Solutions

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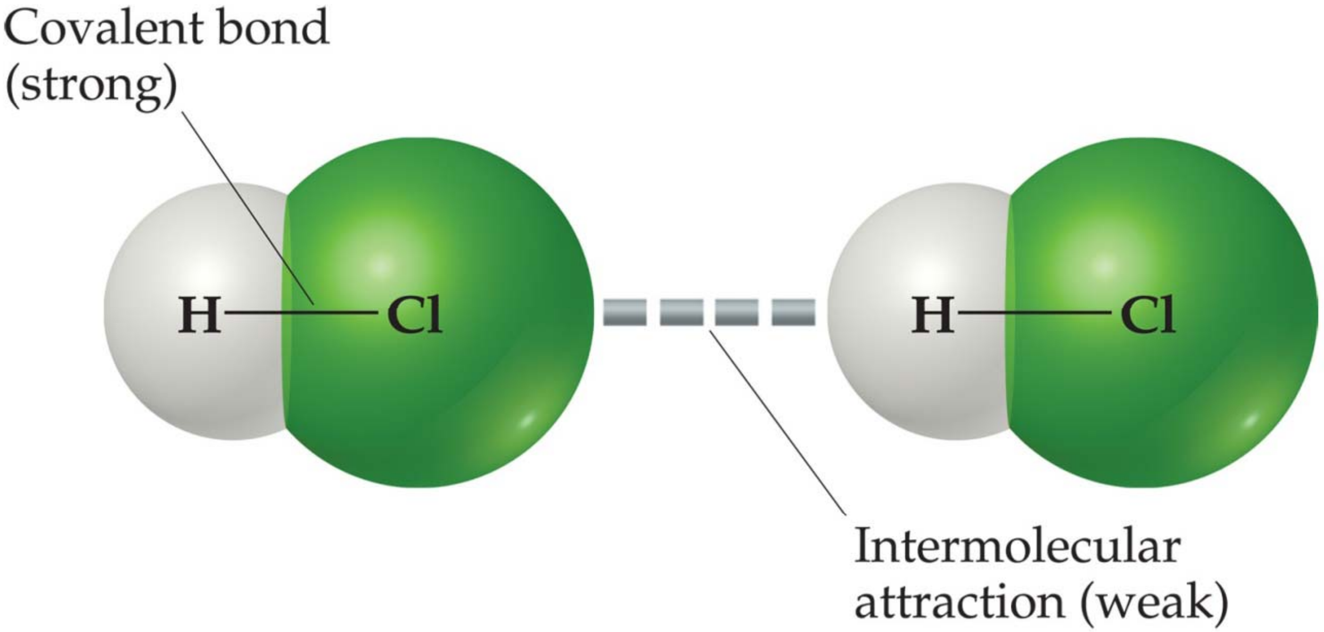
Intermolecular Forces

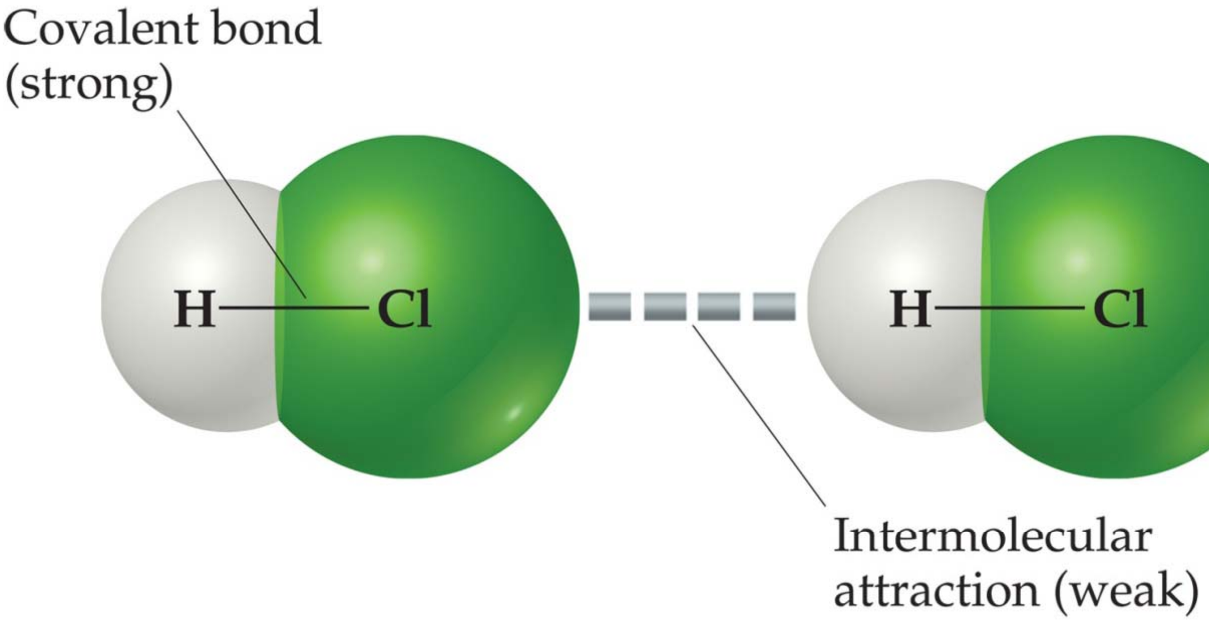
A Review

Intermolecular Forces



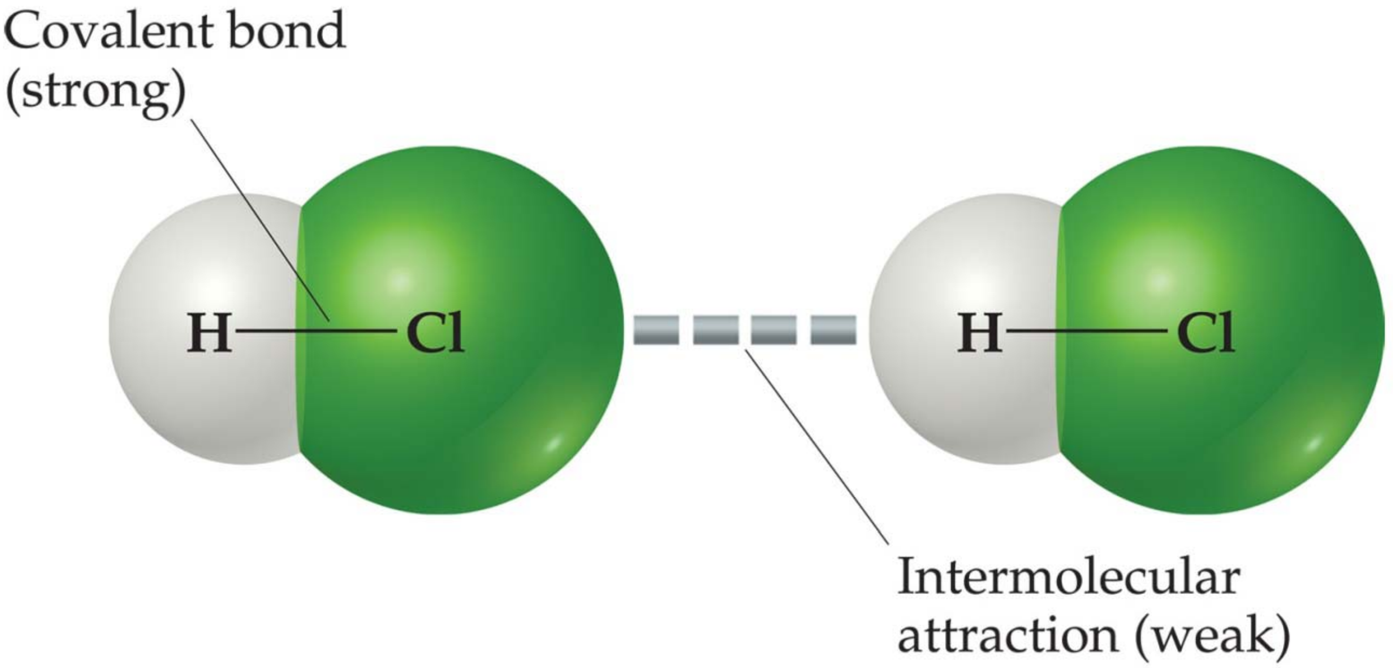
The attractions between molecules are not nearly as strong as the intramolecular attractions that hold compounds together.

