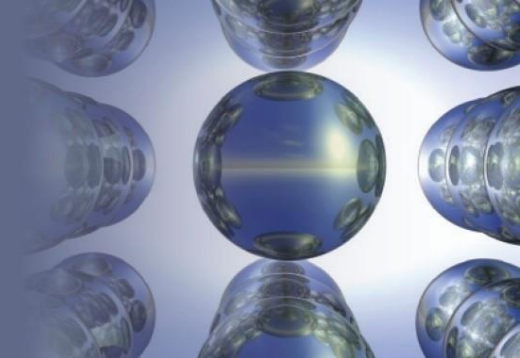


## Chapter 11

### *Properties of Solutions*

# Section 11.1

## *Solution Composition*



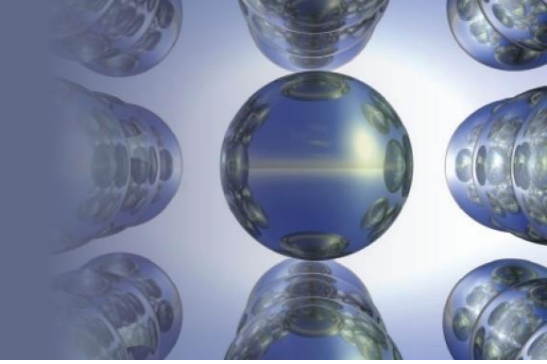
## Various Types of Solutions

**Table 11.1** | Various Types of Solutions

Example	State of Solution	State of Solute	State of Solvent
Air, natural gas	Gas	Gas	Gas
Vodka, antifreeze	Liquid	Liquid	Liquid
Brass	Solid	Solid	Solid
Carbonated water	Liquid	Gas	Liquid
Seawater, sugar solution	Liquid	Solid	Liquid
Hydrogen in platinum	Solid	Gas	Solid

# Section 11.1

## *Solution Composition*



## Solution Composition

$$\text{Molarity (} M \text{)} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$\text{Mass (weight) percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

$$\text{Mole fraction (} \chi_A \text{)} = \frac{\text{moles}_A}{\text{total moles of solution}}$$

$$\text{Molality (} m \text{)} = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

# Section 11.1

## *Solution Composition*

### **EXERCISE 11.1**

A solution is prepared by mixing 1.00 g ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) with 100.0 g water to give a final volume of 101 mL. Calculate the molarity, mass percent, mole fraction, and molality of ethanol in this solution.



## Solution

### Molarity

The moles of ethanol can be obtained from its molar mass (46.07 g/mol):

$$1.00 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}} = 2.17 \times 10^{-2} \text{ mol C}_2\text{H}_5\text{OH}$$

$$\text{Volume} = 101 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.101 \text{ L}$$

$$\begin{aligned} \text{Molarity of C}_2\text{H}_5\text{OH} &= \frac{\text{moles of C}_2\text{H}_5\text{OH}}{\text{liters of solution}} = \frac{2.17 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} \\ &= 0.215 \text{ M} \end{aligned}$$

### Mass Percent

$$\begin{aligned} \text{Mass percent C}_2\text{H}_5\text{OH} &= \left( \frac{\text{mass of C}_2\text{H}_5\text{OH}}{\text{mass of solution}} \right) \times 100\% \\ &= \left( \frac{1.00 \text{ g C}_2\text{H}_5\text{OH}}{100.0 \text{ g H}_2\text{O} + 1.00 \text{ g C}_2\text{H}_5\text{OH}} \right) \times 100\% \\ &= 0.990\% \text{ C}_2\text{H}_5\text{OH} \end{aligned}$$

## Mole Fraction

$$\text{Mole fraction of C}_2\text{H}_5\text{OH} = \frac{n_{\text{C}_2\text{H}_5\text{OH}}}{n_{\text{C}_2\text{H}_5\text{OH}} + n_{\text{H}_2\text{O}}}$$

$$n_{\text{H}_2\text{O}} = 100.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = 5.56 \text{ mol}$$

$$\begin{aligned}\chi_{\text{C}_2\text{H}_5\text{OH}} &= \frac{2.17 \times 10^{-2} \text{ mol}}{2.17 \times 10^{-2} \text{ mol} + 5.56 \text{ mol}} \\ &= \frac{2.17 \times 10^{-2}}{5.58} = 0.00389\end{aligned}$$

## Molality

$$\begin{aligned}\text{Molality of C}_2\text{H}_5\text{OH} &= \frac{\text{moles of C}_2\text{H}_5\text{OH}}{\text{kilogram of H}_2\text{O}} = \frac{2.17 \times 10^{-2} \text{ mol}}{100.0 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}}} \\ &= \frac{2.17 \times 10^{-2} \text{ mol}}{0.1000 \text{ kg}} \\ &= 0.217 \text{ m}\end{aligned}$$

# Section 11.1

## *Solution Composition*

### ***EXERCISE!***

You have 1.00 mol of sugar in 125.0 mL of solution. Calculate the concentration in units of **molarity**.

**8.00 M**

# Section 11.1

## *Solution Composition*

### ***EXERCISE!***

You have a 10.0 M sugar solution. What **volume** of this solution do you need to have 2.00 mol of sugar?

0.200 L



# Section 11.1

## *Solution Composition*

### **EXERCISE!**

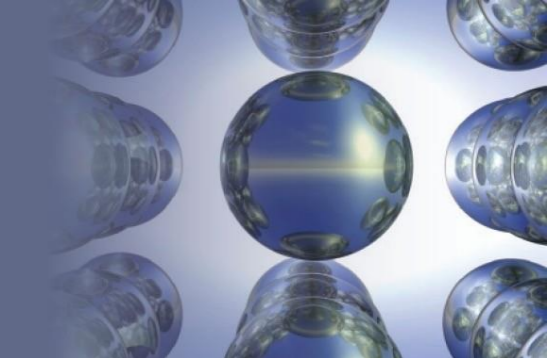
Consider separate solutions of NaOH and KCl made by dissolving 100.0 g of each solute in 250.0 mL of solution. Calculate the concentration of each solution in units of **molarity**.

10.0 M NaOH

5.37 M KCl

# Section 11.1

## *Solution Composition*

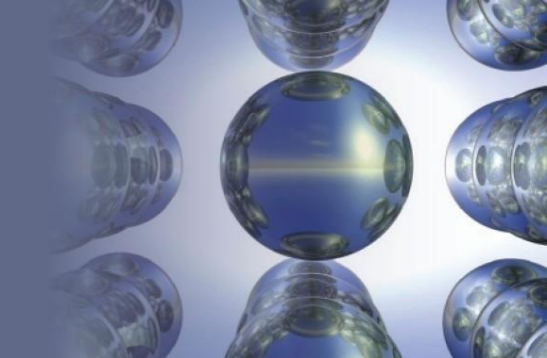


**Normality** is defined as the number of equivalents per liter of solution, where the definition of an equivalent depends on the reaction taking place in the solution.

Acid or Base	Molar Mass	Equivalent Mass	Relationship of Molarity and Normality
HCl	36.5	36.5	$1 M = 1 N$
H <sub>2</sub> SO <sub>4</sub>	98	$\frac{98}{2} = 49$	$1 M = 2 N$
NaOH	40	40	$1 M = 1 N$
Ca(OH) <sub>2</sub>	74	$\frac{74}{2} = 37$	$1 M = 2 N$

# Section 11.1

## *Solution Composition*



## Mass Percent

$$\text{Mass (weight) percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

# Section 11.1

## *Solution Composition*

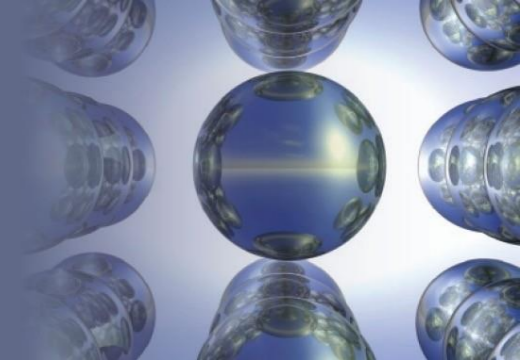
### **EXERCISE!**

What is the **percent-by-mass** concentration of glucose in a solution made by dissolving 5.5 g of glucose in 78.2 g of water?

**6.6%**

# Section 11.1

## *Solution Composition*



## Mole Fraction

$$\text{Mole fraction } (\chi_A) = \frac{\text{moles}_A}{\text{total moles of solution}}$$



# Section 11.1

## *Solution Composition*

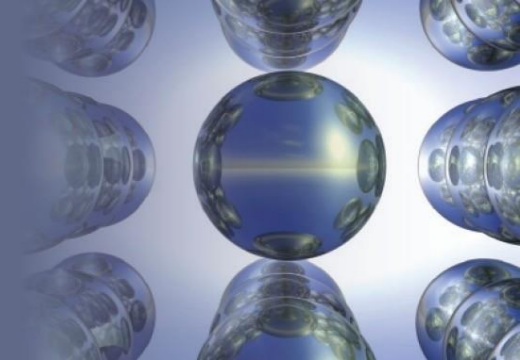
### **EXERCISE!**

A solution of phosphoric acid was made by dissolving 8.00 g of  $\text{H}_3\text{PO}_4$  in 100.0 mL of water. Calculate the **mole fraction** of  $\text{H}_3\text{PO}_4$ . (Assume water has a density of 1.00 g/mL.)

0.0145

# Section 11.1

## *Solution Composition*



## Molality

$$\text{Molality } (m) = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

# Section 11.1

## *Solution Composition*

### **EXERCISE!**

A solution of phosphoric acid was made by dissolving 8.00 g of  $\text{H}_3\text{PO}_4$  in 100.0 mL of water. Calculate the **molality** of the solution. (Assume water has a density of 1.00 g/mL.)

**0.816 m**

# Section 11.1

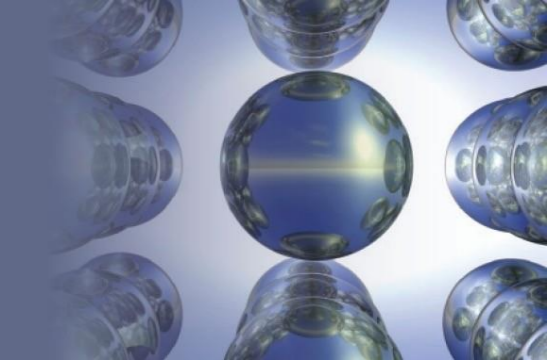
## *Solution Composition*

### **EXERCISE 11.2**

The electrolyte in automobile lead storage batteries is a 3.75 *M* sulfuric acid solution that has a density of 1.230 g/mL. Calculate the mass percent, molality, and normality of the sulfuric acid.

