.

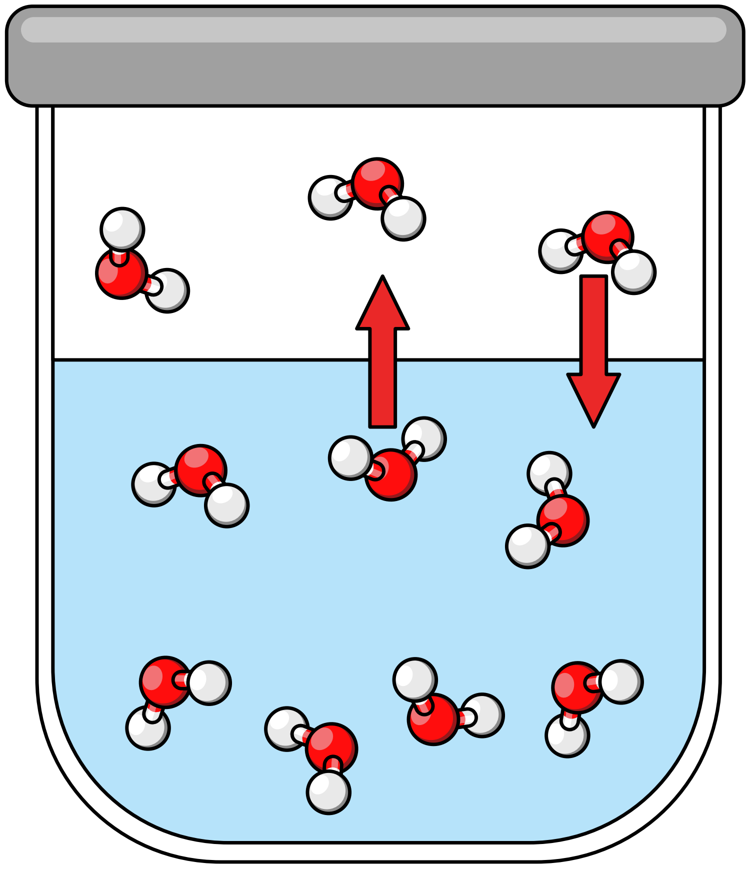
This creates an equilibrium between evaporation and condensation processes in the jar.

There is a relatively constant amount of vapor above the surface of the water because the rates of evaporation and condensation are essentially equivalent.

Any gas will exert pressure on a surface.

For example, atmospheric pressure is due to the gases in the air exerting pressure on a surface.

The vapor in the jar will exert a pressure on the surface of the liquid, which is called the vapor pressure.



Definition: Vapor Pressure

Vapor pressure is the pressure exerted by a vapor above its liquid (or solid) when they are at dynamic equilibrium and in a closed system at constant temperature and pressure.

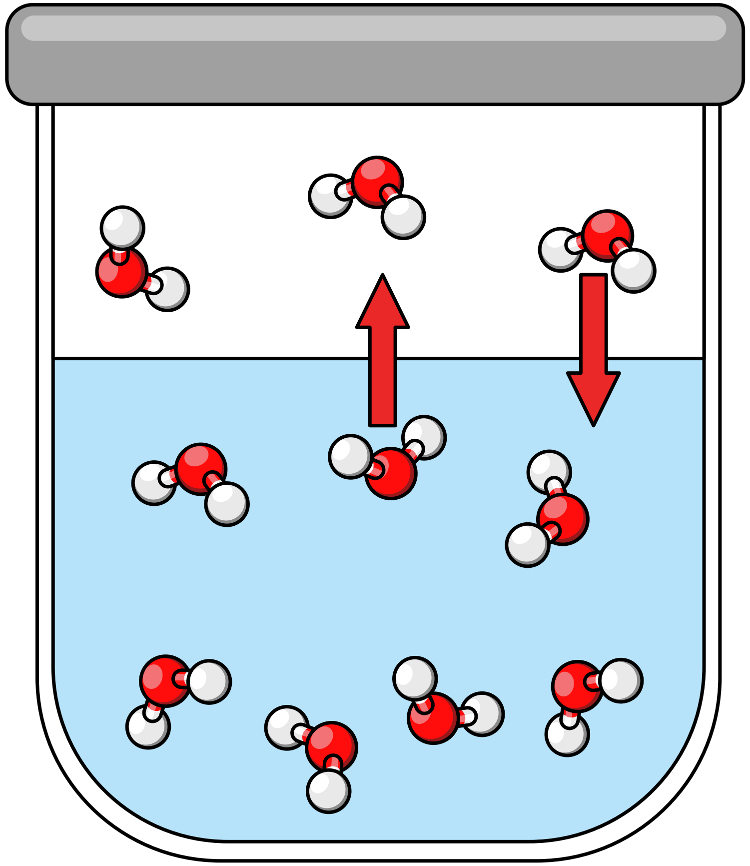
What Is Vapor Pressure? (Continued)

The vapor pressure in the jar of water will be constant as long as the equilibrium in the jar is not disturbed.

However, there are several factors that can affect the vapor pressure.

If we increase the temperature of the jar of water, more water molecules will have enough kinetic energy to escape the liquid phase and enter the vapor (gaseous) phase.

This will cause the vapor pressure to increase because there are more water molecules in the vapor phase.



What Is Vapor Pressure? (Continued)

Increasing the temperature will continue to increase the vapor pressure until the vapor pressure is equal to the pressure outside the container.

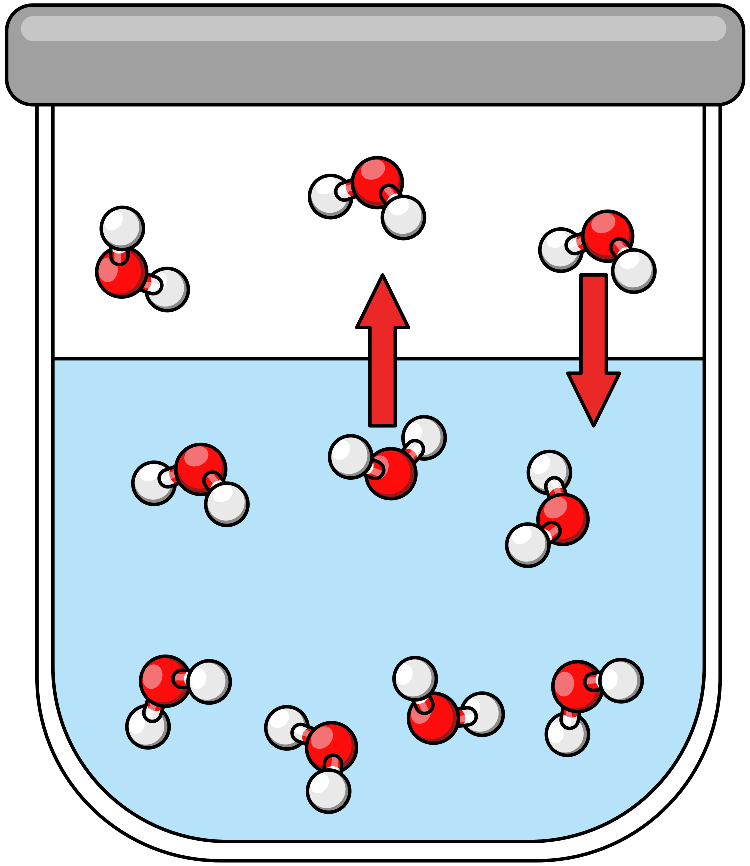
At this point, the water has reached its boiling point and it will begin to boil.

If the container is open instead of closed, the water will boil when the vapor pressure equals the atmospheric pressure.

The temperature at which a liquid boils can be used to indicate the purity of that liquid.

If the normal boiling point of a liquid is equal to its measured boiling point, then the liquid is pure.

However, if the normal boiling point is different from the measured boiling point, then the liquid likely contains impurities.



What Is Vapor Pressure? (Continued)

The identity of the liquid will also affect the vapor pressure because the strength of the intermolecular forces between the molecules of a liquid affects the rate of evaporation.

If the intermolecular forces are weak, it will require less energy for molecules of that substance to become a vapor.

Therefore, when comparing the vapor pressure of two substances at the same temperature, the substance with weaker intermolecular forces will have a higher vapor pressure.

This also explains the difference in boiling points between liquids.

If a liquid has a higher vapor pressure, the temperature of the liquid will not need to increase as much for the vapor pressure to reach the external pressure.

In other words, substances with weak intermolecular forces will have high vapor pressures and lower boiling points.

What Is Vapor Pressure? (Continued)

For example, let's compare water and bromine. Bromine has a vapor pressure of 0.3 atm at 25°C and boils at 59°C.