Intermolecular Forces



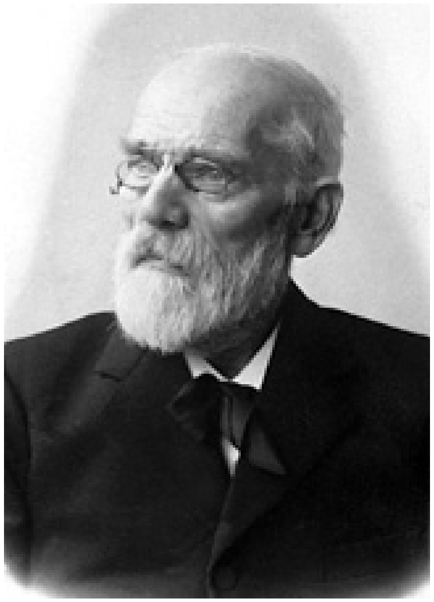
They are, however, strong enough to control physical properties such as boiling and melting points, vapor pressures, viscosities, surface tension, and related properties.

Intermolecular Forces



These intermolecular forces as a group are referred to as van der Waals forces.

Johannes Diderik van der Waals
(1837-1923)

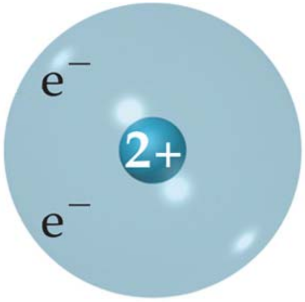


- In 1873 he obtained his doctor's degree for a thesis entitled *Over de Continuïteit van den Gas - en Vloeistoftoestand* (On the continuity of the gas and liquid state)
- In this thesis he put forward an "Equation of State" embracing both the gaseous and the liquid state; he demonstrated that these two states of aggregation not only merge into each other in a continuous manner, but that they are in fact of the same nature.
- Van der Waals saw the necessity of taking into account the volumes of molecules and the intermolecular forces ("Van der Waals forces", as they are now known) in establishing the relationship between the pressure, volume and temperature of gases and liquids.

Intermolecular Forces

- London dispersion forces
- Dipole-induced dipole interactions
- Dipole-dipole interactions
- Hydrogen bonding
- Ion-induced dipole interactions
- Ion-dipole interactions

London Dispersion Forces



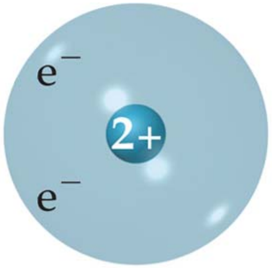
Helium atom 2

The electrons in the 1*s* orbital of helium repel each other.

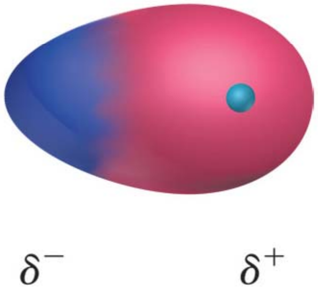
Although they are paired, they tend to stay away from each other

In their normal motion in the 1s energy level, they occasionally wind up on the same side of the atom.

London Dispersion Forces



Helium atom 2

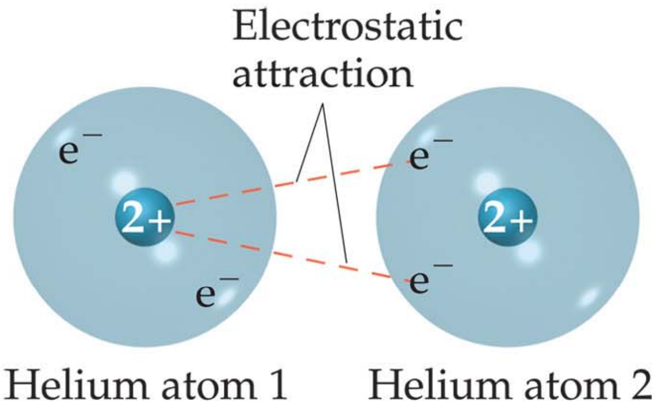


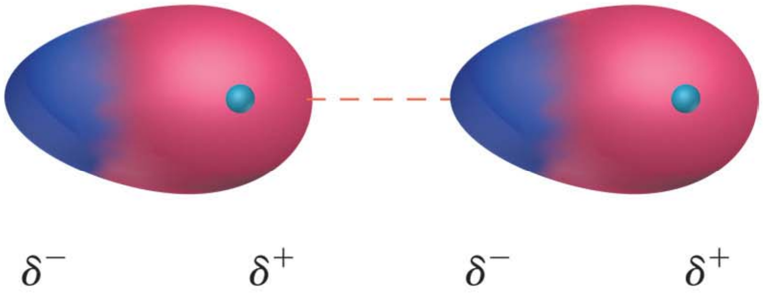
At that instant, as shown in the diagram above, the helium atom is polar, with its electrons on the left side and no electrons on the right side.

This is called an instantaneous dipole

This can be diagrammed as shown on the right, above.

London Dispersion Forces

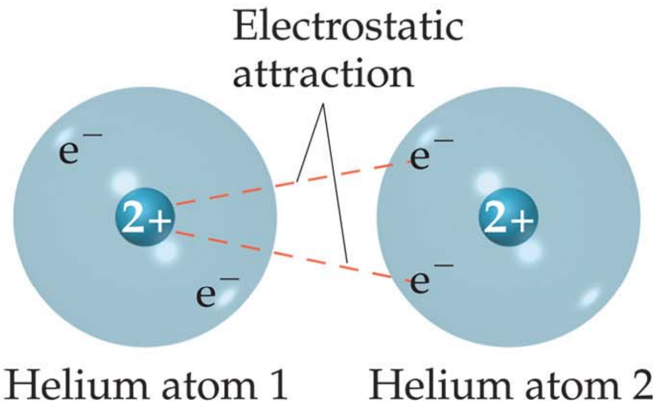


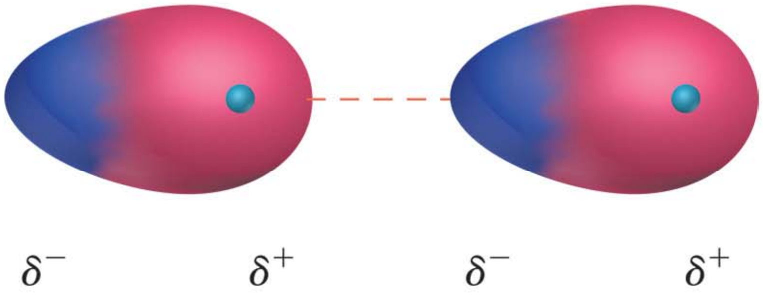


Another helium nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.