# Section 11.2

## *The Energies of Solution Formation*



### Formation of a Liquid Solution

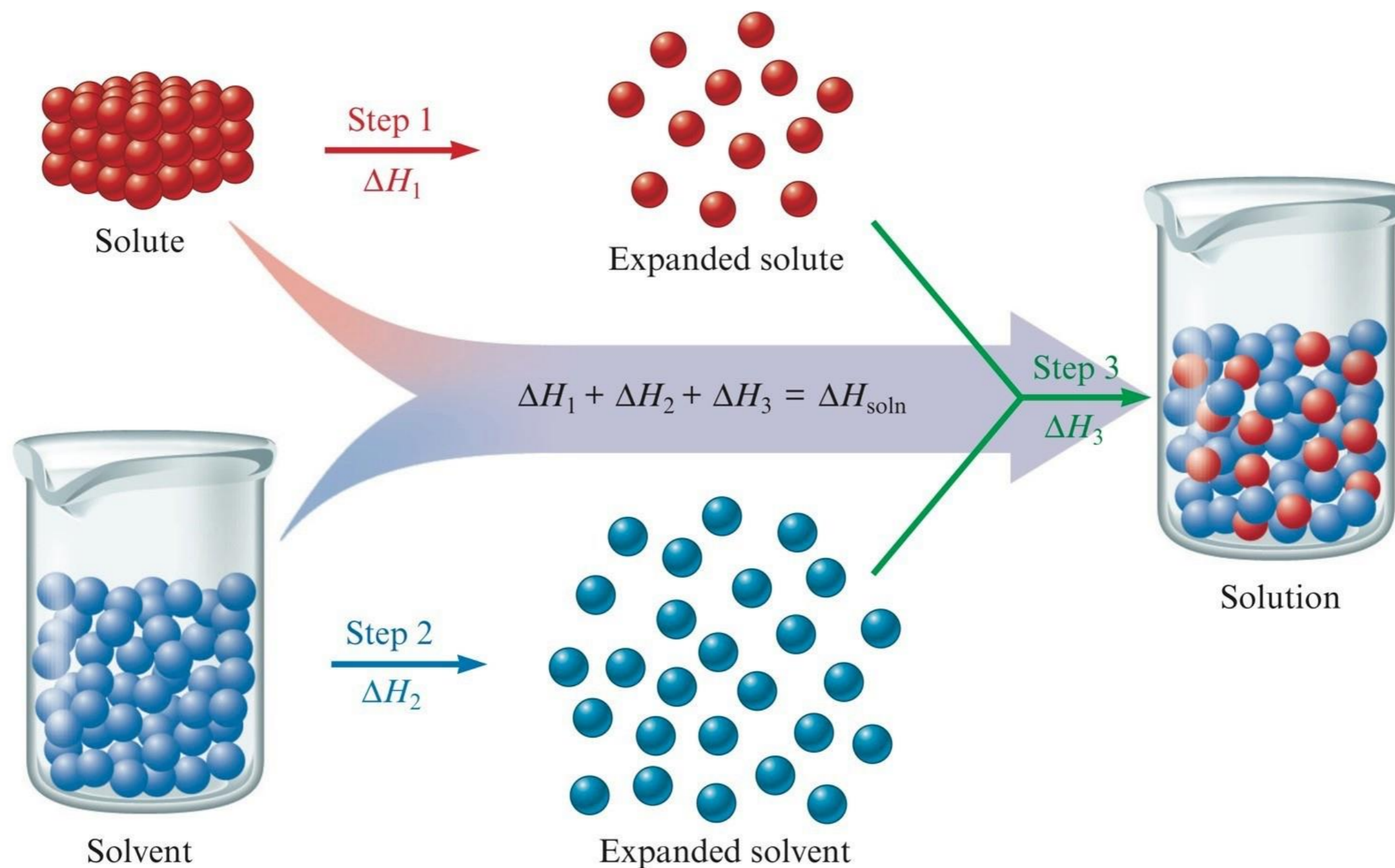
1. Separating the solute into its individual components (expanding the solute).
2. Overcoming intermolecular forces in the solvent to make room for the solute (expanding the solvent).
3. Allowing the solute and solvent to interact to form the solution.



# Section 11.2

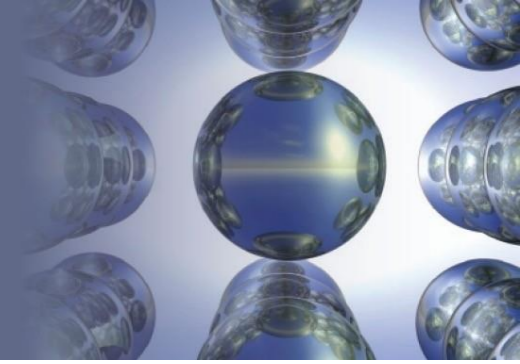
## The Energies of Solution Formation

### Steps in the Dissolving Process



## Section 11.2

# *The Energies of Solution Formation*

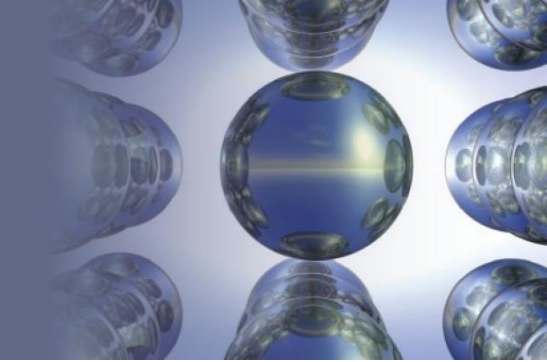


## Steps in the Dissolving Process

- Steps 1 and 2 require energy, since forces must be overcome to expand the solute and solvent.
- Step 3 usually releases energy.
- Steps 1 and 2 are **endothermic**, and step 3 is often **exothermic**.

## Section 11.2

# *The Energies of Solution Formation*



## Enthalpy (Heat) of Solution

- Enthalpy change associated with the formation of the solution is the sum of the  $\Delta H$  values for the steps:

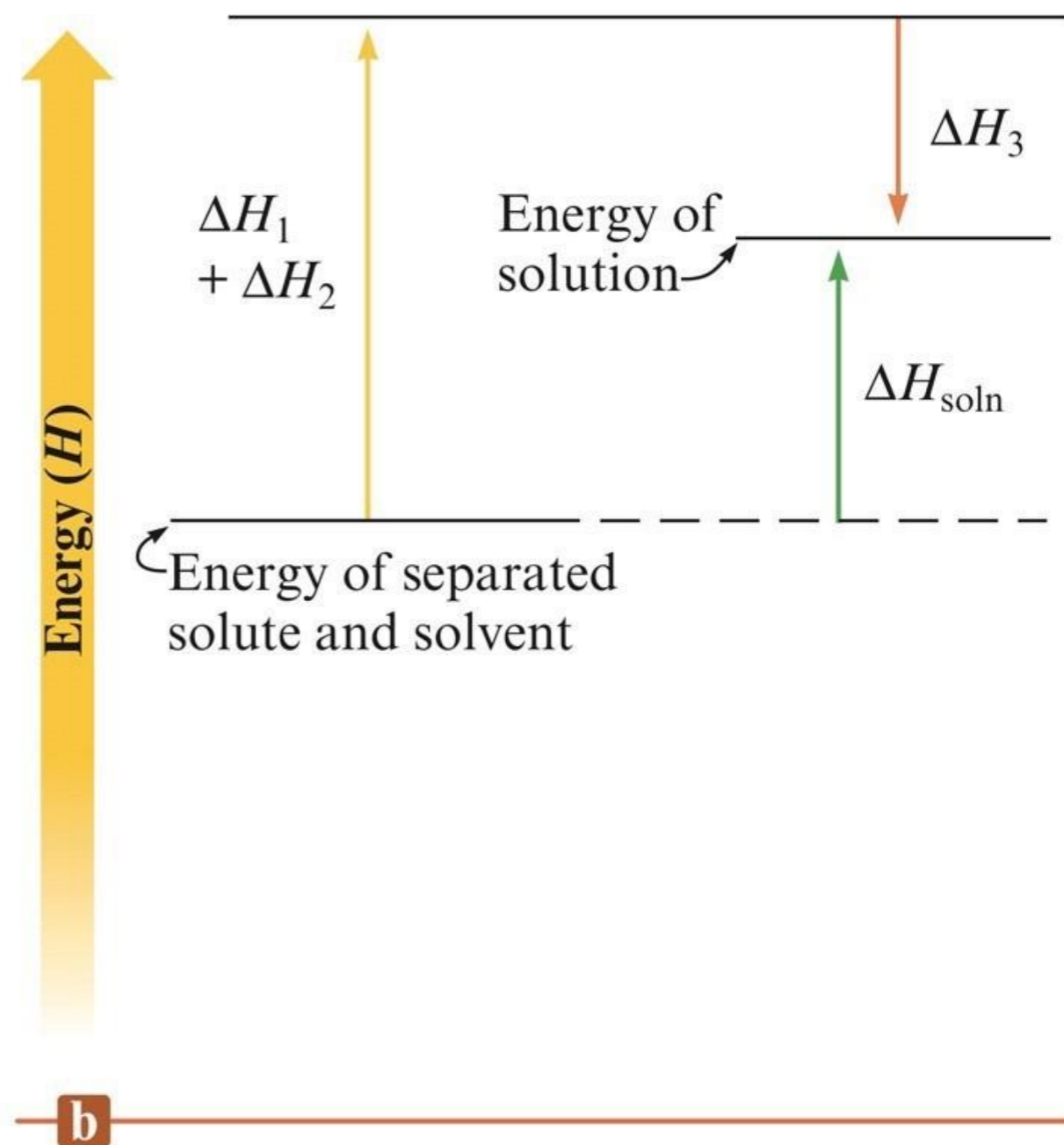
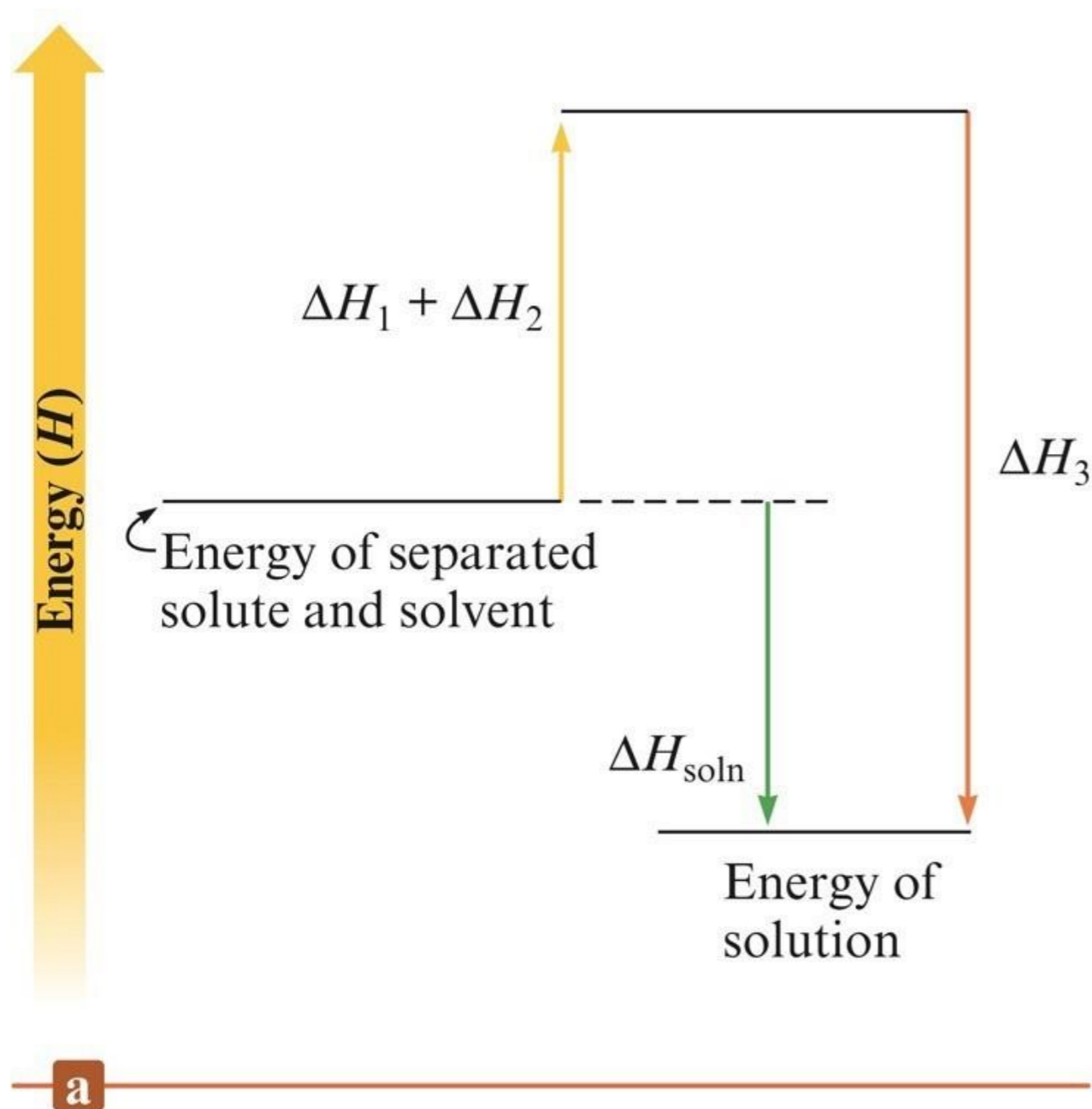
$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

- $\Delta H_{\text{soln}}$  may have a **positive sign (energy absorbed)** or a **negative sign (energy released)**.