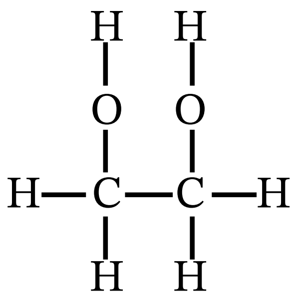
Water has a vapor pressure of 0.03 atm at 25°C and boils at 100°C.

Bromine molecules experience relatively weak London dispersion forces, while water molecules experience stronger hydrogen bonding intermolecular interactions.

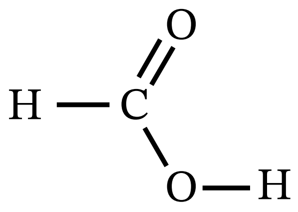
This difference in intermolecular attraction forces explains why bromine has a higher vapor pressure and lower boiling point than water.

Example 1: Determining Which Liquid Will Have the Greatest Vapor Pressure Given the Displayed Formula

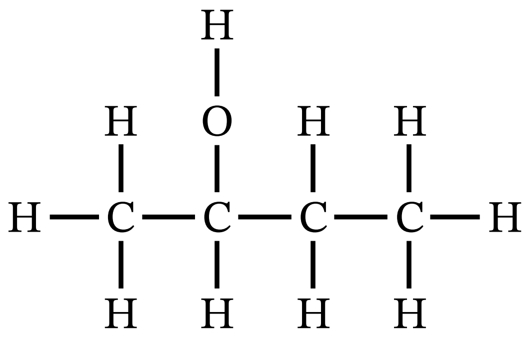
Which of the following liquids would have the greatest vapor pressure at 25°C?



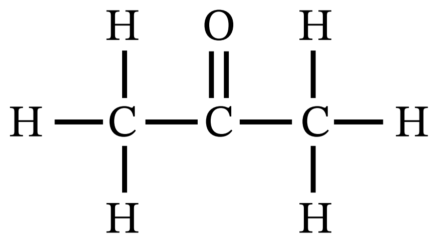
(A)



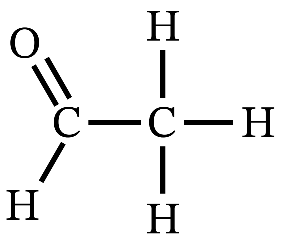
(B)



(C)



(D)



(E)

Example 1 (Continued)

Answer

The vapor pressure of a liquid is the equilibrium pressure exerted by a vapor on the surface of the liquid phase. This vapor above the surface of the liquid is produced by the process of evaporation.

Substances with weaker intermolecular forces evaporate more readily, and this causes them to have a relatively high vapor pressure value. Therefore, the liquid with the greatest vapor pressure will be the one that has the weakest intermolecular forces.

The structures shown in options A, B, and C all have a hydrogen atom bonded to an oxygen atom, meaning that there will be hydrogen bonding between the molecules of these liquids.

Hydrogen bonding is an extremely strong intermolecular force, so these liquids should have a lower vapor pressure than liquids that cannot form hydrogen bonds.

Options D and E do not have the capacity to form hydrogen bonds, and they must be held together with weaker intermolecular forces than options A, B, or C.

Example 1 (Continued)

Options D and E both have a polar CO bond, so they will have similar dipole–dipole intermolecular interactions.

Additionally, the liquids will have London dispersion forces, which are present between any covalently bonded molecules.

The strength of London dispersion forces depends on molecular mass values.

Heavier molecules experience stronger London dispersion forces and lighter molecules experience weaker London dispersion forces. Option D is heavier than option E.

The option D molecule should experience stronger intermolecular forces of attraction than the option E molecule.

The option E molecule must have the greatest vapor pressure because it experiences the weakest intermolecular forces of attraction. So, the correct answer is choice E.

The Relation between the Volatility and Vapor Pressure

The vapor pressure of a substance can be related to its volatility.

The volatility of a substance indicates how readily it evaporates.

There is no quantitative measurement of volatility, but we can observe some trends and relationships between volatility, vapor pressure, and boiling point.

The more volatile a substance is, the greater its vapor pressure is at a given temperature.

A volatile substance will therefore have a high vapor pressure and readily evaporate.

Typically, a substance with a high volatility will have a low boiling point.

The Relation between the Volatility and Vapor Pressure (Continued)

The table below lists the vapor pressure of several liquids at 20°C.

Liquid	**Vapor Pressure at** 20°C (kPa)	**Boiling point** (°C)
Water	2.339	100.0
Diethyl ether	58.662	34.6
Ethylene glycol	0.008	197.3
Ethanol	5.950	78.2

The data in the table show that diethyl ether has the greatest vapor pressure at the given temperature and therefore is the most volatile.

Furthermore, diethyl ether also has the lowest boiling point of the liquids given in the table.

Alternatively, the vapor pressure of ethylene glycol is very low and is therefore a relatively nonvolatile substance.

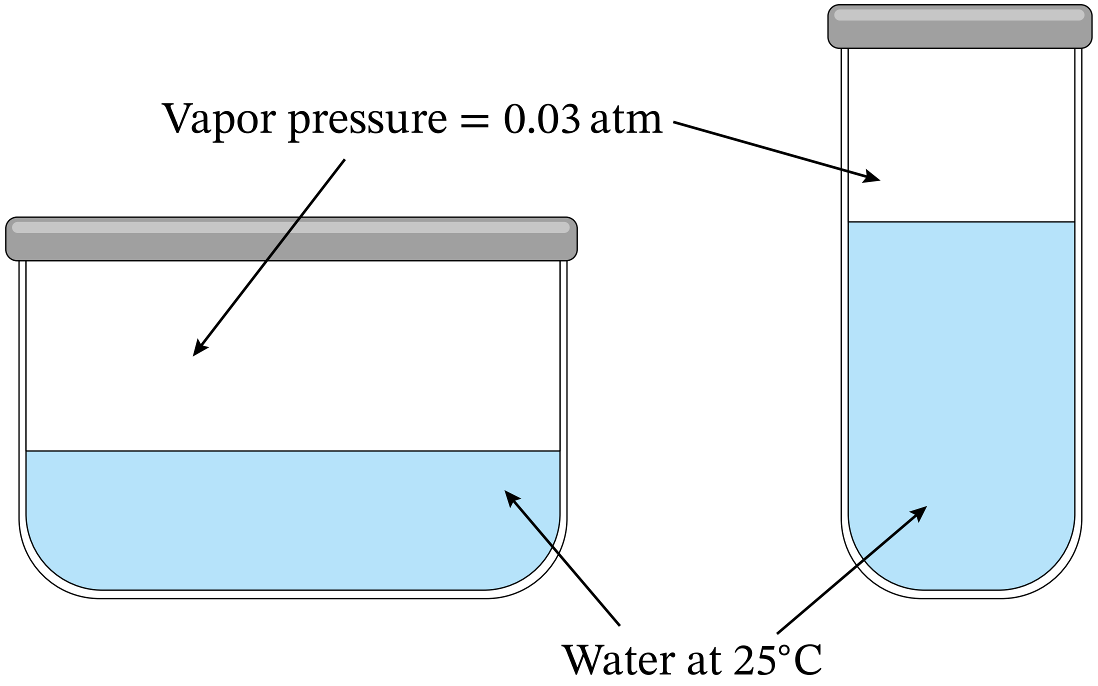
Colligative Properties and Vapor Pressure

It may seem like surface area would impact the vapor pressure of a liquid because the rate of evaporation is higher when the surface area is larger.

However, the surface area has no effect on vapor pressure.

Increasing the surface area also increases the rate of condensation because the vapor molecules can collide with a larger liquid surface area.

The vapor pressure stays the same as the surface area increases because the rates of evaporation and condensation increase at the same rate.