The second helium atom has an induced dipole

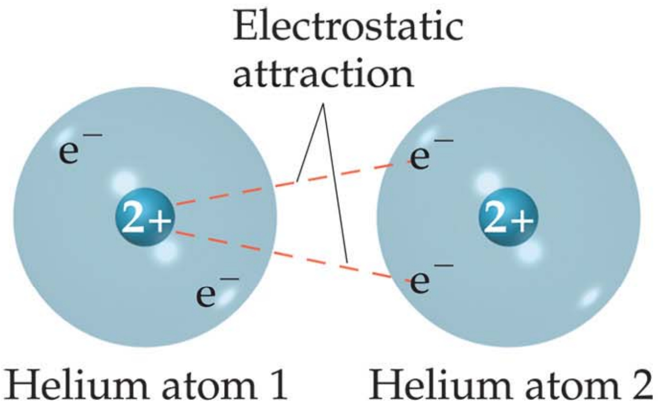
London Dispersion Forces

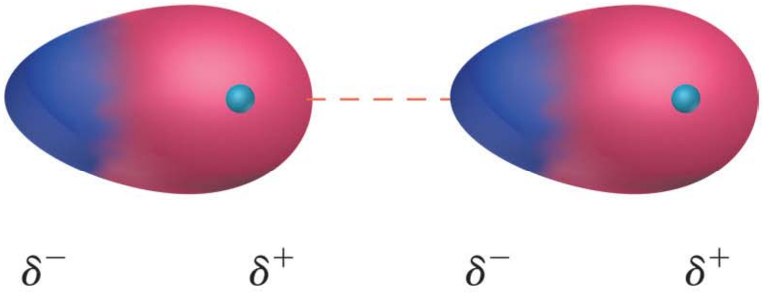




London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole.

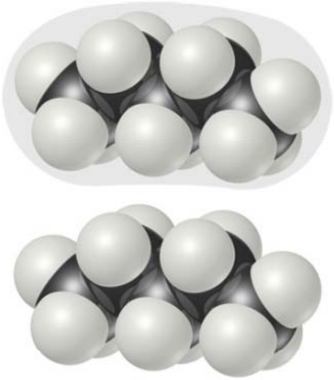
London Dispersion Forces



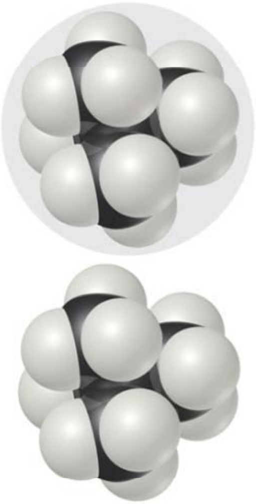


- These forces are present in *all* molecules, whether they are polar or nonpolar.
- The tendency of an electron cloud to distort in this way is called **polarizability**.

Factors Affecting London Forces



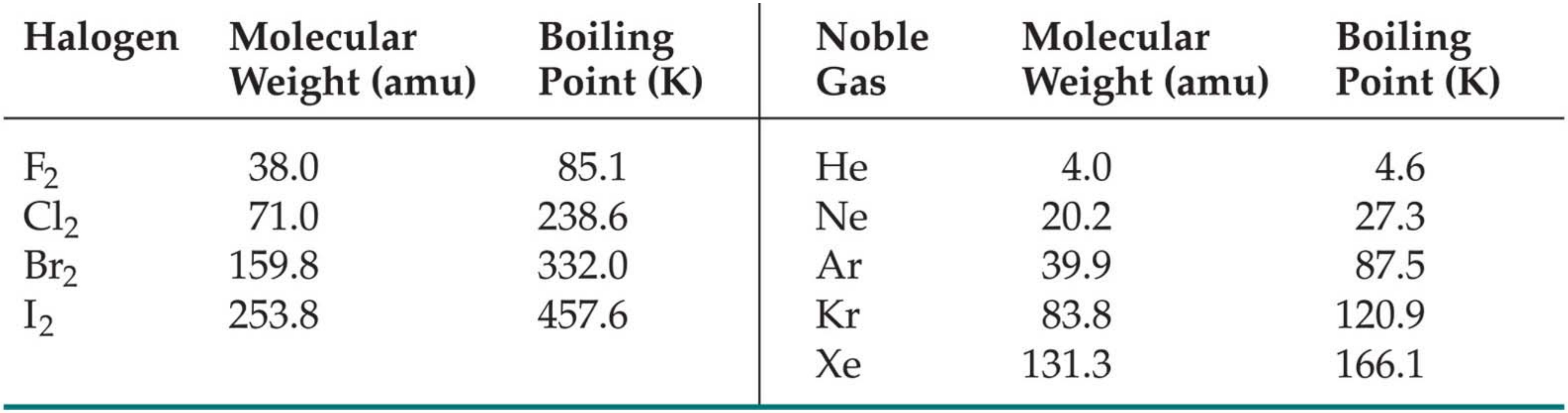
n-Pentane
(bp = 309.4 K)



Neopentane
(bp = 282.7 K)

- The shape of the molecule affects the strength of dispersion forces:
  - long, skinny molecules (like *n*-pentane) tend to have stronger dispersion forces
  - short, fat molecules (like neopentane, 2,2-dimethylpropane) have weaker dispersion forces
  - This is due to the increased surface area in *n*-pentane.

Factors Affecting London Forces

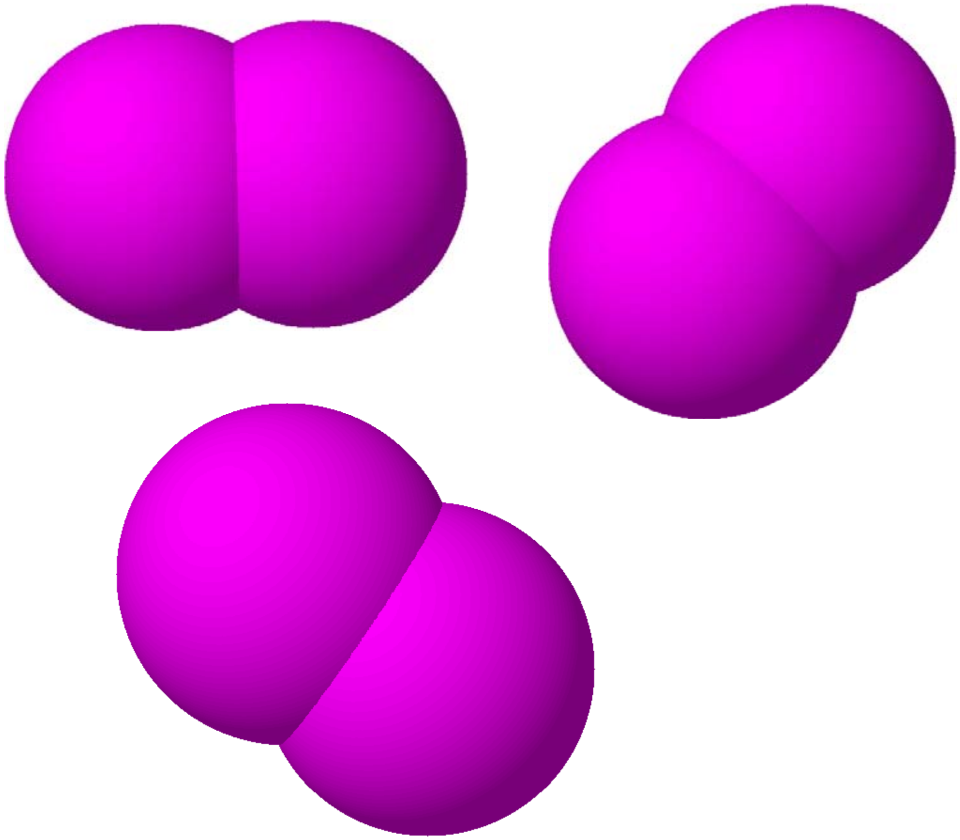


Halogen	Molecular Weight (amu)	Boiling Point (K)	Noble Gas	Molecular Weight (amu)	Boiling Point (K)
F_2	38.0	85.1	He	4.0	4.6
Cl_2	71.0	238.6	Ne	20.2	27.3
Br_2	159.8	332.0	Ar	39.9	87.5
I_2	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

- The strength of dispersion forces tends to increase with increased molecular weight.
- Larger atoms have larger electron clouds, which are easier to polarize.