# Section 11.2

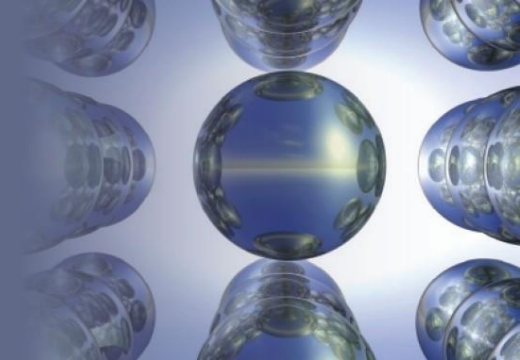
## The Energies of Solution Formation

### Enthalpy (Heat) of Solution



# Section 11.2

## *The Energies of Solution Formation*



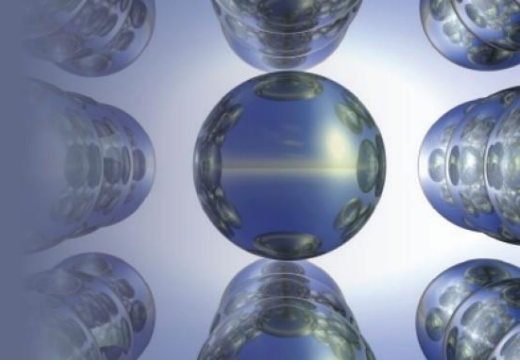
### The Energy Terms for Various Types of Solutes and Solvents

	$\Delta H_1$	$\Delta H_2$ $\Delta H_3$		$\Delta H_{\text{soln}}$	<i>Outcome</i>
<b>Polar solute, polar solvent</b>	<b>Large</b>	<b>Large</b>	<b>Large, negative</b>	<b>Small</b>	<b>Solution forms</b>
<b>Nonpolar solute, polar solvent</b>	<b>Small</b>	<b>Large</b>	<b>Small</b>	<b>Large, positive</b>	<b>No solution forms</b>
<b>Nonpolar solute, nonpolar solvent</b>	<b>Small</b>	<b>Small</b>	<b>Small</b>	<b>Small</b>	<b>Solution forms</b>
<b>Polar solute, nonpolar solvent</b>	<b>Large</b>	<b>Small</b>	<b>Small</b>	<b>Large, positive</b>	<b>No solution forms</b>



# Section 11.2

## *The Energies of Solution Formation*

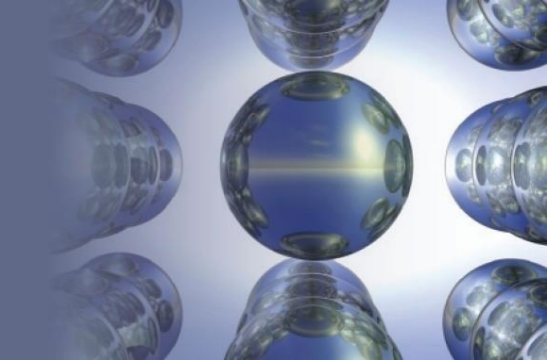


### **CONCEPT CHECK!**

Explain why water and oil (a long chain hydrocarbon) **do not mix**. In your explanation, be sure to address how  $\Delta H$  plays a role.

## Section 11.2

# *The Energies of Solution Formation*



### In General

- Processes that require large amounts of energy tend not to occur.
- Overall, remember that “like dissolves like”.

## Section 11.2

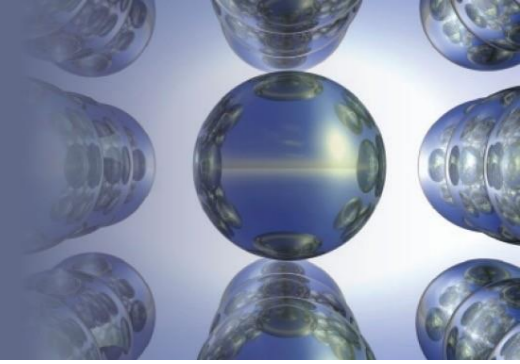
# *The Energies of Solution Formation*

### **EXERCISE 11.3**

Decide whether liquid hexane ( $\text{C}_6\text{H}_{14}$ ) or liquid methanol ( $\text{CH}_3\text{OH}$ ) is the more appropriate solvent for the substances grease ( $\text{C}_{20}\text{H}_{42}$ ) and potassium iodide (KI).

# Section 11.3

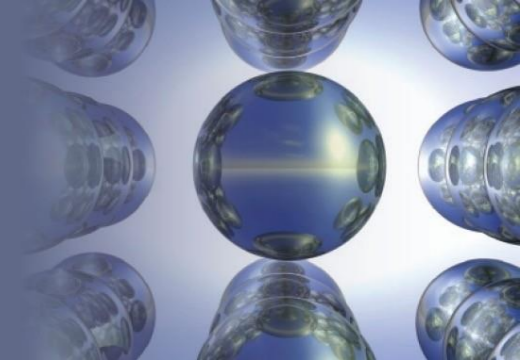
## *Factors Affecting Solubility*



- Structure Effects:
  - Polarity
- Pressure Effects:
  - Henry's law
- Temperature Effects:
  - Affecting aqueous solutions

# Section 11.3

## *Factors Affecting Solubility*



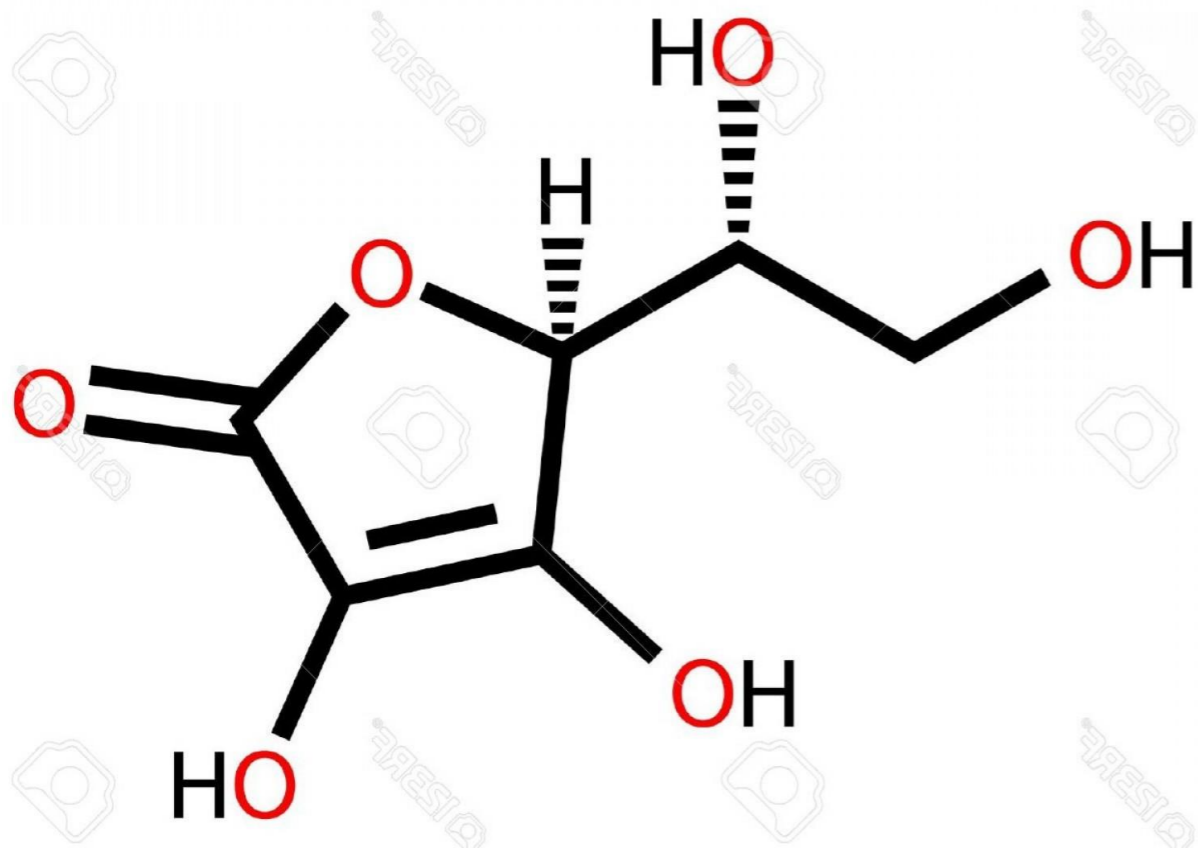
### Structure Effects

- Hydrophobic (water fearing)
  - Non-polar substances
- Hydrophilic (water loving)
  - Polar substances

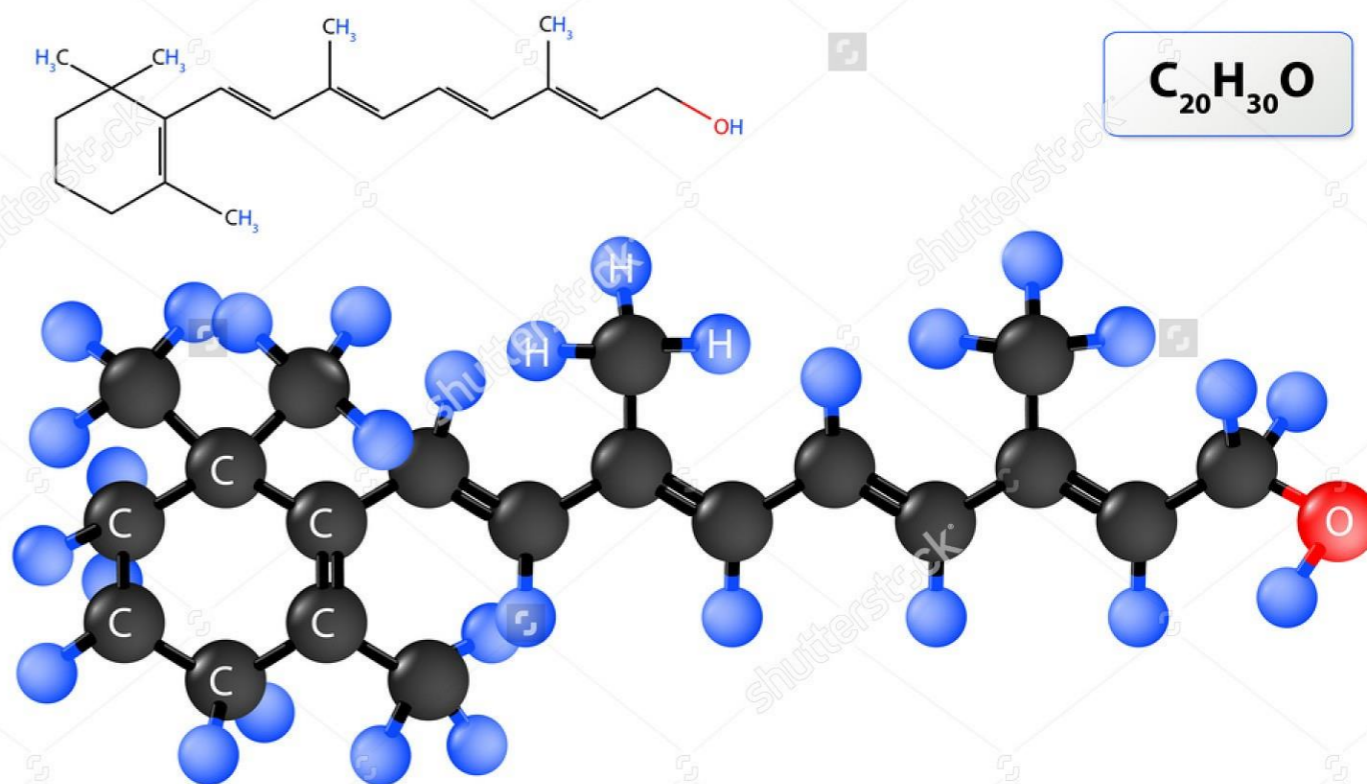
# Section 11.3

## Factors Affecting Solubility

### Vitamin C



### Vitamin A (retinol)



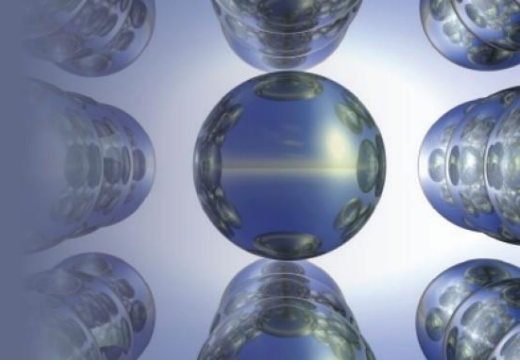
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# Section 11.3