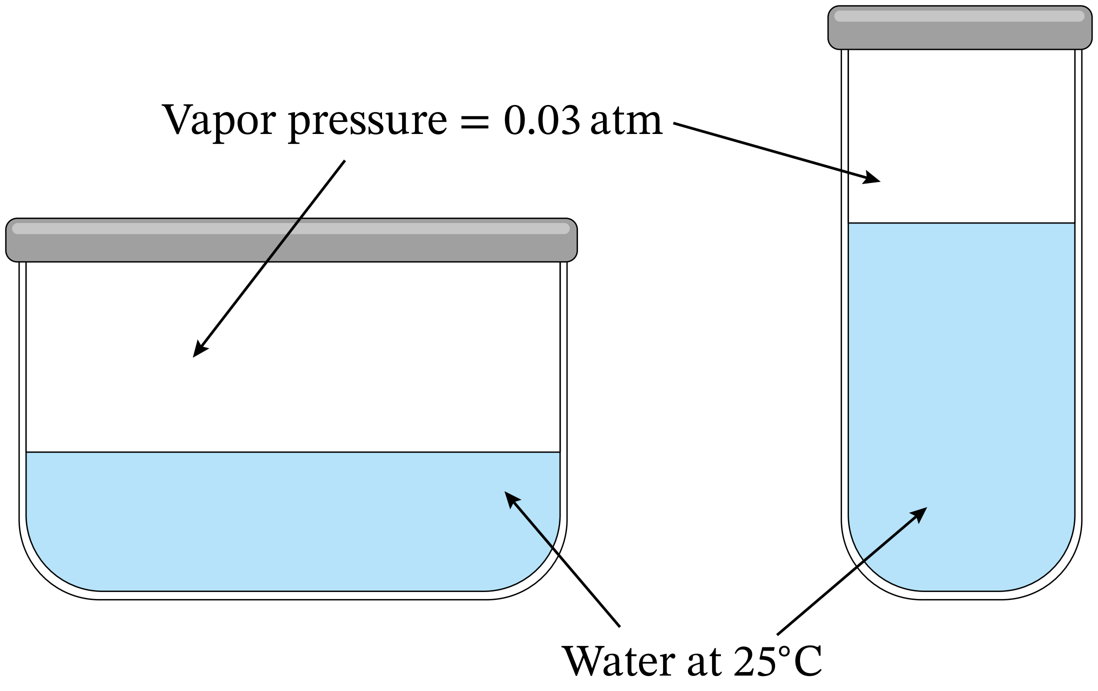
Colligative Properties and Vapor Pressure (Continued)

The final factor that affects the vapor pressure of a liquid is the presence of a solute, such as a salt.

When a nonvolatile solute is dissolved into a solvent, the properties of the solution differ from those of the pure solvent.

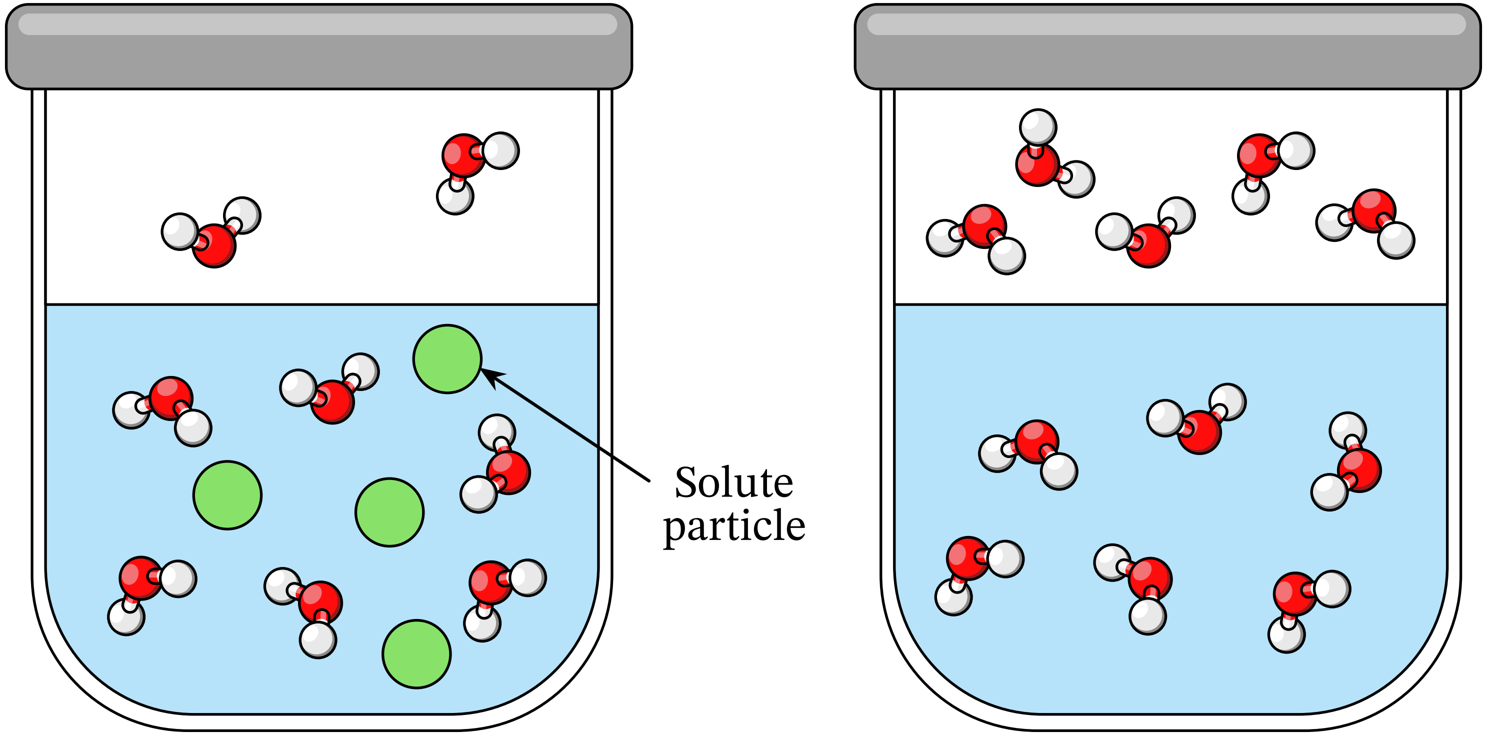
These properties are known collectively as colligative properties and include vapor pressure lowering, boiling point elevation, and freezing point depression.

Colligative properties are affected by the ratio of the number of solute particles to the number of solvent particles.



Colligative Properties and Vapor Pressure

Solute particles will interfere with the ability of the solvent molecules to escape the liquid phase, and this tends to decrease the vapor pressure.



Definition: Colligative Properties

Colligative properties are the properties of a solution that depend on the number of solute particles but not on the identity of the solute.

Example 2: Identifying Factors That Affect the Vapor Pressure of a Liquid

Which of the following factors does **not** affect the vapor pressure of a liquid?

A. Concentration of solutions
B. Volume of the liquid
C. Temperature
D. Intermolecular forces

Answer

The vapor pressure of a liquid is the equilibrium pressure exerted by the vapor on the surface of the liquid phase.

The amount of vapor above the surface of the liquid, and therefore the vapor pressure, remains constant over time due to a dynamic equilibrium between the evaporation and condensation processes.

Example 2 (Continued)

Any factor that increases or decreases the rate of evaporation without affecting the rate of condensation will change the vapor pressure of the liquid.

If a solute is added to a liquid, the liquid molecules will not be able to evaporate as readily, which would decrease the vapor pressure.

The more solute is added to the liquid, the more the vapor pressure tends to decrease. This means the concentration of solutions, answer choice A, does affect the vapor pressure of a liquid.

If the volume of a liquid increases, the rate of evaporation generally would not change.

However, the rate of evaporation would increase if the surface area increased as well.

Even in this case, the rate of condensation would also increase by the same amount, causing no change to the vapor pressure.

So, answer choice B does **not** affect the vapor pressure of liquid and is the correct answer.

Example 2 (Continued)

Increasing the temperature increases the kinetic energy of molecules.

This means the rate of evaporation will increase because more molecules in the liquid phase will be able to overcome the intermolecular forces that hold them together.

The vapor pressure will increase with temperature because the rate of evaporation increases with temperature.

Intermolecular forces determine the forces of the attraction between molecules in any liquid. Molecules have to overcome intermolecular forces of attraction to escape from a liquid and enter into a vapor or gaseous state.

A liquid with stronger intermolecular forces will not evaporate as easily as liquids with weaker intermolecular forces.

Example 2 (Continued)

In other words, liquids with stronger intermolecular forces generally have a lower vapor pressure than liquids with weaker intermolecular forces.

The only answer choice that does **not** affect the vapor pressure of the factors given is the volume of the liquid, answer choice B.

Colligative Properties and Vapor Pressure (Continued)

The vapor pressure will become progressively lower as more particles are added to a liquid. This means that substances will have a low vapor pressure if they contain a high concentration of a nonelectrolyte substance such as a monosaccharide or disaccharide sugar.

Substances will have even lower vapor pressure values if they contain the same concentration of a substance that can dissolve in water because the substance can break down into a greater number of particles.

The colligative properties, such as vapor pressure lowering, are also affected by whether the solute is an electrolyte or a nonelectrolyte.

Sucrose, sodium chloride (NaCl), and calcium chloride ($CaCl_2$) will all dissolve in water.

However, as a nonelectrolyte, when sucrose is dissolved in water, only one particle is produced.

In other words, the sucrose does not dissociate into ions; 1 mole of sucrose will produce 1 mole of sucrose.

Colligative Properties and Vapor Pressure (Continued)

When a strong electrolyte such as NaCl is dissolved in water, each mole of NaCl dissolves to produce 2 moles of ions in solution: 1 mole of Na^+ ions and 1 mole of Cl^- ions.

Compared with sucrose, the dissolution of NaCl produces twice as many solute particles and so will depress the vapor pressure much more than sucrose.