Intermolecular forces in I_2

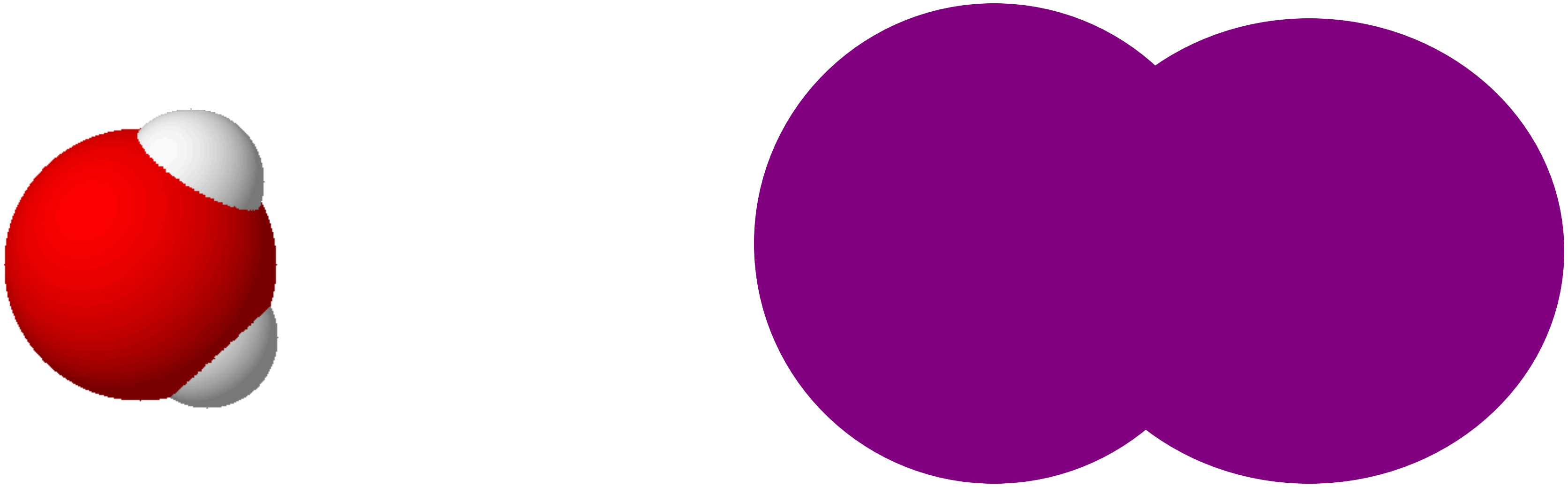
1. Iodine vapor
2. Iodine-hexane: Nonpolar interactions (London forces)



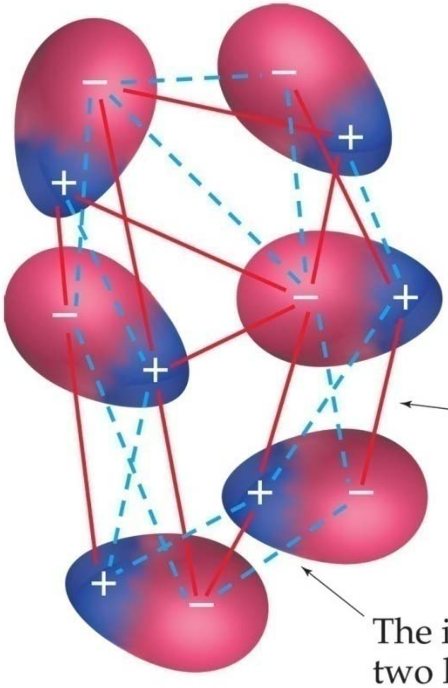
Dipole-Induced Dipole Interactions
Intermolecular forces using I_2

Molecules that have permanent dipoles can induce a dipole on a non-polar atom or molecule

Demonstration: iodine in water



Dipole-Dipole Interactions



The interaction between any two opposite charges is attractive (solid red lines).

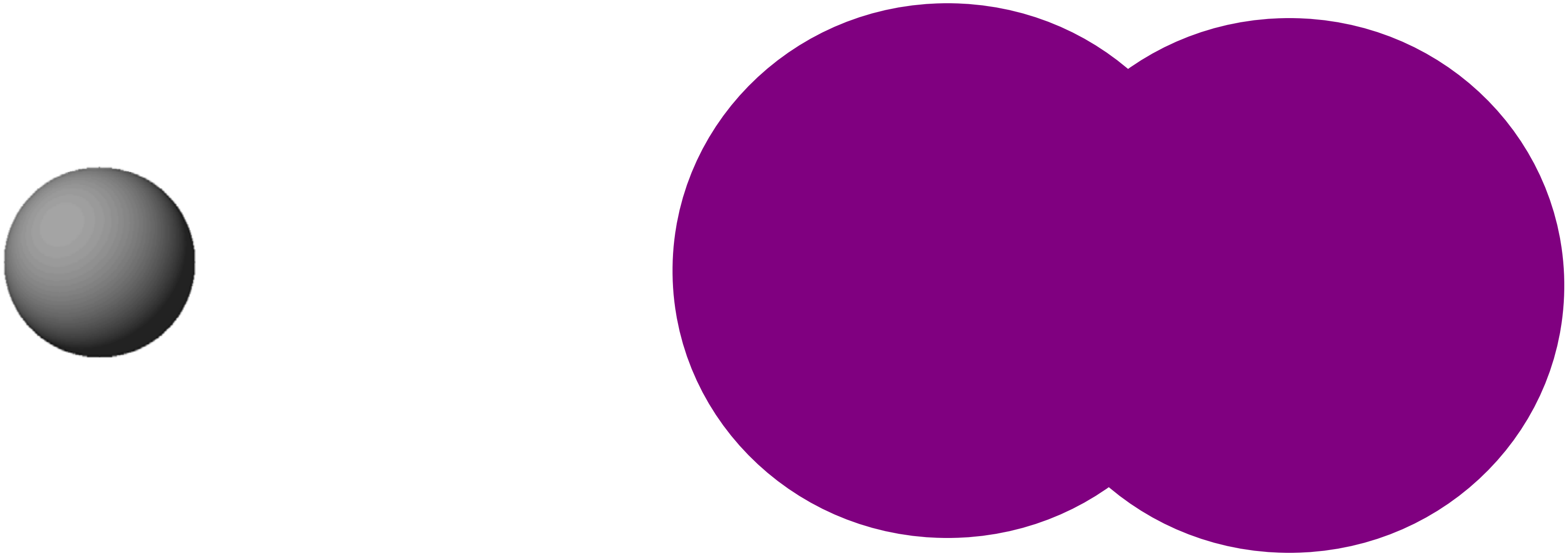
The interaction between any two like charges is repulsive (dashed blue lines).

- Molecules that have permanent dipoles are attracted to each other.
  - The positive end of one is attracted to the negative end of the other and vice-versa.
  - These forces are only important when the molecules are close to each other.