## *Factors Affecting Solubility*

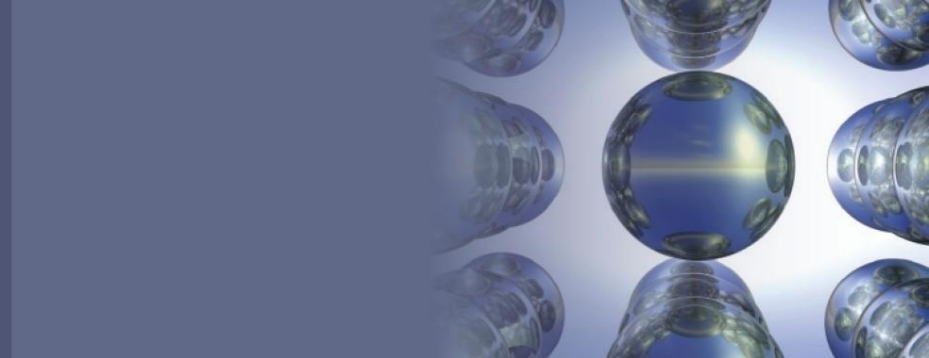


### Pressure Effects

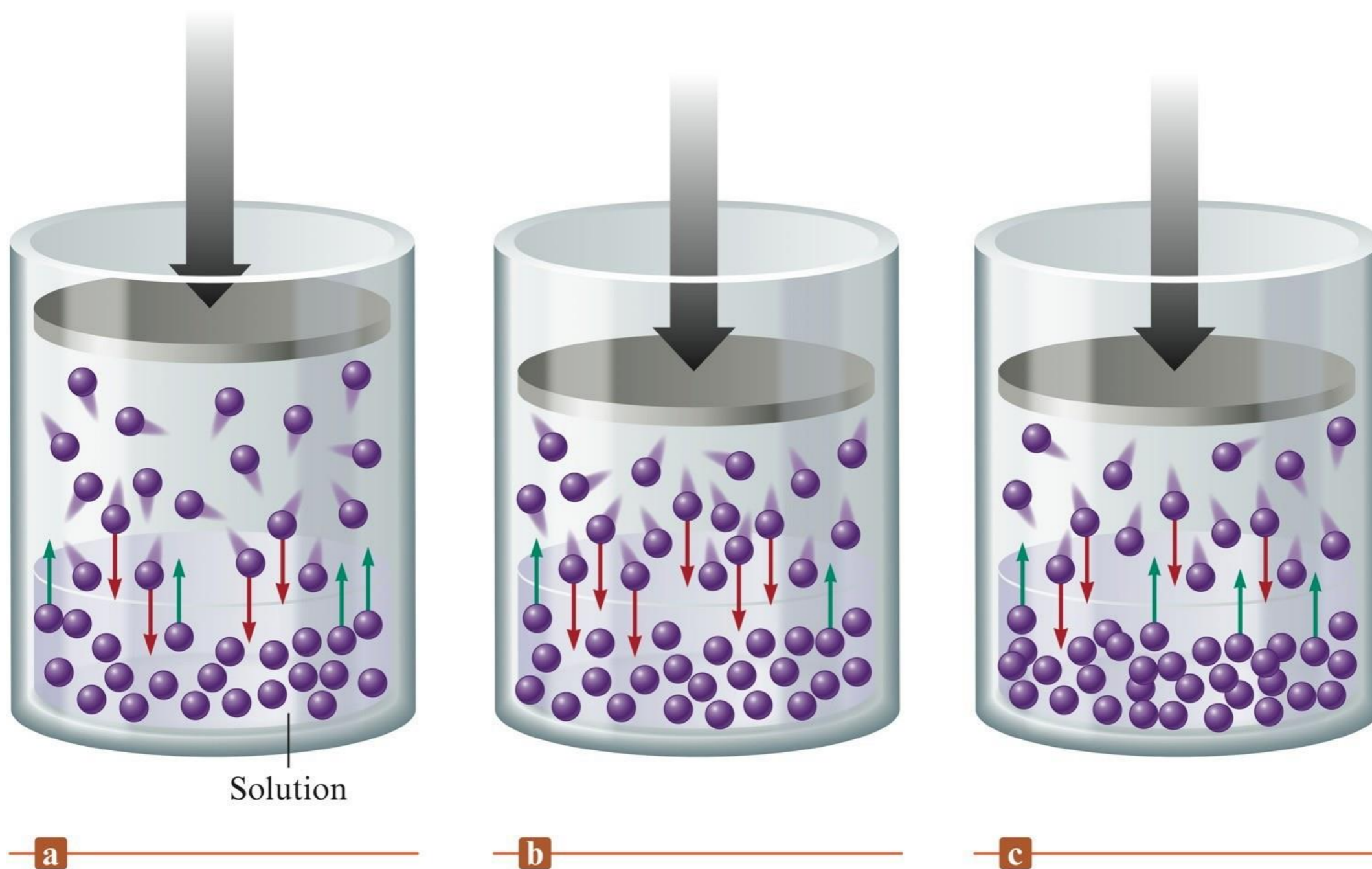
- Little effect on solubility of solids or liquids
- Henry's law:  $C = kP$ 
  - $C$  = concentration of dissolved gas
  - $k$  = constant
  - $P$  = partial pressure of gas solute above the solution
- Amount of gas dissolved in a solution is directly proportional to the pressure of the gas above the solution.


# Section 11.3

## *Factors Affecting Solubility*

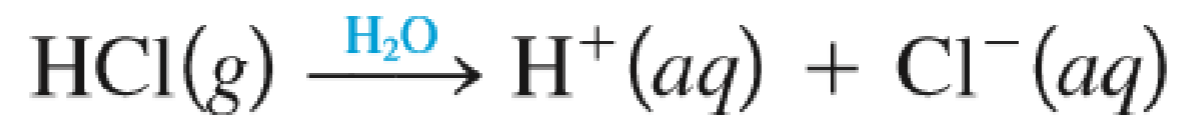


### A Gaseous Solute





Henry's law is obeyed most accurately for dilute solutions of gases that do not dissociate in or react with the solvent. For example, Henry's law is obeyed by oxygen gas in water, but it does not correctly represent the behavior of gaseous hydrogen chloride in water because of the dissociation reaction



# Section 11.3

## *Factors Affecting Solubility*

### **EXERCISE 11.4**

A certain soft drink is bottled so that a bottle at 25C contains CO<sub>2</sub> gas at a pressure of 5.0 atm over the liquid. Assuming that the partial pressure of CO<sub>2</sub> in the atmosphere is  $4.0 \times 10^{-4}$  atm, calculate the equilibrium concentrations of CO<sub>2</sub> in the soda both before and after the bottle is opened. The Henry's law constant for CO<sub>2</sub> in aqueous solution is  $3.1 \times 10^{-2}$  mol/L.atm at 25C.

## Solution

What is Henry's law for  $\text{CO}_2$ ?

$$C_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CO}_2}$$

where  $k_{\text{CO}_2} = 3.1 \times 10^{-2} \text{ mol/L} \cdot \text{atm}$ .

What is the  $C_{\text{CO}_2}$  in the unopened bottle?

In the *unopened* bottle,  $P_{\text{CO}_2} = 5.0 \text{ atm}$  and

$$\text{> } C_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CO}_2} = (3.1 \times 10^{-2} \text{ mol/L} \cdot \text{atm})(5.0 \text{ atm}) = 0.16 \text{ mol/L}$$

In the *opened* bottle, the  $\text{CO}_2$  in the soda eventually reaches equilibrium with the atmospheric  $\text{CO}_2$ , so  $P_{\text{CO}_2} = 4.0 \times 10^{-4} \text{ atm}$  and

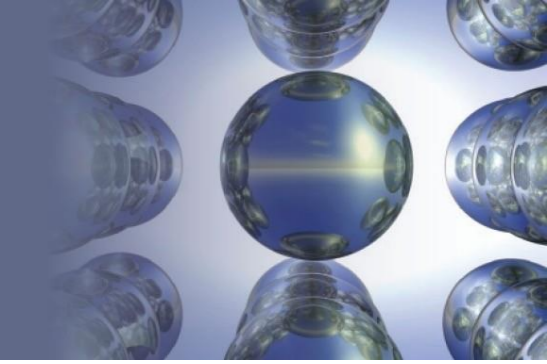
$$\text{> } C_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CO}_2} = \left( 3.1 \times 10^{-2} \frac{\text{mol}}{\text{L} \cdot \text{atm}} \right) (4.0 \times 10^{-4} \text{ atm}) = 1.2 \times 10^{-5} \text{ mol/L}$$

Note the large change in concentration of  $\text{CO}_2$ . This is why soda goes “flat” after being open for a while.



# Section 11.3

## *Factors Affecting Solubility*



### Temperature Effects (for Aqueous Solutions)

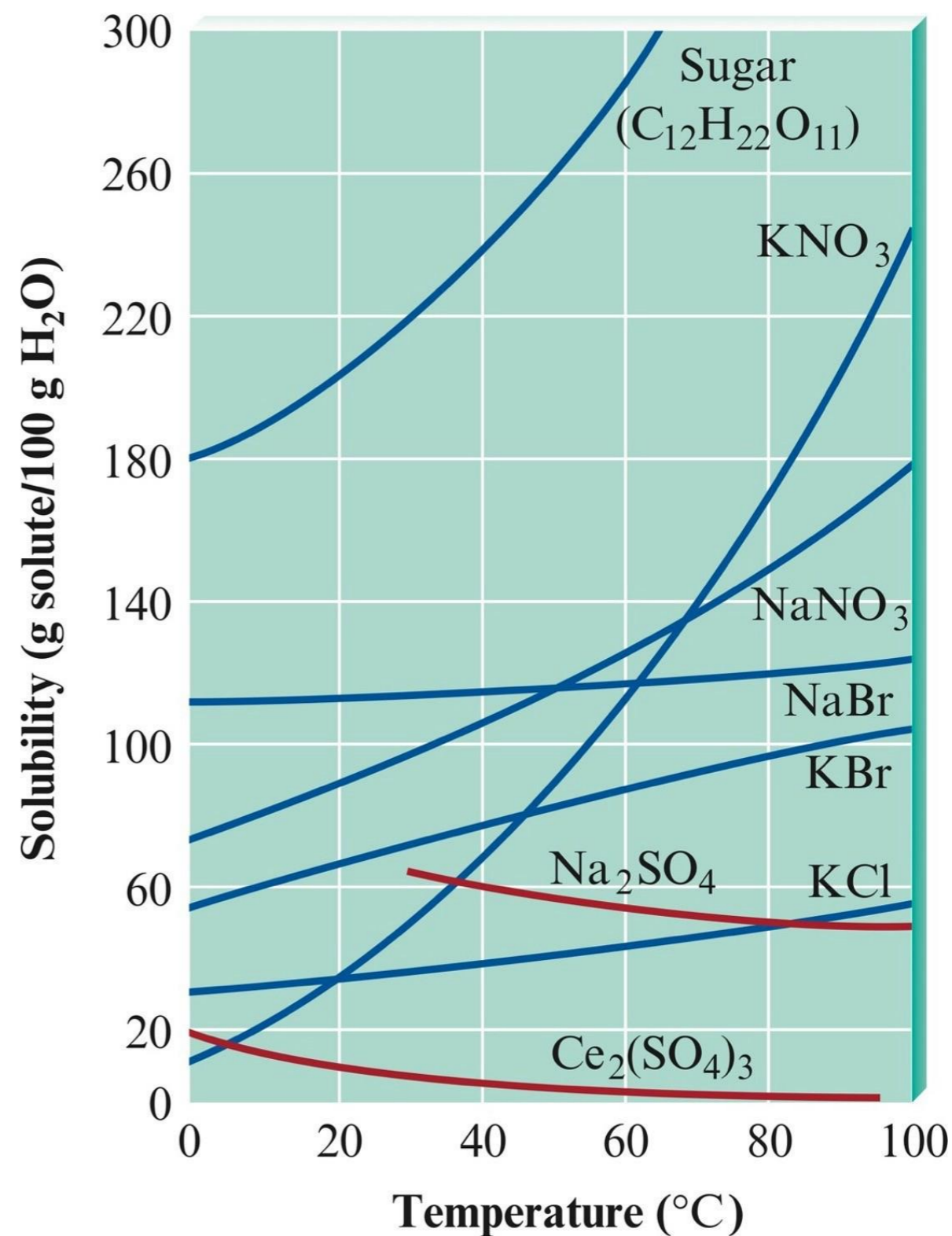
- Although the solubility of most solids in water increases with temperature, the solubilities of some substances decrease with increasing temperature.
- Predicting temperature dependence of solubility is very difficult.
- Solubility of a gas in solvent typically decreases with increasing temperature.