$CaCl_2$ is another strong electrolyte.

However, the dissolution of 1 mole of $CaCl_2$ in water will produce 3 moles of ions: 1 mole of Ca^{2+} ions and 2 moles of Cl^- ions.

As a result, the vapor pressure will be depressed more than for NaCl.

In general, the depression of vapor pressure increases more for electrolytes than nonelectrolytes.

Colligative Properties and Vapor Pressure (Continued)

Let’s first consider how higher concentrations of a soluble sugar can affect the vapor pressure, and then we can consider soluble salts as well.

We will start by considering a 1 M and 2 M solution of sucrose.

The vapor pressure will be lower in the 2 M sucrose solution since it contains a higher concentration of sucrose particles than the 1 M solution.

There is a higher concentration of sugar molecules in the 2 M sucrose solution, and this disrupts the evaporation and condensation processes at the water–air interface more substantially.

Now, let’s compare a 1 M solution of sucrose with a 1 M solution of NaCl.

The solutions have the same concentration of solute substances, but sucrose does not dissociate in solution and NaCl does dissociate into sodium (Na^+) and chloride (Cl^-) ions.

The 1 M NaCl solution has twice as many solute particles as the 1 M sucrose solution.

We can use this information to determine that the vapor pressure will be lower in the 1 M NaCl solution and higher in the 1 M sucrose solution.

Example 3: Identifying the Solution with the Highest Concentration of a Solute Given the Vapor Pressures

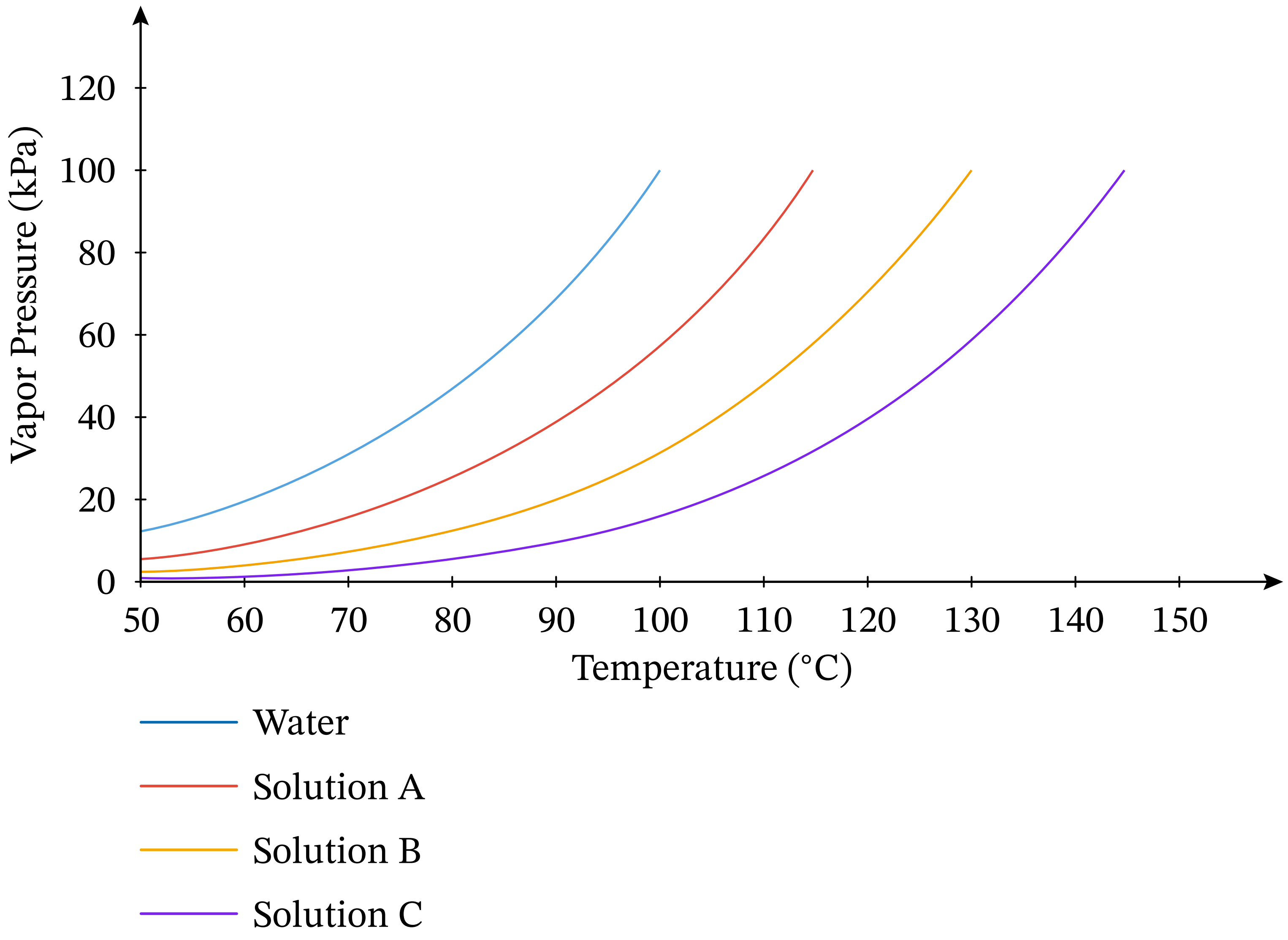
The given graph shows vapor pressure against temperature for three solutions of NaCl and pure water.

Which solution has the highest concentration?

A. Solution A

B. Solution B

C. Solution C



Example 3 (Continued)

Answer

The vapor pressure of a liquid is the equilibrium pressure exerted by a vapor on the surface of the liquid phase. This vapor above the surface of the liquid is produced through the process of evaporation.

When a solute, such as NaCl, is added to a liquid, the solute particles interfere with the process of evaporation, which decreases the vapor pressure of the liquid.

We can see this in the graph in the question: the vapor pressure for all three NaCl solutions is lower than the vapor pressure of pure water at all temperatures.

A higher concentration of solute will decrease the vapor pressure by a more significant amount.

Therefore, the NaCl solution with the highest concentration will correspond to the curve with the lowest vapor pressure.

The curve with the lowest vapor pressure is solution C, so solution C has the highest concentration of NaCl.

Example 4: Determining Which Solution Will Have the Lowest Vapor Pressure

Which of the following solutions would you expect to have the lowest vapor pressure? Assume all solutions are at the same temperature.

A. 0.2 M solution of urea
B. 0.2 M solution of $MgSO_4$
C. 0.2 M solution of KCl
D. 0.2 M solution of $AlCl_3$
E. 0.2 M solution of LiBr

Answer

The vapor pressure of a liquid is the equilibrium pressure exerted by a vapor on the surface of the liquid phase. This vapor above the surface of the liquid is produced by the process of evaporation.

When a solute is added to a liquid, the solute particles interfere with the process of evaporation, which decreases the vapor pressure of the liquid.

Example 4 (Continued)

The more particles that are present in the solution, the lower the vapor pressure will be.

The solutions in this question all have the same concentration, but the solutes dissociate into different numbers of particles in solution.

The solution containing the solute that dissociates into the greatest number of particles will have the lowest vapor pressure.

Urea does not dissociate in solution.

$MgSO_4$ dissociates into two particles: Mg^{2+} and $SO_4{}^{2+}$.

KCl dissociates into two particles: K^+ and Cl^-.

$AlCl_3$ dissociates into four particles: Al^{3+} and 3 Cl^-.

LiBr dissociates into two particles: Li^+ and Br^-.

$AlCl_3$ dissociates into the greatest number of particles, and this indicates that it has the lowest vapor pressure. So, the answer is choice D.

Vapor Pressure and Boiling Point

When the vapor pressure decreases due to adding a solute, the solution will need to be heated to a higher temperature in order for the vapor pressure to equal the external or atmospheric pressure.

In other words, adding a solute will increase the boiling point of a liquid; this is known as boiling point elevation.

Boiling point elevation is affected by whether the solute is an electrolyte or a nonelectrolyte and by the number of moles of ions produced when the solute dissolves.

One mole of a nonelectrolyte, like sucrose, will produce one mole of sucrose molecules when dissolved in water.

However, one mole of an electrolyte, like NaCl, will produce 2 moles of ions when dissolved in water.

As a result, the boiling point elevation for a solution containing 1 mole of NaCl would be expected to be twice as much as for a solution containing 1 mole of sucrose.

Similarly, a solution containing one mole of $CaCl_2$ would be expected to raise the boiling point by three times as much as one mole of sucrose.

Vapor Pressure and Boiling Point (Continued)

The number of particles present in a solution is also affected by the concentration of solute, and so we would expect the boiling point elevation to be directly proportional to the number of solute particles in the solution.

The table below shows the expected boiling points for pure water and aqueous solutions containing different electrolytes.