Ion-Induced Dipole Interactions
Intermolecular forces using I_2

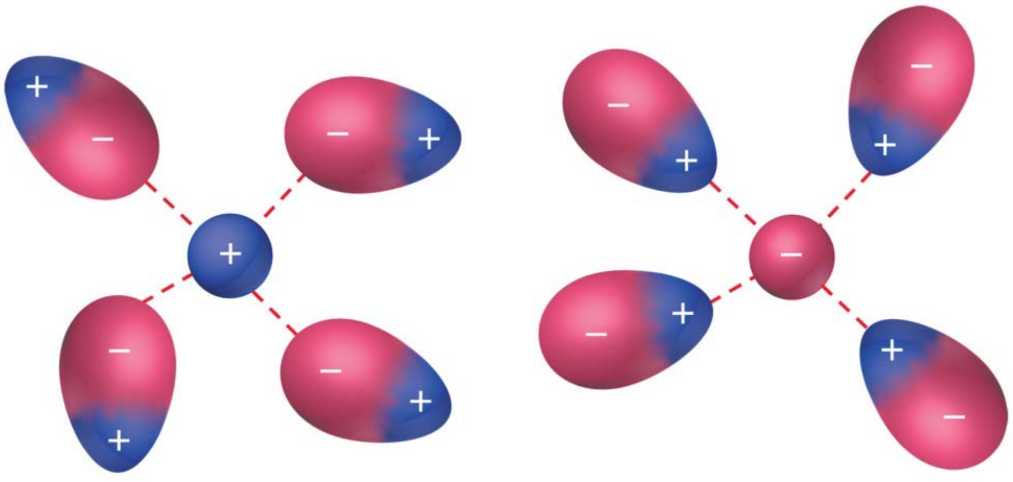
Ions can induce a dipole on a non-polar atom or molecule

Demonstration: Add potassium iodide to iodine in water



Ion-Dipole Interactions

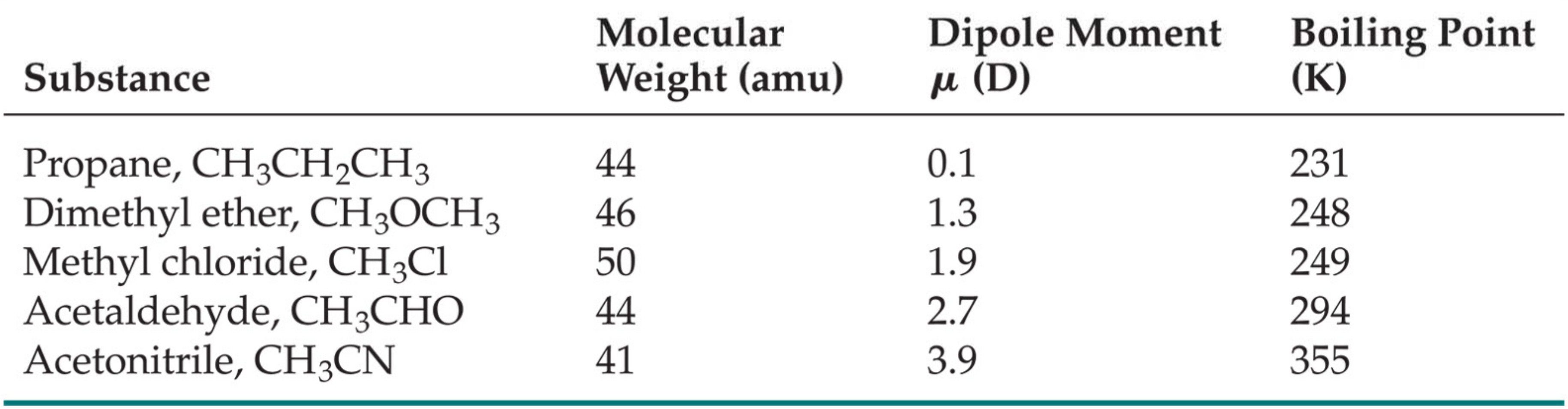
- Ion-dipole interactions are an important force in solutions of ions.
- The strength of these forces are what make it possible for ionic substances to dissolve in polar solvents.



Cation-dipole attractions

Anion-dipole attractions

Dipole-Dipole Interactions



Substance	Molecular Weight (amu)	Dipole Moment μ (D)	Boiling Point (K)
Propane, $CH_3CH_2CH_3$	44	0.1	231
Dimethyl ether, CH_3OCH_3	46	1.3	248
Methyl chloride, CH_3Cl	50	1.9	249
Acetaldehyde, CH_3CHO	44	2.7	294
Acetonitrile, CH_3CN	41	3.9	355

The more polar the molecule, the higher is its boiling point.

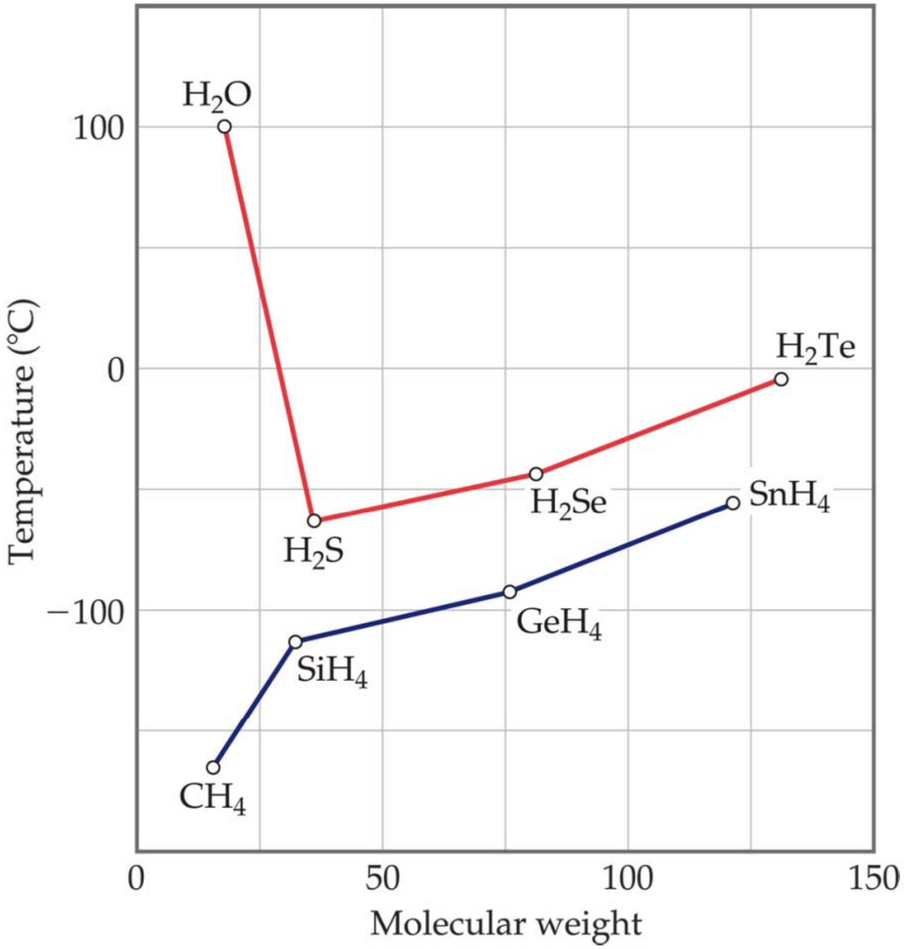
NOTE: To better see the polarity of these molecules, draw their structures.

Which Have a Greater Effect:

Dipole-Dipole Interactions or Dispersion Forces?

- If two substances have molecules that are of comparable size and shape
  - Dispersion forces are approximately equal in the two substances
  - If there is any polarity in the molecules, then dipole-dipole interactions will be the dominating force.
- If two substances differ where one molecule is much larger than another
  - If they are non-polar, substances, dispersion forces in the substance consisting of larger molecules will be stronger.