# Section 11.3

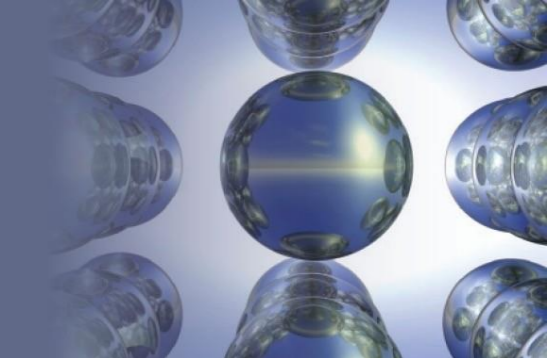
## *Factors Affecting Solubility*

The Solubilities of Several Solids as a Function of Temperature

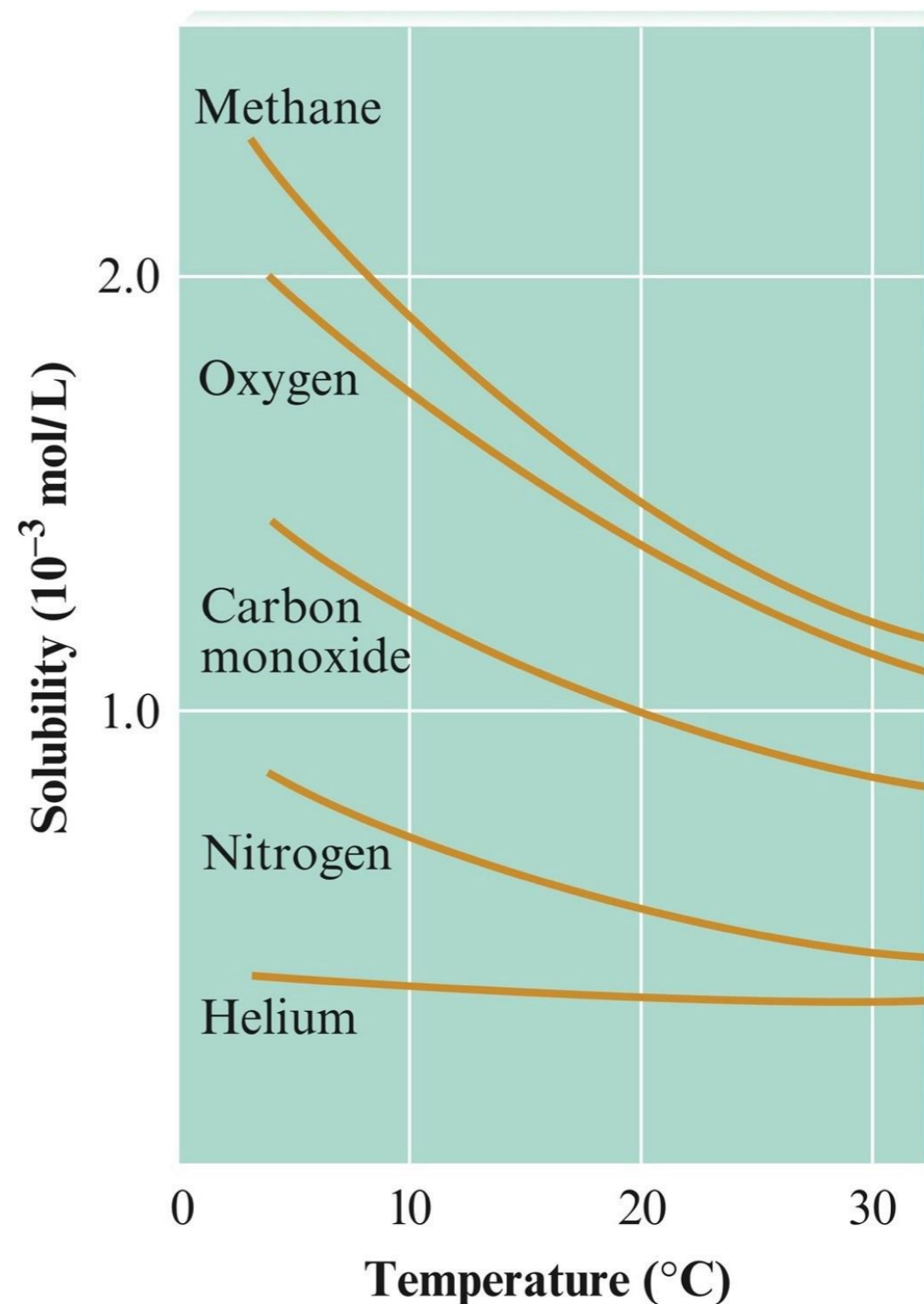


# Section 11.3

## *Factors Affecting Solubility*

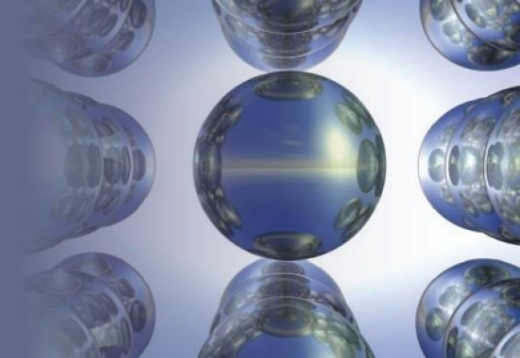


The Solubilities of Several Gases in Water



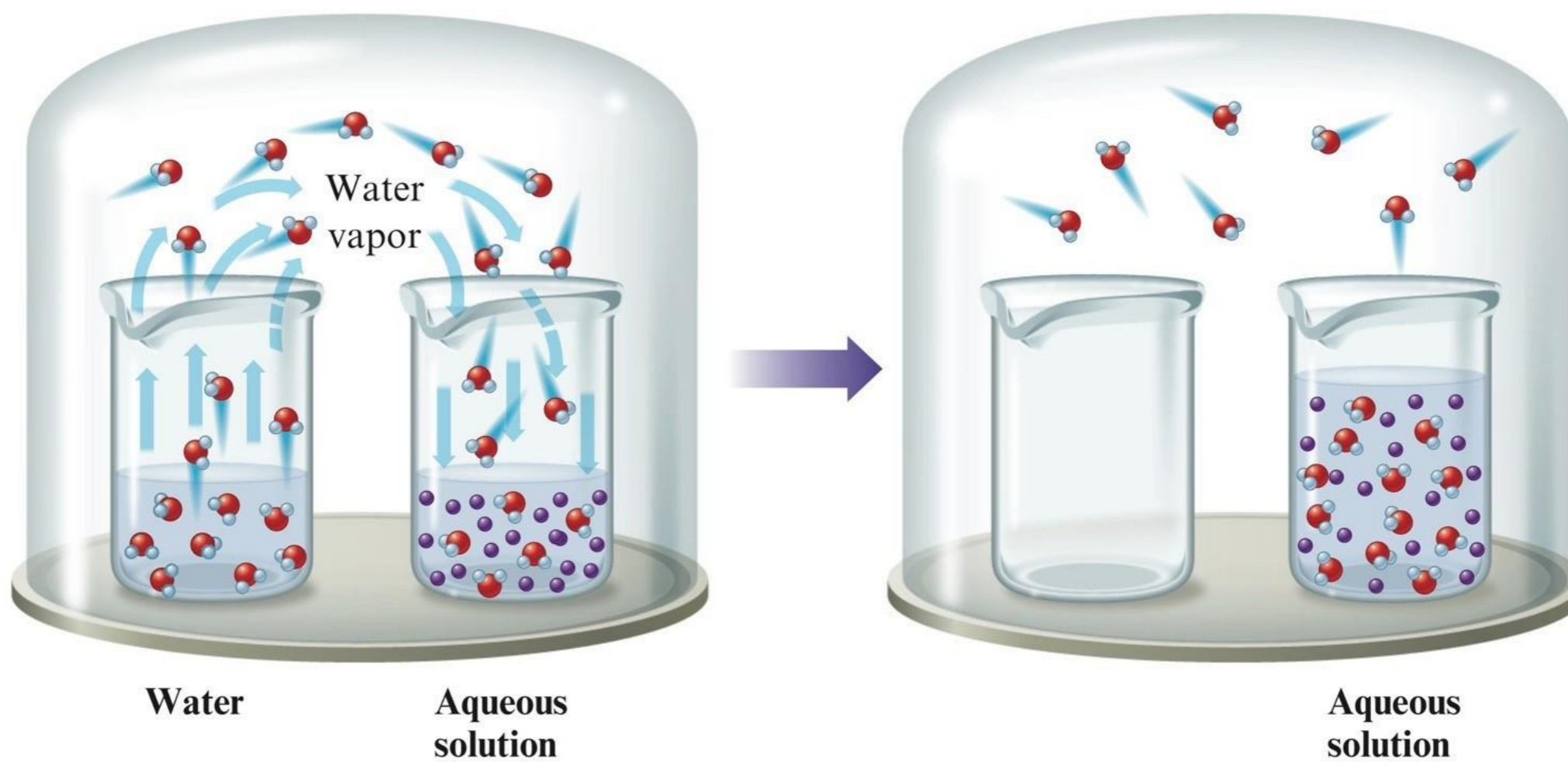
# Section 11.4

## *The Vapor Pressures of Solutions*



### An Aqueous Solution and Pure Water in a Closed Environment

The vapor pressure of the pure solvent is greater than that of the solution.



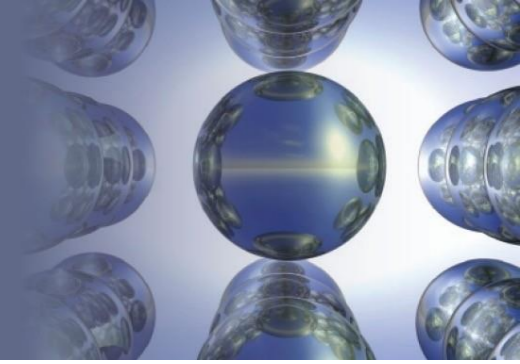
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## Section 11.4

# *The Vapor Pressures of Solutions*



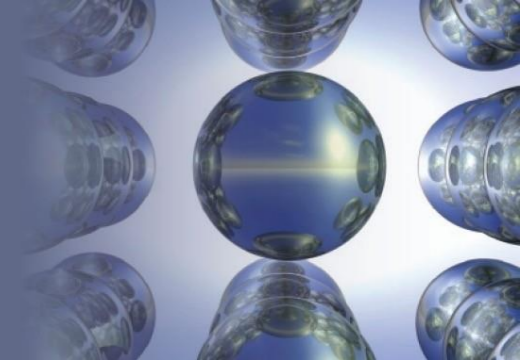
## Vapor Pressure Lowering: Addition of a Solute

<https://youtu.be/i0FrxbPsT8>

<https://youtu.be/CfagHzOtIDM>

# Section 11.4

## *The Vapor Pressures of Solutions*



### Vapor Pressures of Solutions

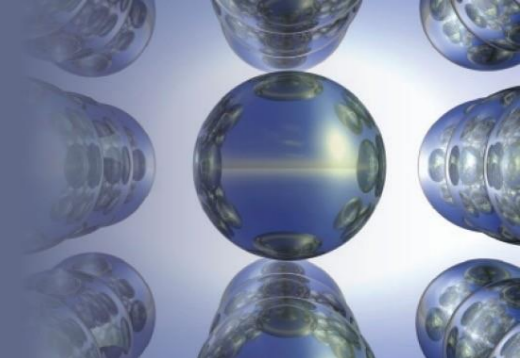
- Nonvolatile solute lowers the vapor pressure of a solvent.