Substance	**Expected Boiling Point (°C) at 1 atm**
Pure water	100.0
A 1 mol aqueous solution of sucrose	100.5
A 1 mol aqueous solution of NaCl	101.0
A 1 mol aqueous solution of $CaCl_2$	101.5

Vapor Pressure and Boiling Point (Continued)

We can calculate this increase in boiling point using the equation

$$\Delta T_b = K_b \cdot m \cdot i,$$

where ΔT_b is the change in boiling point, K_b is the boiling point elevation constant (which has a specific value depending on the identity of the solvent), m is the molality of the solute, and i is the van't Hoff factor, which is equal to the number of particles the solute dissociates into.

Definition: Boiling Point Elevation

Boiling point elevation is the difference in temperature between the boiling point of the pure solvent and that of a solution.

Vapor Pressure and Freezing Point

Introducing a solute to liquid also has an effect on the freezing point.

When a substance freezes, liquid particles come closer together to form a solid.

When a solute is added, the solute particles interfere with this process, which has the effect of lowering the freezing point of a substance. This is known as freezing point depression.

Freezing point depression is also affected by whether the solute is an electrolyte or a nonelectrolyte and by the number of moles of ions produced when the solute dissolves.

It is expected, therefore, that the freezing point depression for a solution containing 1 mole of NaCl would be twice as much as for a solution containing 1 mole of sucrose.

Similarly, a solution containing 1 mole of $CaCl_2$ would be expected to lower the freezing point by three times as much as 1 mole of sucrose.

Vapor Pressure and Freezing Point (Continued)

The number of particles present in a solution is also affected by the concentration of solute, and so we would expect the freezing point depression to be directly proportional to the number of solute particles in the solution.

The table below shows the expected freezing points for pure water and aqueous solutions containing different electrolytes.

Substance	**Expected Freezing Point (°C) at 1 atm**
Pure water	0.0
A 1 mol aqueous solution of sucrose	−1.86
A 1 mol aqueous solution of NaCl	−3.72
A 1 mol aqueous solution of $CaCl_2$	−5.58

Vapor Pressure and Freezing Point (Continued)

This is why roads are salted in the winter in areas where snowfall is common.

The salt decreases the freezing point of the water on the roads, preventing the formation of ice.

We can calculate the decrease in freezing point using the equation

$$\Delta T_f = K_f \cdot m \cdot i,$$

where ΔT_f is the change in freezing point, K_f is the freezing point constant (which has a specific value depending on the identity of the solvent), m is the molality of the solute, and i is the van't Hoff factor.

Vapor Pressure and Freezing Point (Continued)

For example, the freezing point value of water is 0°C; therefore, when adding 1 mole of the nonelectrolyte sucrose to 1 000 g of water, the freezing point would be expected to lower to -1.86°C.

However, when adding 1 mole of the electrolyte NaCl to 1 000 g of water, 2 moles of ions are produced.

As a result, the freezing point would be expected to be twice as low as for sucrose.

Therefore, the freezing point would be depressed by $2 \times -1.86 = -3.72$°C, and so the freezing point would be -3.72°C.

Similarly, we would expect the freezing point depression for 1 mole of $CaCl_2$ added to 1 000 g of water to be three times as lower as for 1 mole of sucrose.

Definition: Freezing Point Depression

Freezing point depression is the difference in temperature between the freezing point of the pure solvent and that of a solution.

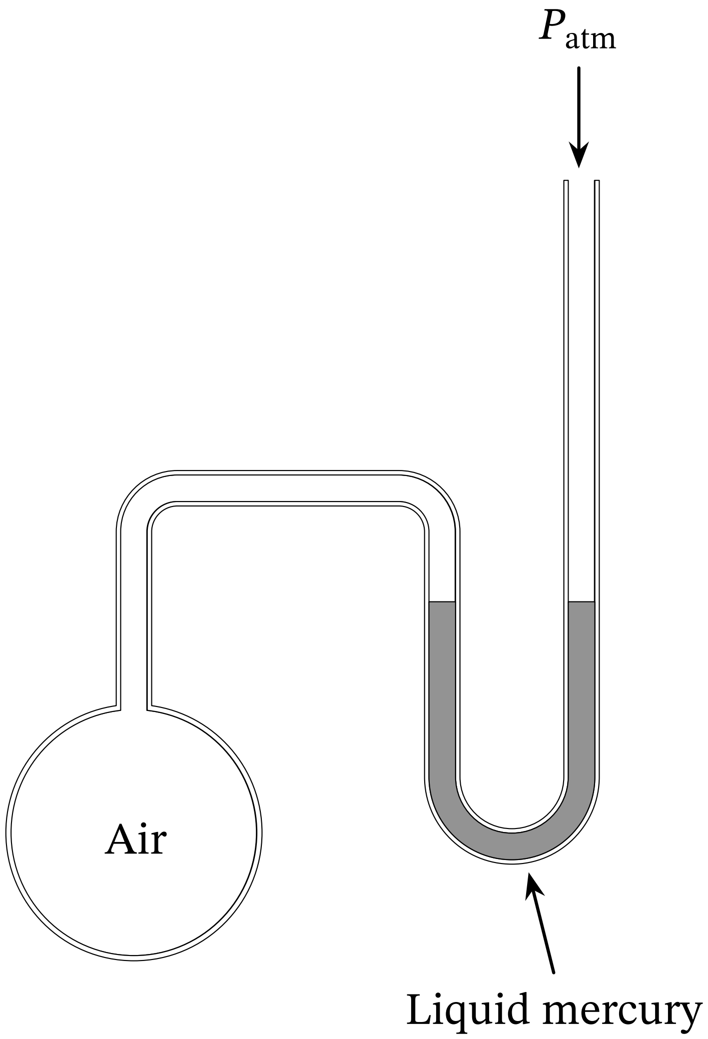
Measuring Vapor Pressure

The vapor pressure of a substance can be measured using a device called a manometer, which consists of a curved glass tube containing a liquid.

The liquid inside a manometer is usually mercury because mercury has an incredibly low vapor pressure, meaning it will have little to no effect on the result of the measurement.

There are several ways to set up a manometer to measure the vapor pressure.

One common experimental setup is shown in the opposite diagram.



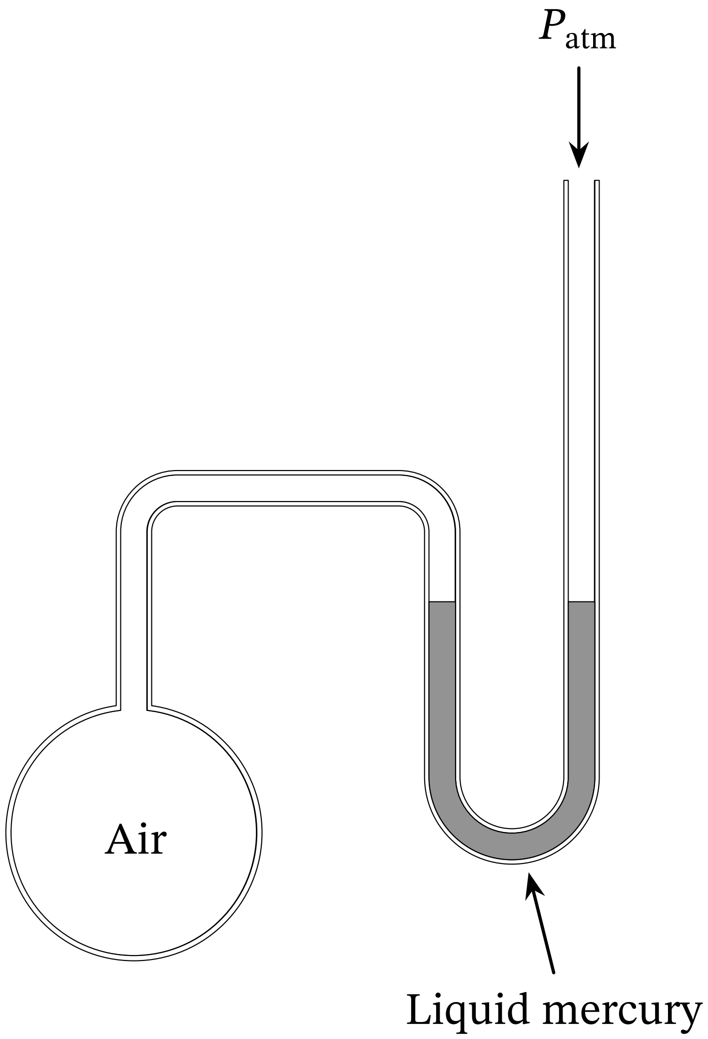
Measuring Vapor Pressure (Continued)

In this diagram, one end of the manometer is open to the atmosphere and the other end is connected to a spherical container.