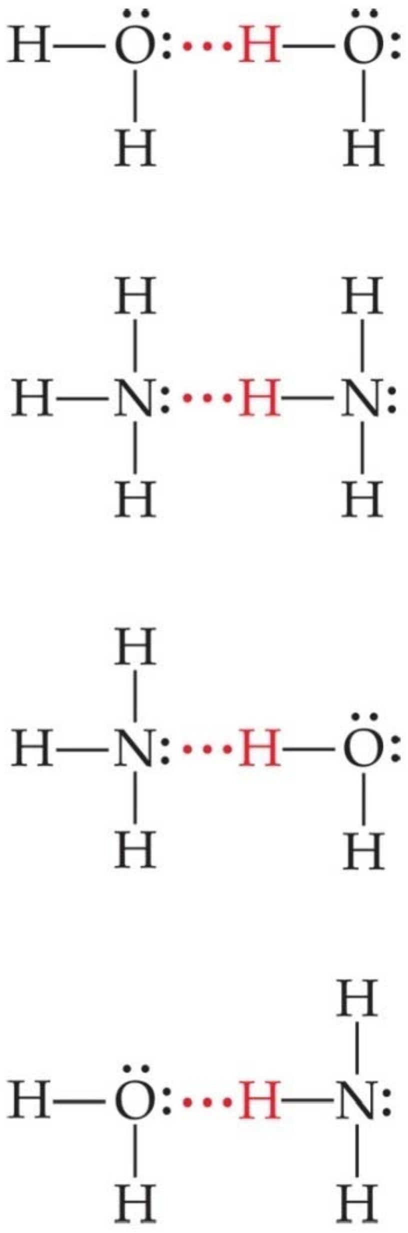
How Do We Explain This?



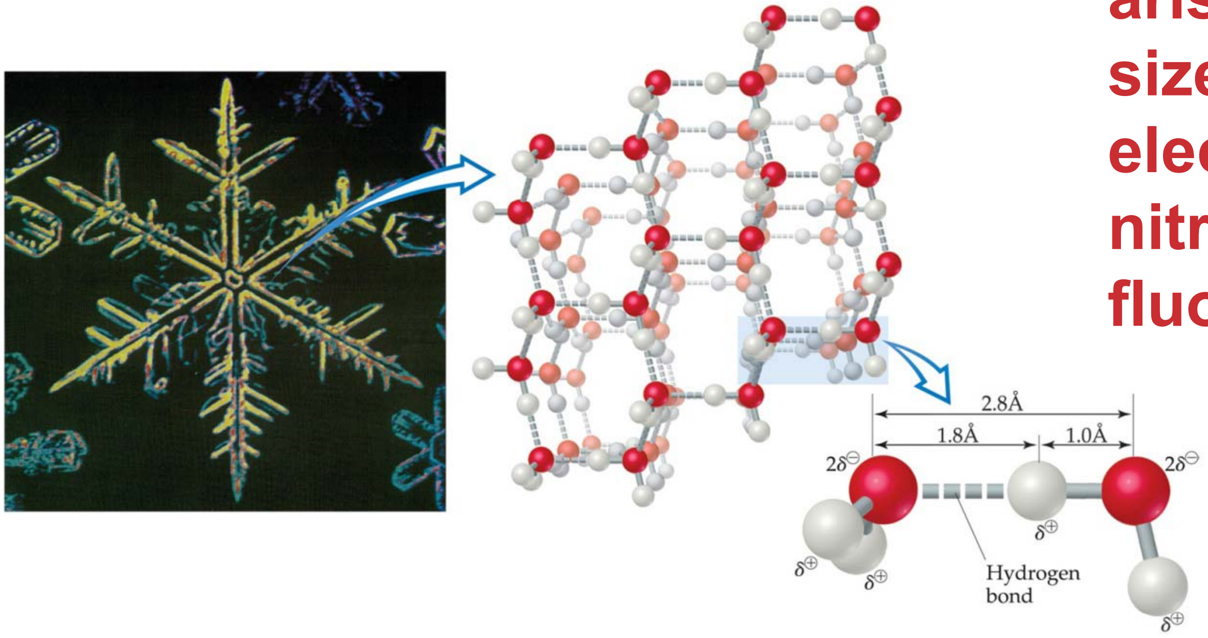
- The nonpolar series (SnH_4 to CH_4) follow the expected trend.
- The polar series follows the trend from H_2Te through H_2S, but water is quite an anomaly.

Hydrogen Bonding

- The dipole-dipole interactions experienced when H is bonded to N, O, or F are unusually strong.
- We call these interactions hydrogen bonds.



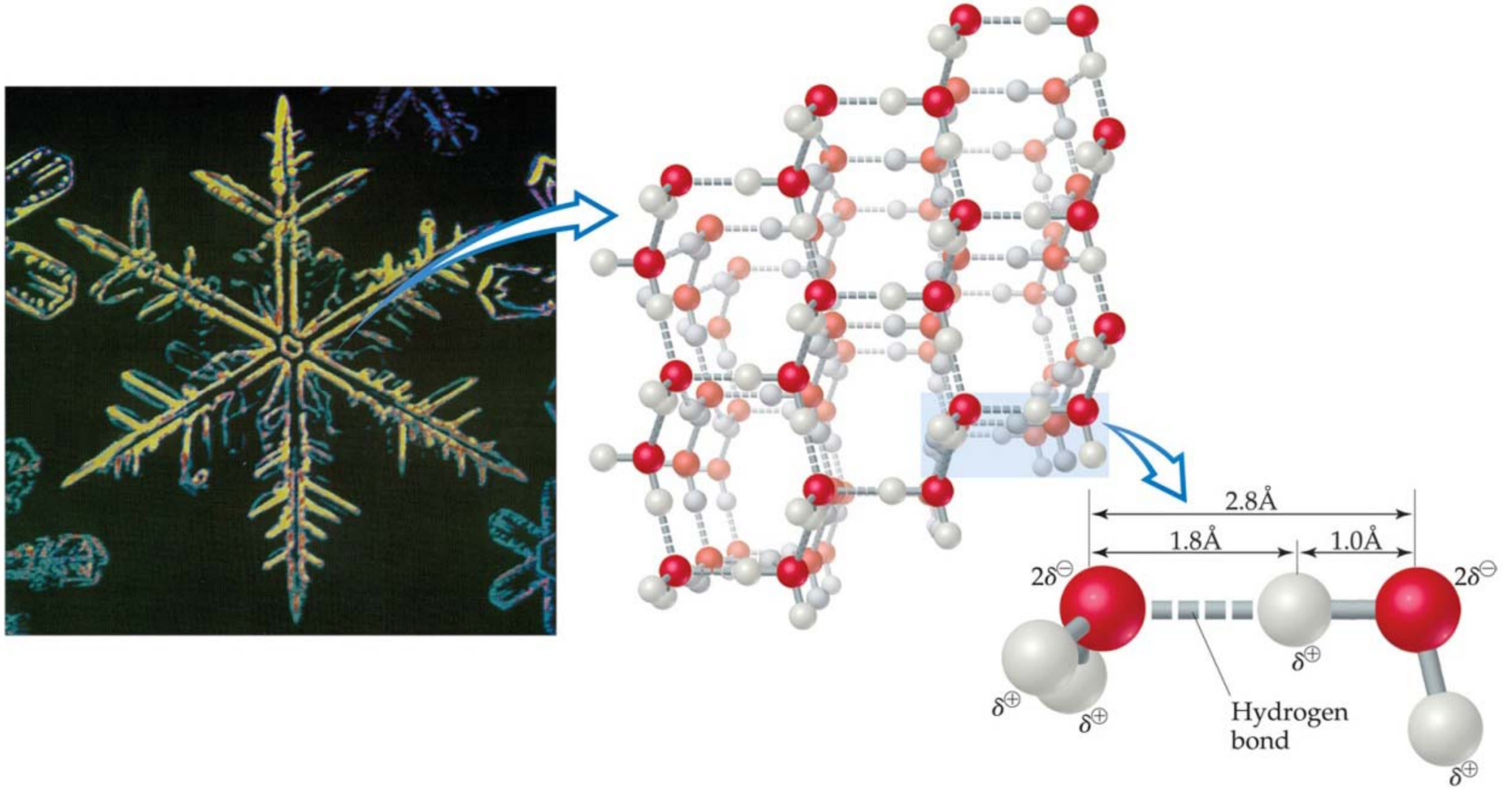
Hydrogen Bonding



Hydrogen bonding arises from the small size and high electronegativity of nitrogen, oxygen, and fluorine.