- **Raoult's Law:**  $P_{\text{soln}} = \chi_{\text{solv}} P_{\text{solv}}^{\circ}$ 
  - $P_{\text{soln}}$  = observed vapor pressure of solution
  - $\chi_{\text{solv}}$  = mole fraction of solvent
  - $P_{\text{solv}}^{\circ}$  = vapor pressure of pure solvent

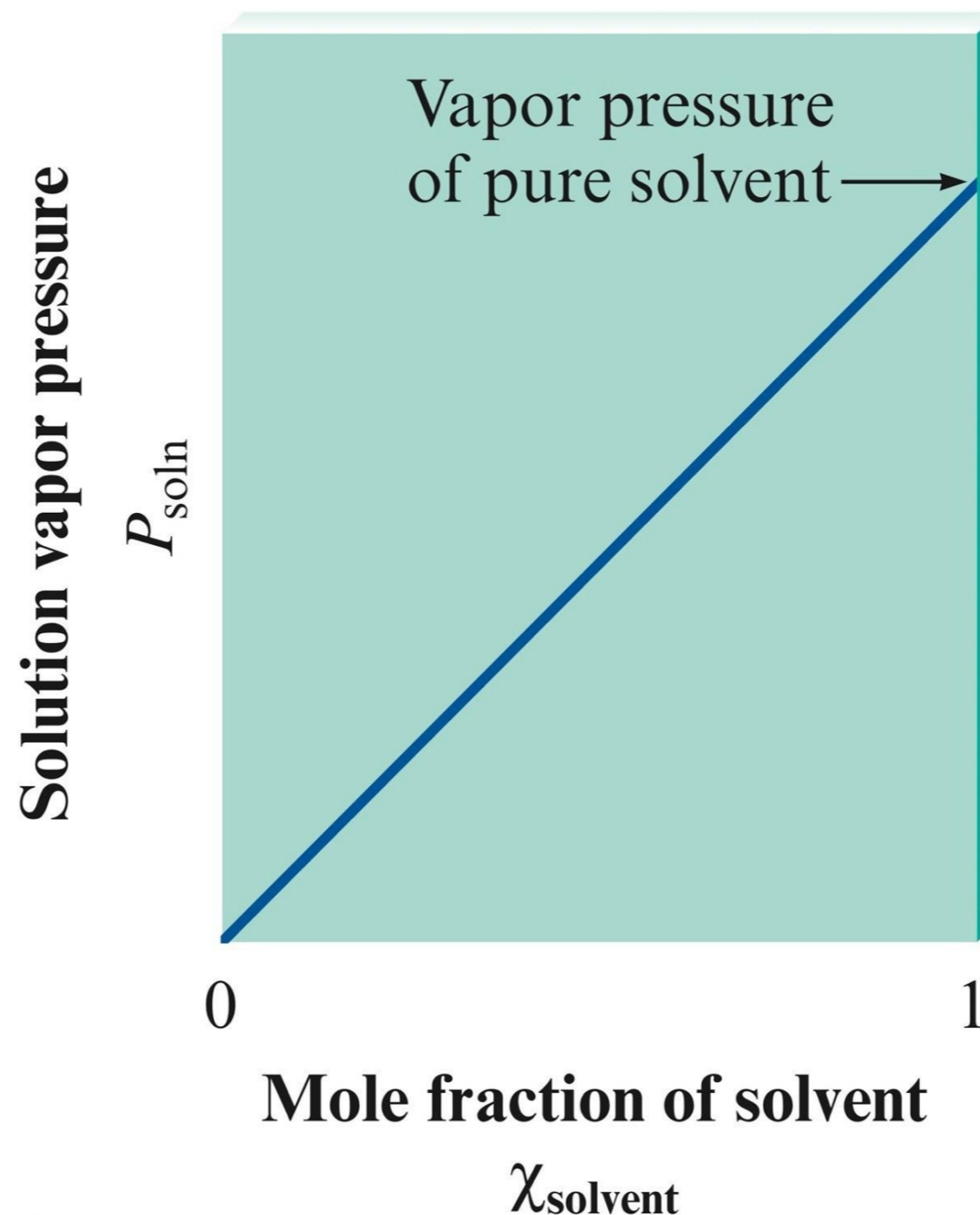


# Section 11.4

## *The Vapor Pressures of Solutions*



### A Solution Obeying Raoult's Law

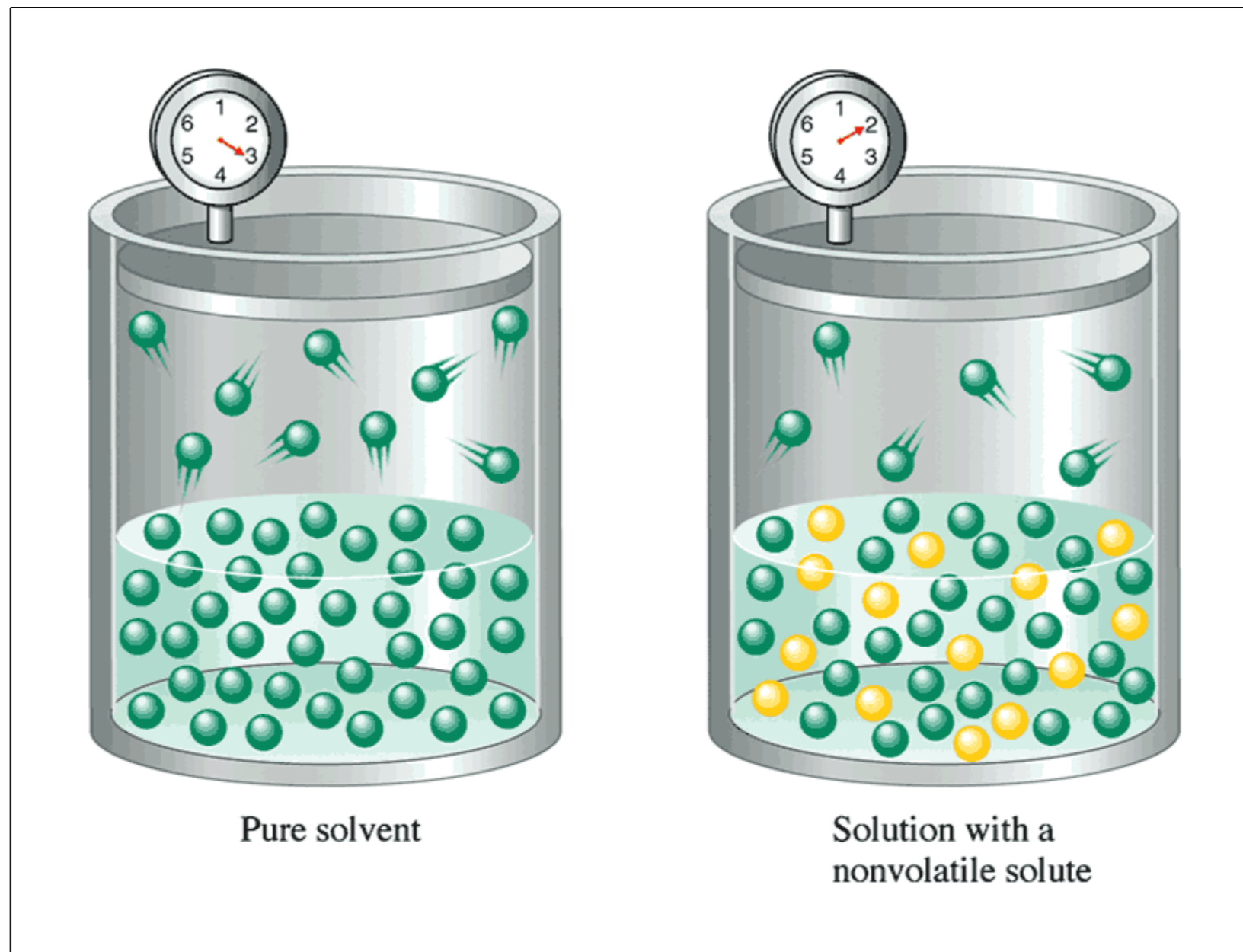




# Section 11.4

## *The Vapor Pressures of Solutions*

**Figure 11.10: The presence of a nonvolatile solute inhibits the escape of solvent molecules from the liquid and so lowers the vapor pressure of the solvent.**



## Section 11.4

# *The Vapor Pressures of Solutions*

### **EXERCISE 11.5**

Calculate the expected vapor pressure at 25C for a solution prepared by dissolving 158.0 g common table sugar (sucrose, molar mass = 342.3 g/mol) in 643.5 cm<sup>3</sup> of water. At 25C, the density of water is 0.9971 g/cm<sup>3</sup> and the vapor pressure is 23.76 torr.

## Solution

*What is Raoult's law for this case?*

$$P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^0$$

To calculate the mole fraction of water in the solution, we must first determine the number of moles of sucrose and the moles of water present.

*What are the moles of sucrose?*

$$\begin{aligned} \text{Moles of sucrose} &= 158.0 \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342.3 \text{ g sucrose}} \\ &= 0.4616 \text{ mol sucrose} \end{aligned}$$

*What are the moles of water?*

To determine the moles of water present, we first convert volume to mass using the density:

$$643.5 \text{ cm}^3 \text{ H}_2\text{O} \times \frac{0.9971 \text{ g H}_2\text{O}}{\text{cm}^3 \text{ H}_2\text{O}} = 641.6 \text{ g H}_2\text{O}$$

The number of moles of water is therefore

$$641.6 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 35.60 \text{ mol H}_2\text{O}$$

*What is the mole fraction of water in the solution?*

$$\begin{aligned} \chi_{\text{H}_2\text{O}} &= \frac{\text{mol H}_2\text{O}}{\text{mol H}_2\text{O} + \text{mol sucrose}} = \frac{35.60 \text{ mol}}{35.60 \text{ mol} + 0.4616 \text{ mol}} \\ &= \frac{35.60 \text{ mol}}{36.06 \text{ mol}} = 0.9873 \end{aligned}$$

- › The vapor pressure of the solution is:  $P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^0 = (0.9872)(23.76 \text{ torr}) = 23.46 \text{ torr}$

Thus the vapor pressure of water has been lowered from 23.76 torr in the pure state to 23.46 torr in the solution. The vapor pressure has been lowered by 0.30 torr.

## Section 11.4

# *The Vapor Pressures of Solutions*

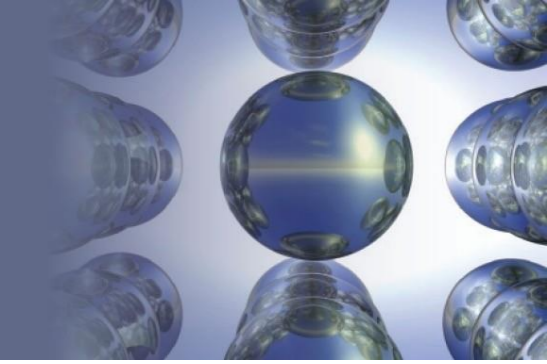
### **EXERCISE 11.6**

Predict the vapor pressure of a solution prepared by mixing 35.0 g solid  $\text{Na}_2\text{SO}_4$  (molar mass = 142.05 g/mol) with 175 g water at 25C. The vapor pressure of pure water at 25C is 23.76 torr .