Air will fill the spherical container if it is not filled with some other type of liquid.

The air will exert pressure on the mercury from one side while the atmosphere exerts pressure from the other side.

The right- and left-hand side mercury levels will be elevated to the same height because the pressure from the atmosphere is equal to the pressure from the air inside the spherical container.

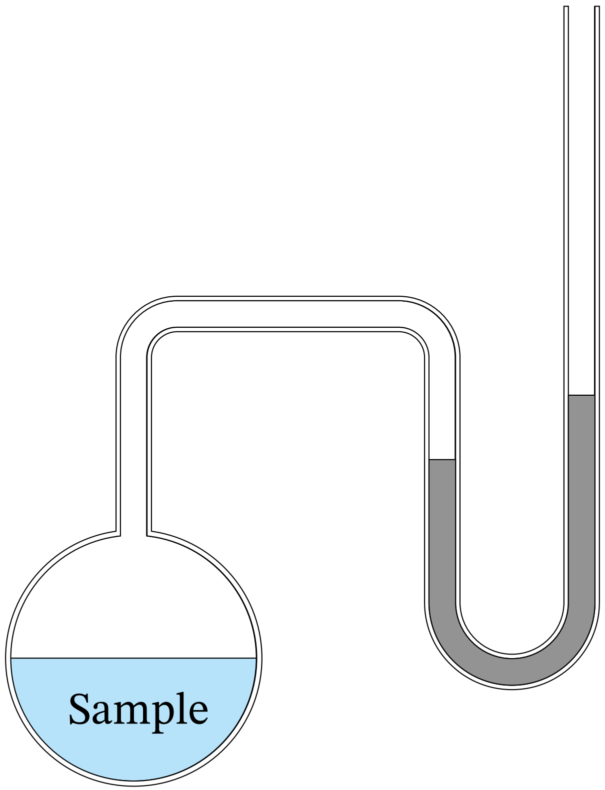


Measuring Vapor Pressure (Continued)

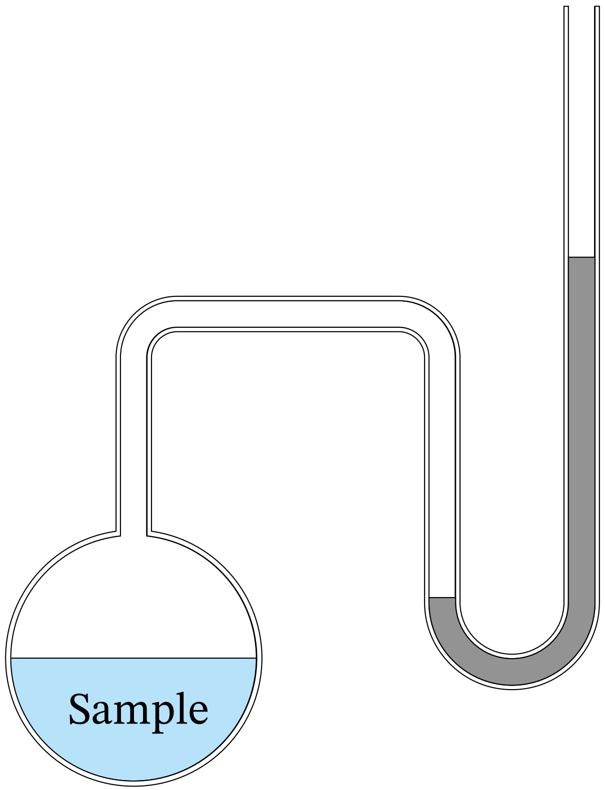
If the container is then filled with a liquid, the pressure of the vapor will be added to the pressure of the air that was in the container.

Therefore, the pressure on that side of the manometer is greater than the pressure on the side open to the atmosphere.

This will cause the mercury in the manometer to rise on the side that is open to the atmosphere.



Lower vapor pressure



Higher vapor pressure

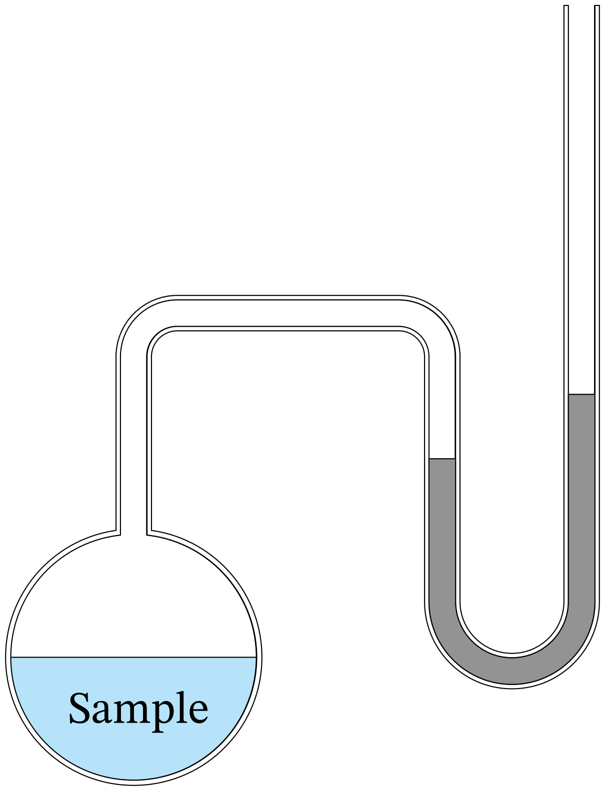
Measuring Vapor Pressure (Continued)

The following equation shows how the pressure and height of the liquid are related to each other:

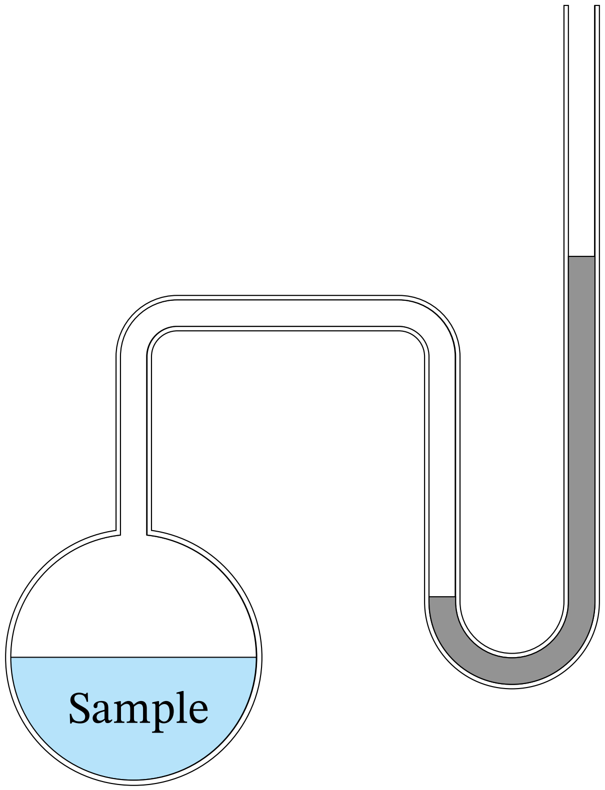
$$P = \rho g h.$$

Here, P is the pressure, ρ is the density of liquid, g is the acceleration due to gravity, and h is the height of the liquid.

This means we can use the difference in height of the mercury between the two sides of the manometer to determine the vapor pressure of the liquid.