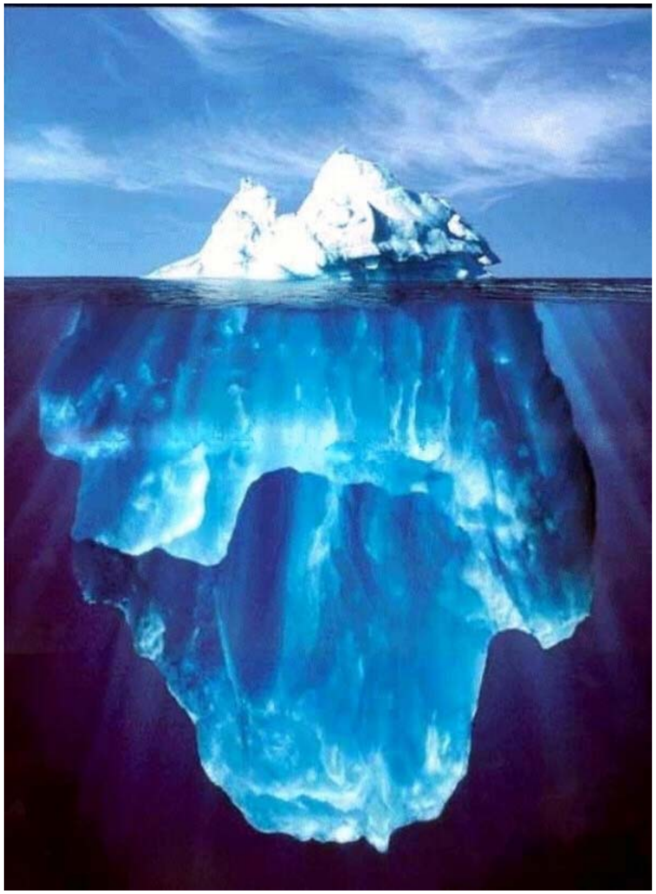
Also, when hydrogen is bonded to one of those small, electronegative elements, the hydrogen nucleus is essentially exposed.

Hydrogen Bonding



The hexagonal shape of a snowflake is a result of the hexagonal, non-planar rings formed by water molecules in ice. When water is cooled below 4°C, the molecules slow down sufficiently so repulsions between the water molecules cause the molecules to move apart causing the density of the cold water or ice to decrease.

Water expands on freezing



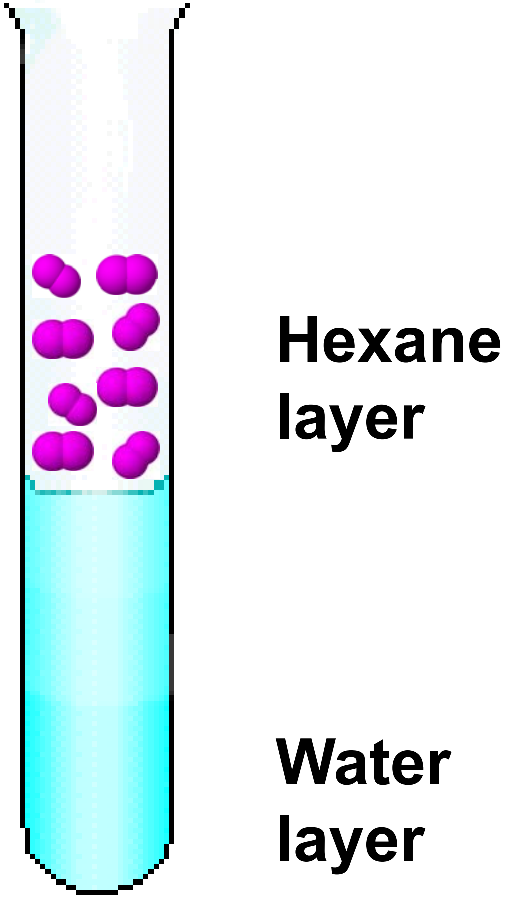
Ice is less dense than liquid water

Intermolecular forces
Intermolecular forces using I_2

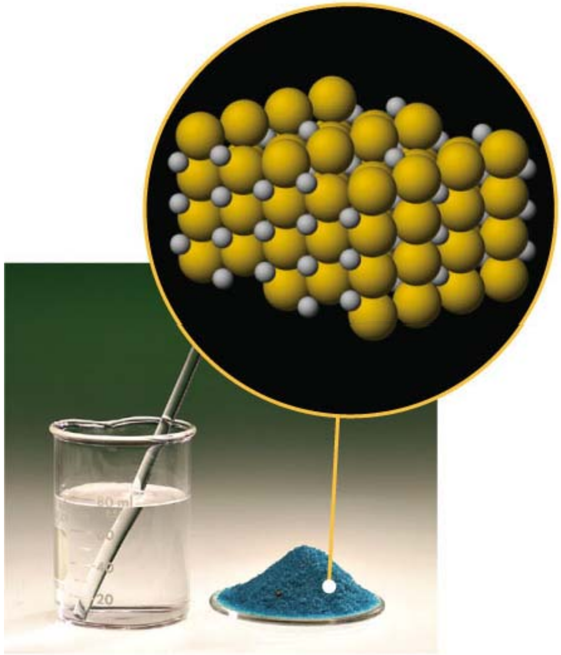
Even though there are these different forces of attraction between particles, there are still preferences.

When given the proper conditions, iodine prefers a non-polar solvent:

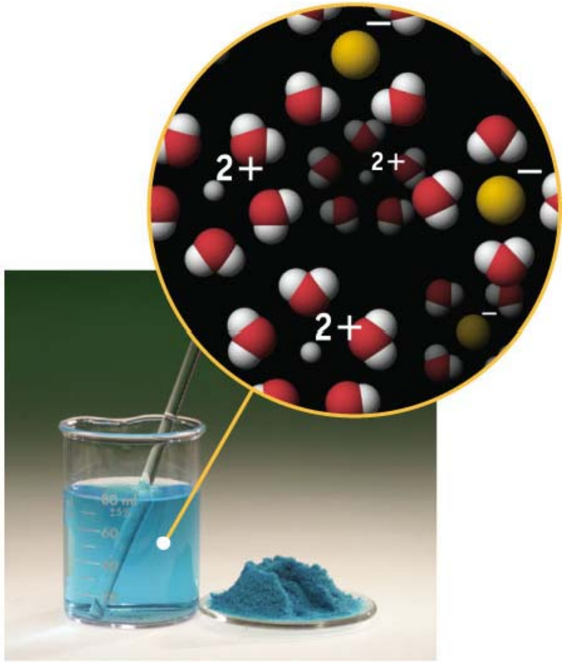
Like dissolves like



Solutions



(a) Copper(II) chloride, the solute, is added to water, the solvent.