# Section 11.4

## *The Vapor Pressures of Solutions*



### Nonideal Solutions

- Liquid-liquid solutions where both components are volatile.
- Modified Raoult's Law:

$$P_{\text{Total}} = P_A + P_B$$


$$P_{\text{Total}} = \chi_A P_A^\circ + \chi_B P_B^\circ$$

▪

A liquid-liquid solution that obeys Raoult's law is called an ideal solution

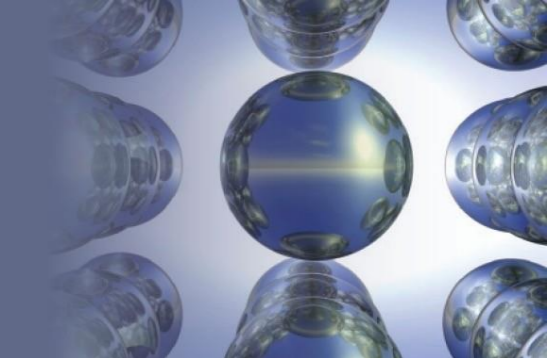
Nonideal solutions behave ideally as the mole fractions approach 0 and 1.



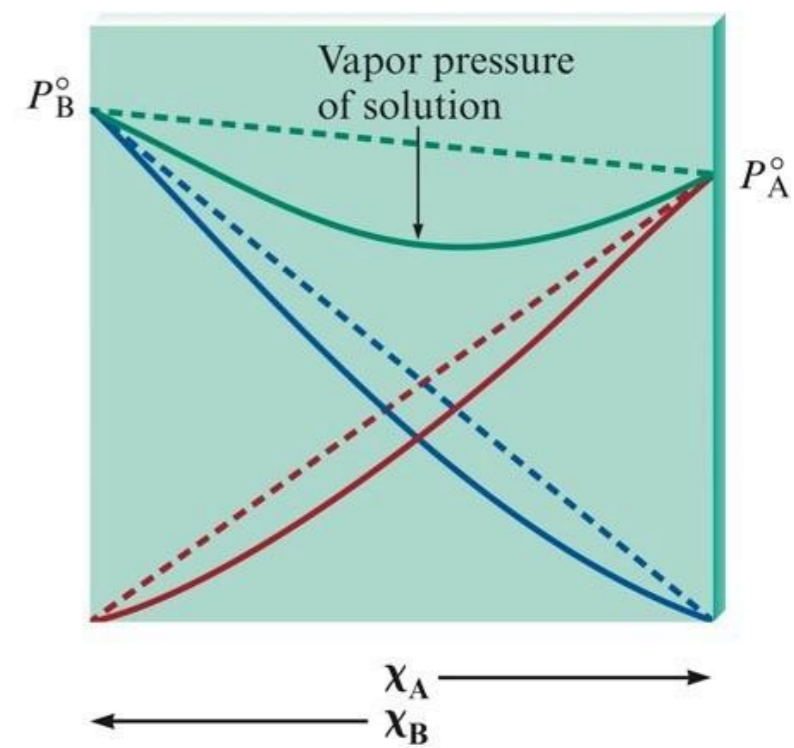
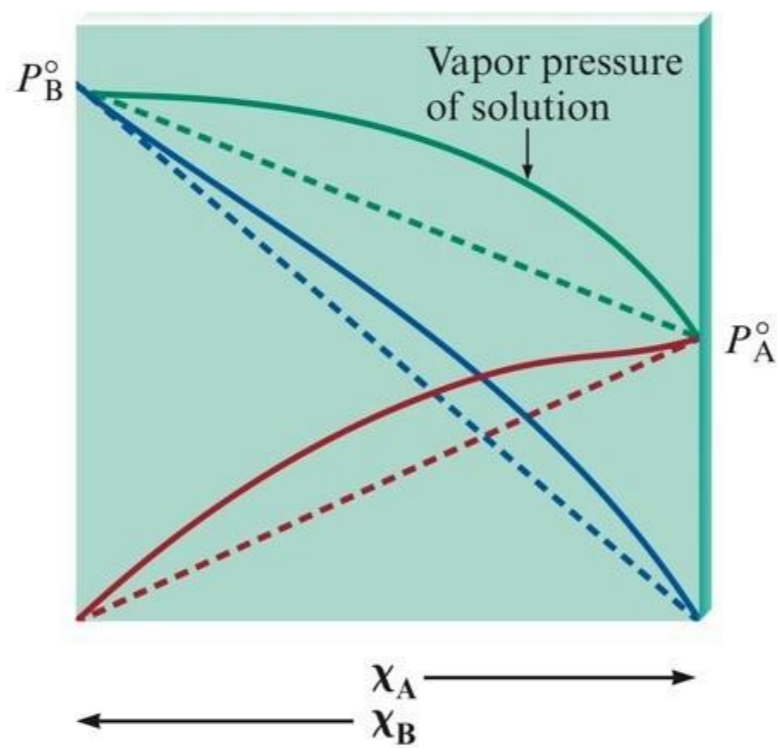
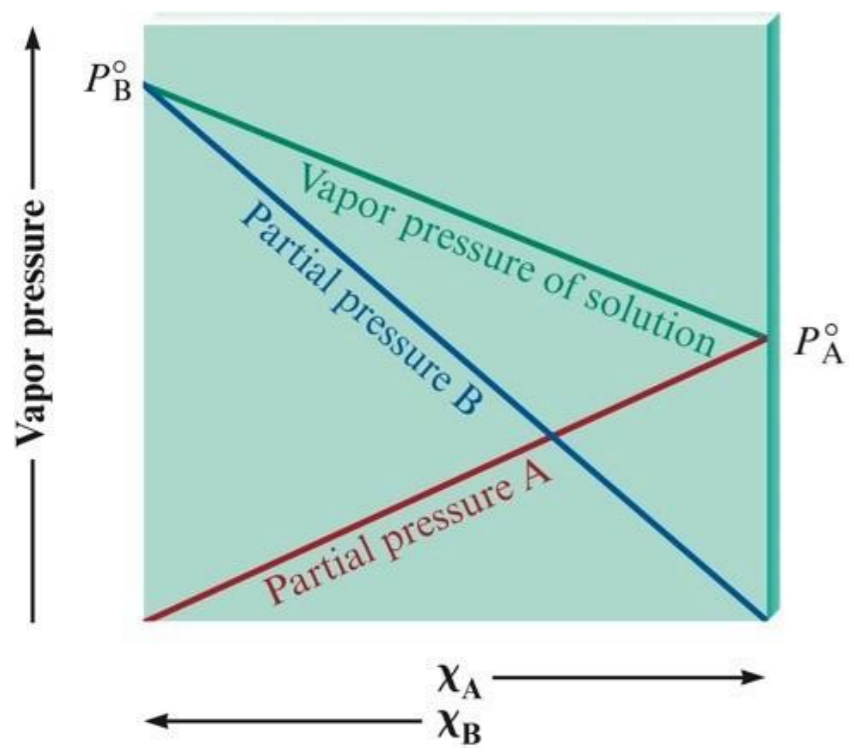
- 
- Nearly ideal behavior is often observed when the solute–solute, solvent–solvent, and solute–solvent interactions are very similar
  - If the solvent has a special affinity for the solute, such as if hydrogen bonding occurs, the tendency of the solvent molecules to escape will be lowered more than expected
  - Thus, vapor pressure will be lower than the value predicted by Raoult’s law; there will be a negative deviation from Raoult’s law.
  - when  $\Delta H_{\text{soln}}$  is large and negative, we can assume that strong interactions exist between the solute and solvent. In this case we expect a negative deviation from Raoult’s law