Lower vapor pressure



Higher vapor pressure

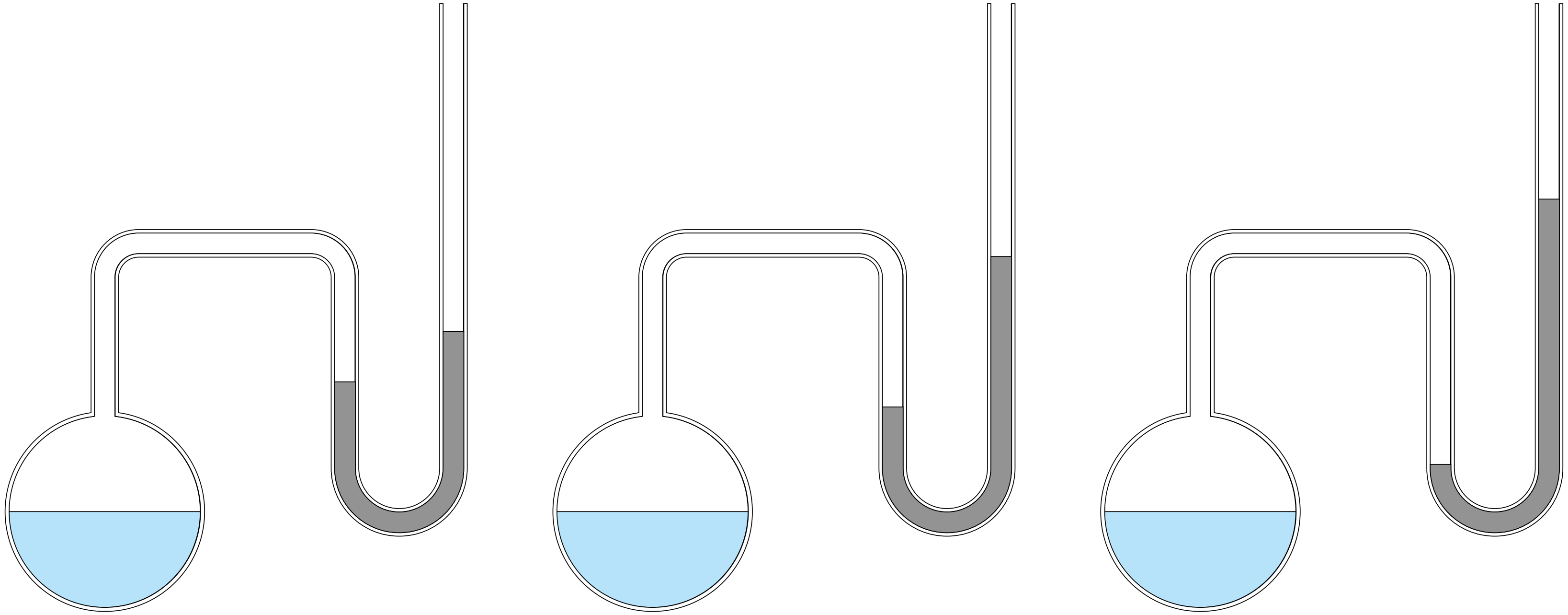
Example 5: Determining Which Manometer Shows the Liquid Sample with the Highest Temperature

The image below shows three manometers, each containing a sample of ethanoic acid. For which manometer is the temperature of the ethanoic acid the highest?

A. A

B. B

C. C



(A) (B) (C)

Example 5 (Continued)

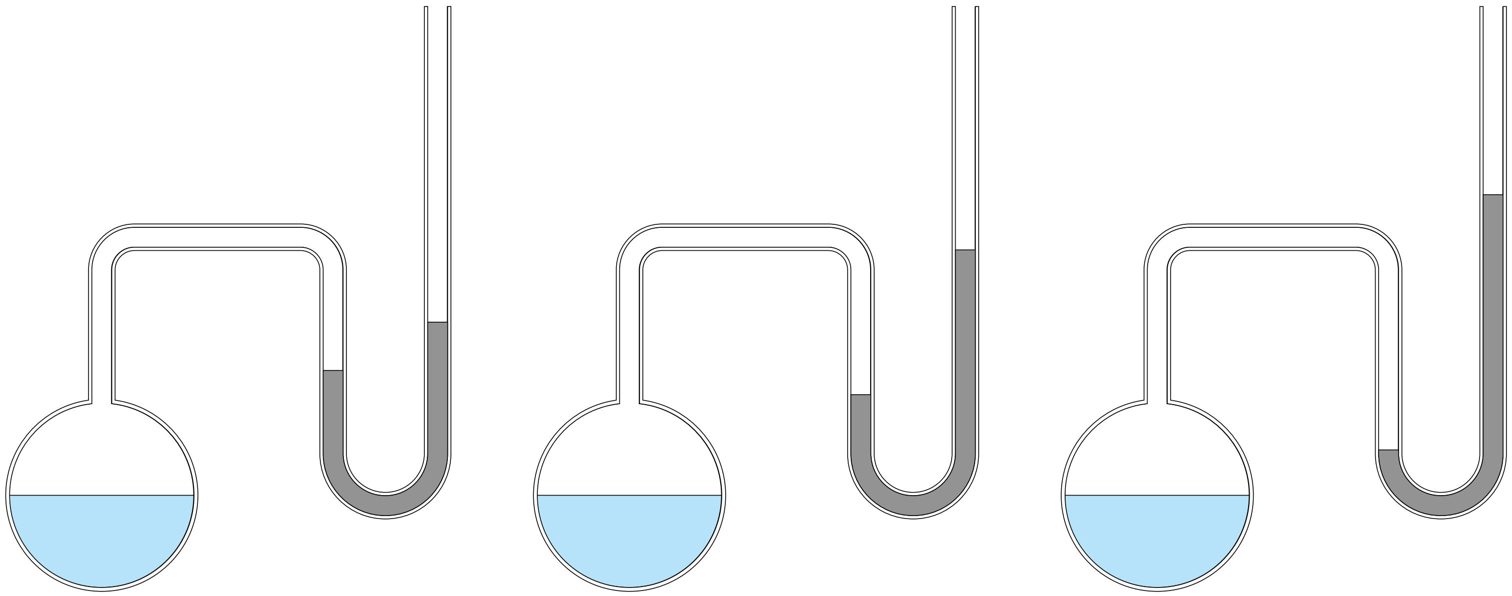
Answer

Manometers are devices that can be used to measure the vapor pressure of a sample.

The manometer consists of a curved glass tube filled with some liquid, usually mercury. There are several experimental setups for manometers.

In the opposite diagram, the manometer is attached to a flask on the left containing the sample of ethanoic acid.

The manometer is open to the atmosphere on the right.



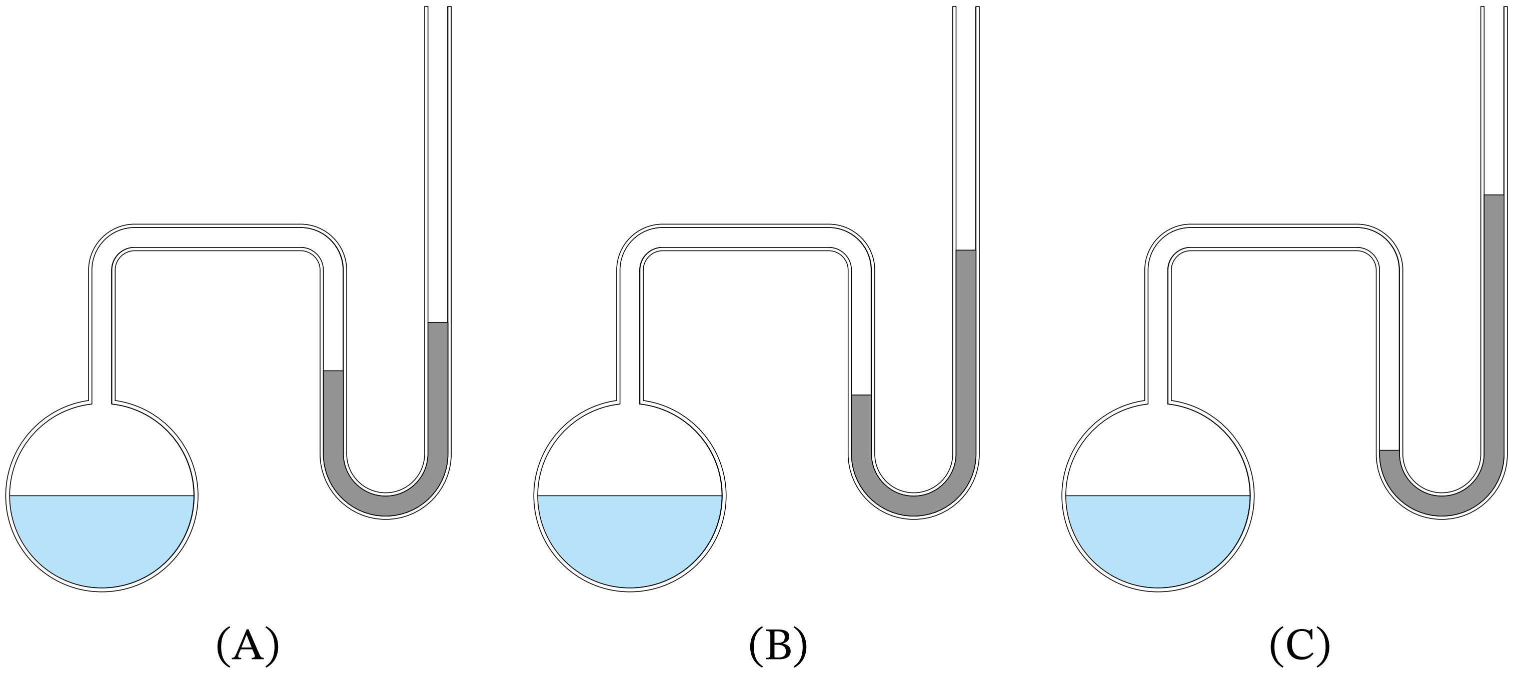
(A) (B) (C)

Example 5 (Continued)

In the flask, there will be some amount of air as well as some ethanoic vapor due to the evaporation of ethanoic acid.

The pressure from the gases on both sides of the liquid will push on the liquid, causing the liquid to be pushed up one side of the tube.

Whichever side has the greater pressure will push more on the liquid in the manometer, causing the liquid to rise up the tube on the other side.

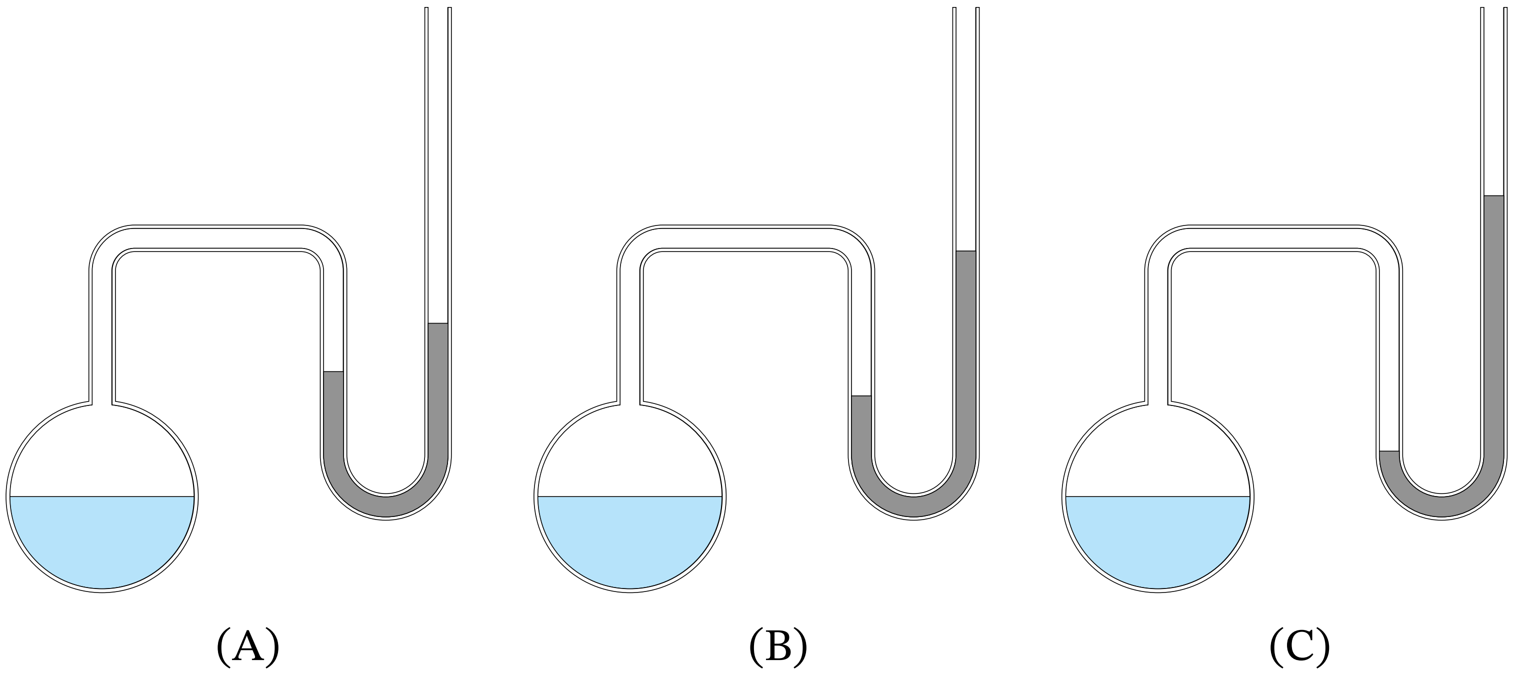


Example 5 (Continued)

Because all three manometers show the liquid rising up the right side of the tube, which is open to the atmosphere, we know the pressure inside the flask in all three manometers is greater than the pressure due to the atmosphere.

We need to determine which manometer contains the sample of ethanoic acid that is at the highest temperature.

When the temperature increases, more of the ethanoic acid will evaporate, which will increase the amount of ethanoic acid vapor in the flask.

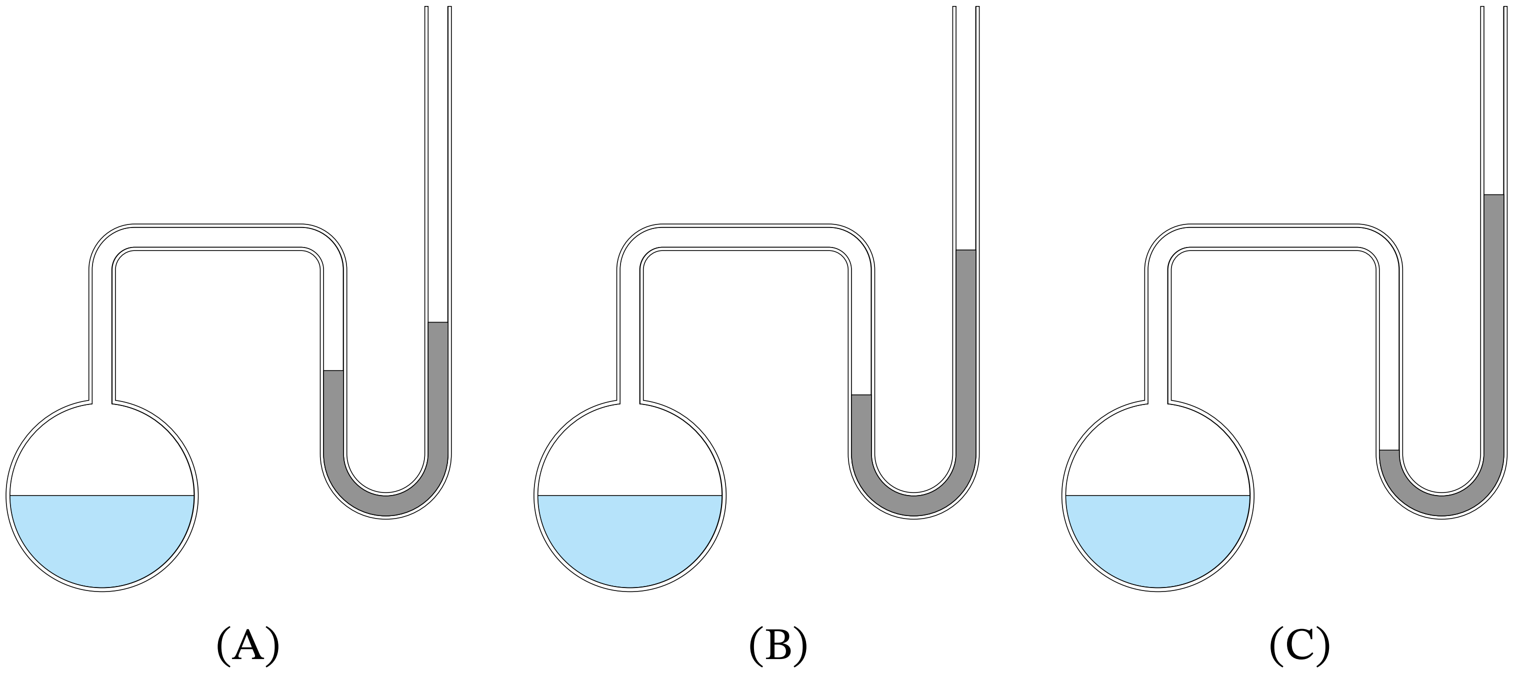


Example 5 (Continued)

More ethanoic acid vapor will result in a larger pressure in the flask. This means the manometer that shows the highest pressure in the flask will be the one with the highest temperature.

From examining the opposite diagram, we can see that manometer C must have the greatest pressure in the flask because the gases in the flask have pushed the liquid up the right side of the tube the furthest.

This means manometer C contains the ethanoic acid that is the highest temperature, so answer choice C is the correct answer.



Key Points

- Vapor pressure is the pressure exerted by a vapor above its liquid (or solid) when they are at dynamic equilibrium and in a closed system at constant temperature and pressure.
- A substance boils when the vapor pressure equals the atmospheric pressure in an open system or the external pressure in a closed system.
- Increasing the temperature will increase the vapor pressure.
- Substances with weaker intermolecular forces will have a higher vapor pressure at any given temperature and will therefore boil at lower temperature.
- Vapor pressure can be measured using a manometer.
- Adding a solute to a substance will affect the colligative properties of the solvent.
- Adding a solute to a substance will decrease the vapor pressure, resulting in an increase to the boiling point (boiling point elevation) or a decrease to the freezing point (freezing point depression).
- The colligative properties of a solution are affected by the ratio of the number of solute particles to the number of solvent particles.
- Solutes that are electrolytes affect the colligative properties of a solution more than a nonelectrolyte, as electrolytes produce more particles when dissolved in the solvent.