# Section 11.4

## The Vapor Pressures of Solutions



### Vapor Pressure for a Solution of Two Volatile Liquids



**a**

Ideal solution

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**b**

Weak solute-solvent interactions

**c**

Strong solute-solvent interactions

Benzene-toluene

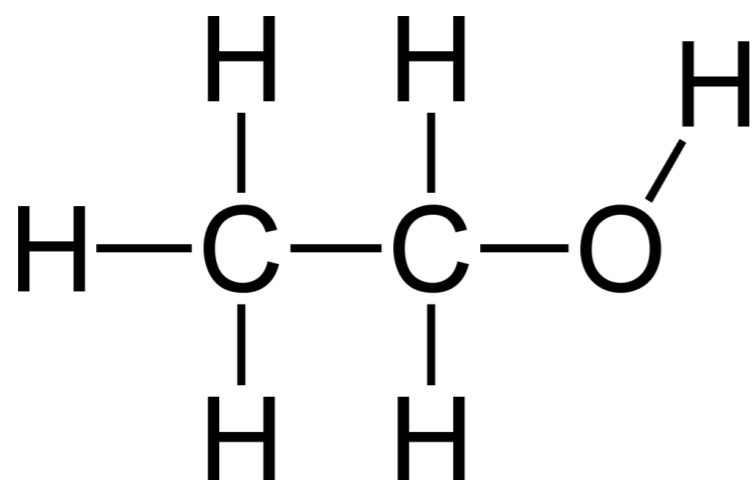
Ethanol-hexane

Acetone-water

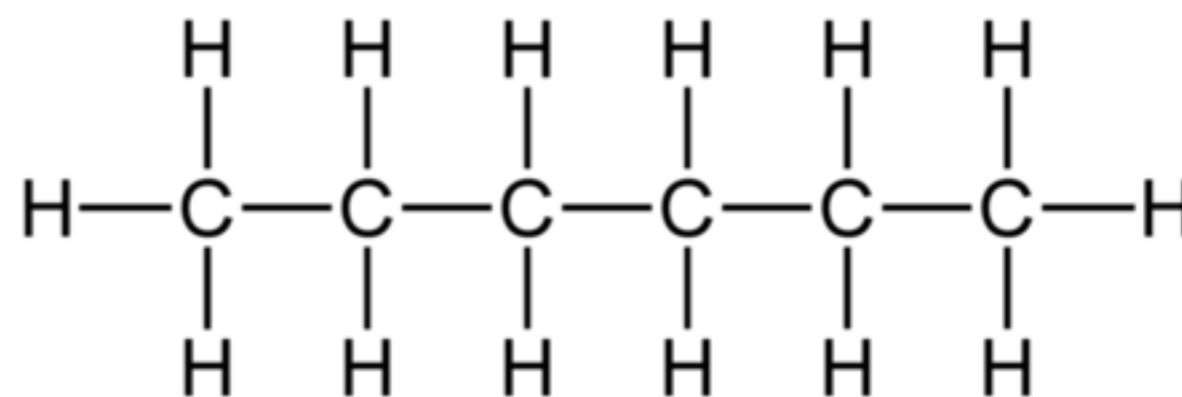
# Section 11.4

## *The Vapor Pressures of Solutions*

**Weak solute–solvent interactions**



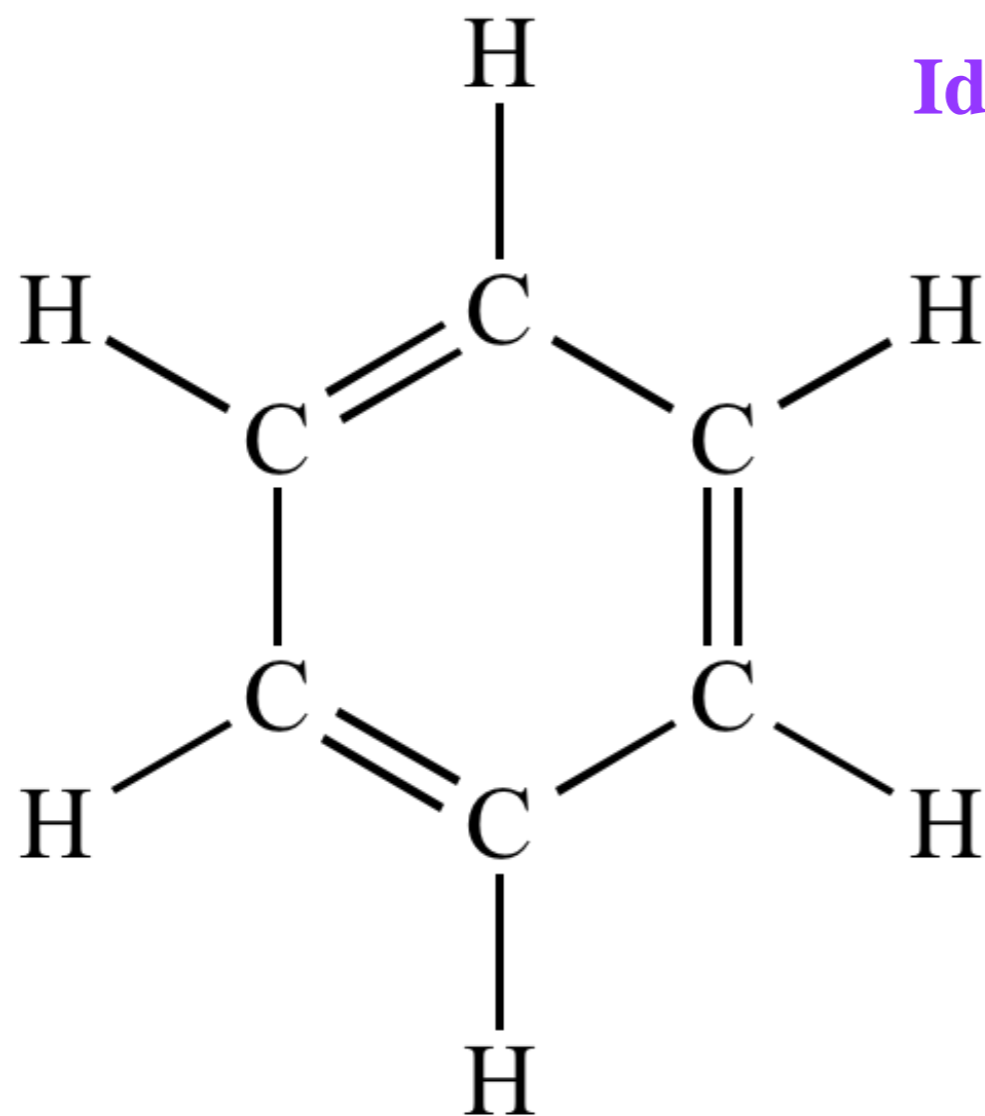
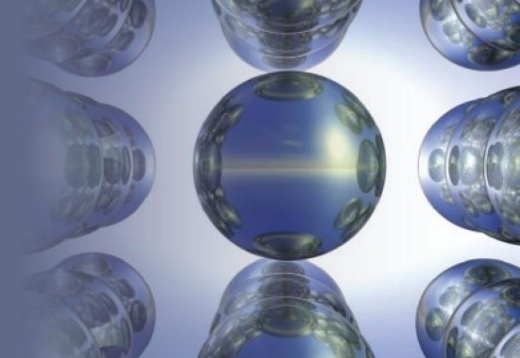
**Ethanol**



**Hexane**

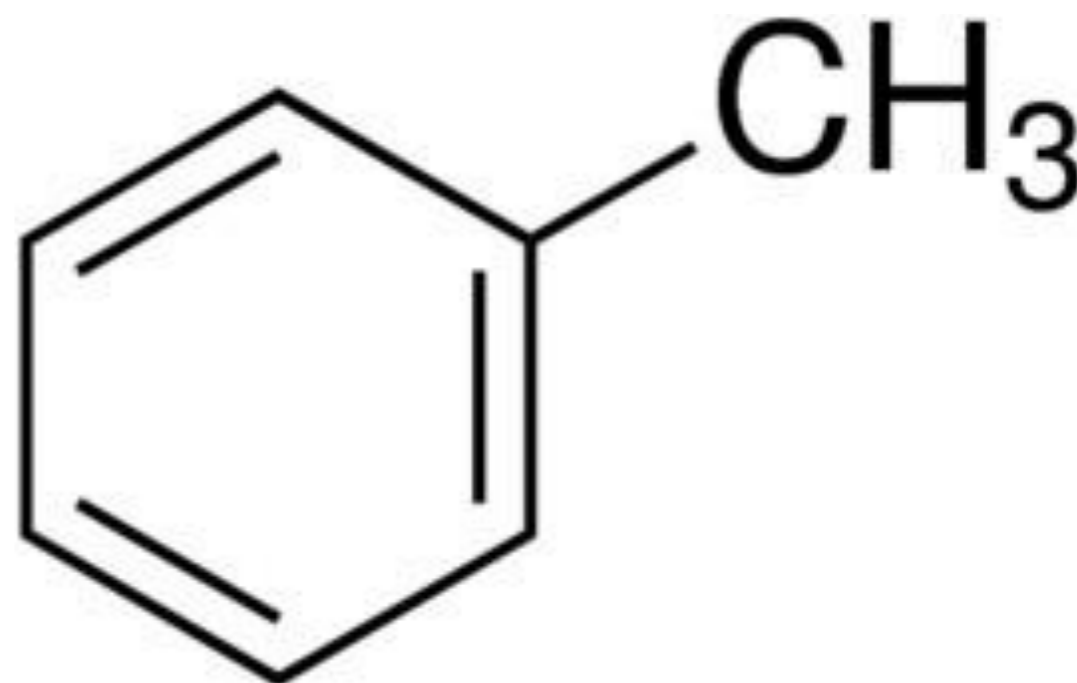
# Section 11.4

## *The Vapor Pressures of Solutions*



Ideal solution

**Benzene**

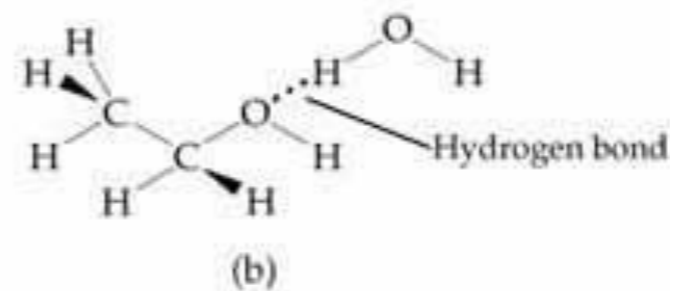
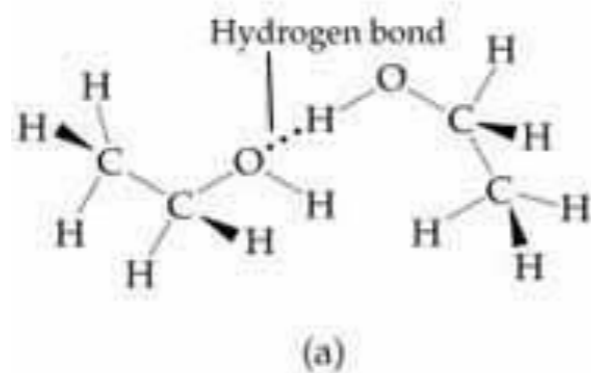
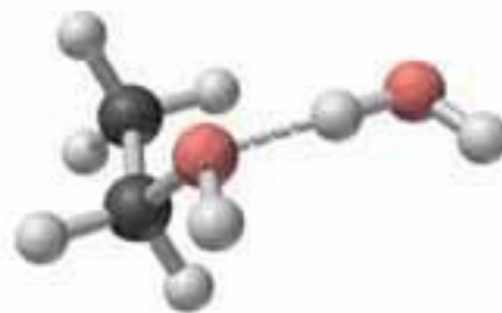
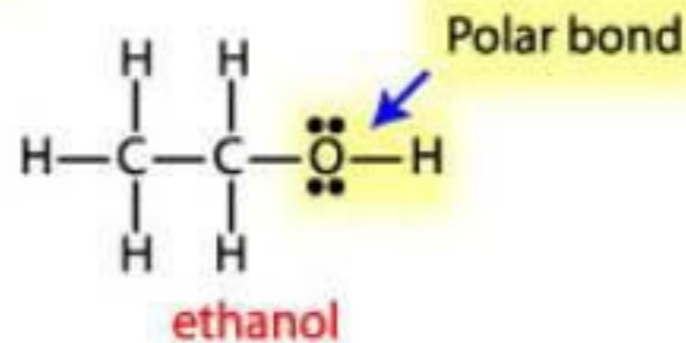


**Toluene**

# Section 11.4

## *The Vapor Pressures of Solutions*

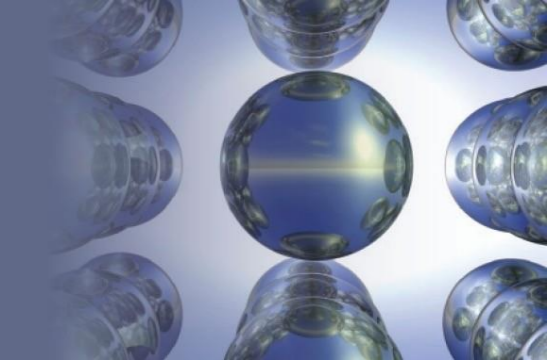
### Strong solute–solvent interactions





# Section 11.4

## *The Vapor Pressures of Solutions*



### Summary of the Behavior of Various Types of Solutions

<i>Interactive Forces Between Solute (A) and Solvent (B) Particles</i>	$\Delta H_{\text{soln}}$	$\Delta T$ for Solution Formation	<i>Deviation from Raoult's Law</i>	<i>Example</i>
$A \leftrightarrow A, B \leftrightarrow B \equiv A \leftrightarrow B$	Zero	Zero	None (ideal solution)	Benzene-toluene
$A \leftrightarrow A, B \leftrightarrow B < A \leftrightarrow B$	Negative (exothermic)	Positive	Negative	Acetone-water
$A \leftrightarrow A, B \leftrightarrow B > A \leftrightarrow B$	Positive (endothermic)	Negative	Positive	Ethanol-hexane



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# The Vapor Pressures of Solutions

### CONCEPT CHECK!

For each of the following solutions, would you expect it to be relatively **ideal** (with respect to Raoult's Law), show a **positive deviation**, or show a **negative deviation**?

a) Hexane ( $C_6H_{14}$ ) and chloroform ( $CHCl_3$ )

**positive deviation**

b) Ethyl alcohol ( $C_2H_5OH$ ) and water

**negative deviation**

c) Hexane ( $C_6H_{14}$ ) and octane ( $C_8H_{18}$ )

**ideal**

# Section 11.4

## *The Vapor Pressures of Solutions*

### **Example 11.7**

A solution is prepared by mixing 5.81 g acetone ( $\text{C}_3\text{H}_6\text{O}$ , molar mass 58.1 g/mol) and 11.9 g chloroform ( $\text{HCCl}_3$ , molar mass 119.4 g/mol). At 35C, this solution has a total vapor pressure of 260. torr. Is this an ideal solution? The vapor pressures of pure acetone and pure chloroform at 35C are 345 and 293 torr, respectively.

## Solution

To decide whether this solution behaves ideally, we first calculate the expected vapor pressure using Raoult's law:

$$P_{\text{TOTAL}} = \chi_{\text{A}}P_{\text{A}}^0 + \chi_{\text{C}}P_{\text{C}}^0$$

where A stands for acetone and C stands for chloroform. The calculated value can then be compared with the observed vapor pressure.

First, we must calculate the number of moles of acetone and chloroform:

$$5.81 \text{ g acetone} \times \frac{1 \text{ mol acetone}}{58.1 \text{ g acetone}} = 0.100 \text{ mol acetone}$$

$$11.9 \text{ g chloroform} \times \frac{1 \text{ mol chloroform}}{119 \text{ g chloroform}} = 0.100 \text{ mol chloroform}$$

Since the solution contains equal numbers of moles of acetone and chloroform, that is,

$$\chi_{\text{A}} = 0.500 \quad \text{and} \quad \chi_{\text{C}} = 0.500$$

the expected vapor pressure is

$$P_{\text{TOTAL}} = (0.500)(345 \text{ torr}) + (0.500)(293 \text{ torr}) = 319 \text{ torr}$$