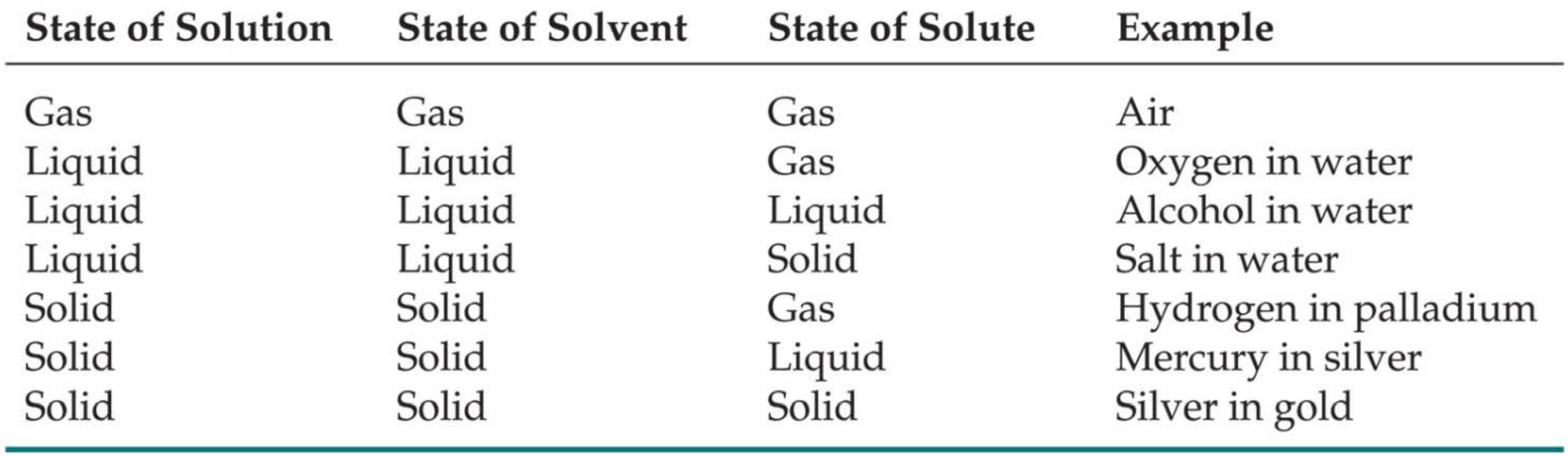
(b) Interactions between water molecules and Cu^{2+} and Cl^{-} ions allow the solid to dissolve. The ions are now sheathed with water molecules.

A solution is a HOMOGENEOUS mixture of 2 or more substances in a single phase.

One constituent is usually regarded as the SOLVENT (usually water) and the others as SOLUTES.

Solutions

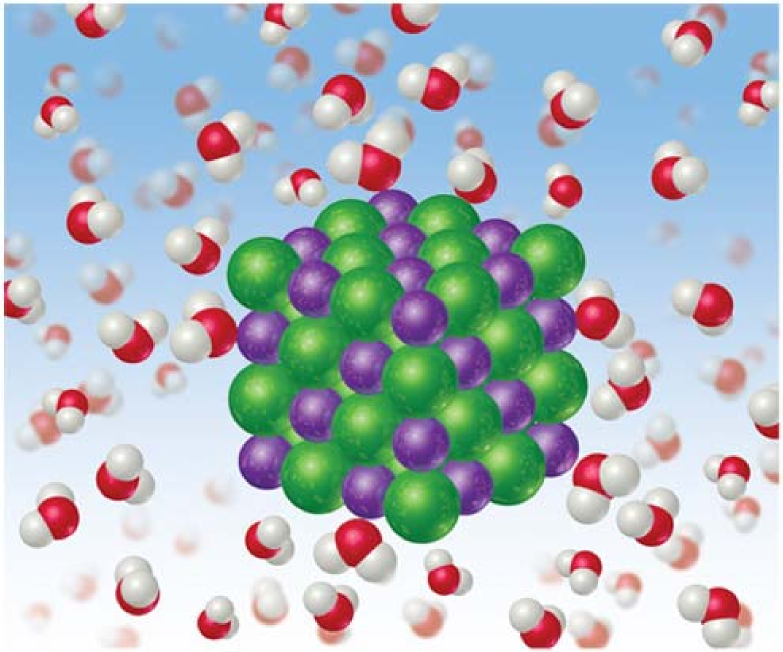
- In a solution, the **solute** is dispersed uniformly throughout the **solvent**.



State of Solution	State of Solvent	State of Solute	Example
Gas	Gas	Gas	Air
Liquid	Liquid	Gas	Oxygen in water
Liquid	Liquid	Liquid	Alcohol in water
Liquid	Liquid	Solid	Salt in water
Solid	Solid	Gas	Hydrogen in palladium
Solid	Solid	Liquid	Mercury in silver
Solid	Solid	Solid	Silver in gold

Intermolecular Forces
Why does a substance dissolve?

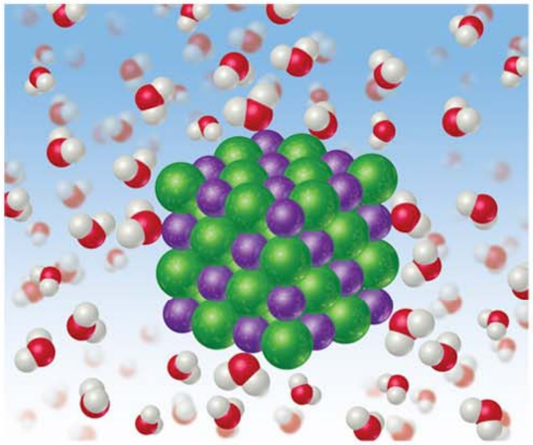
The intermolecular forces between solute and solvent particles must be strong enough to compete with those between solute particles and those between solvent particles.



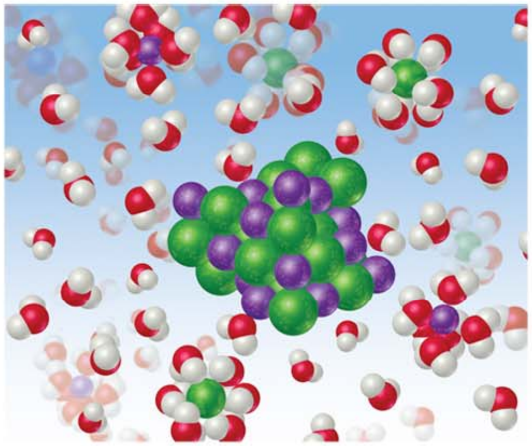
How Does a Solution Form?

In this example, we have an ionic solid, NaCl, and a polar solvent, H_2O.

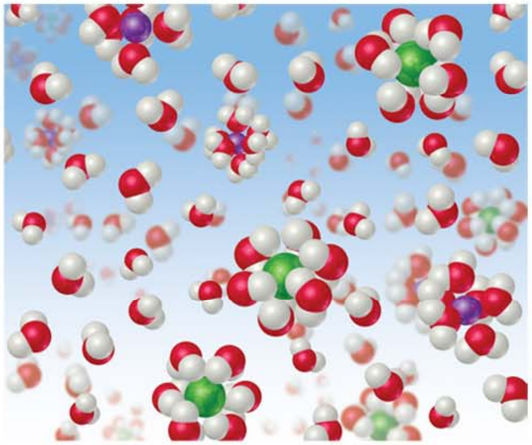
The solution forms because the solvent pulls solute particles apart and surrounds, or **solvates**, them. In water this is called **hydration**.



Solute (NaCl) in water

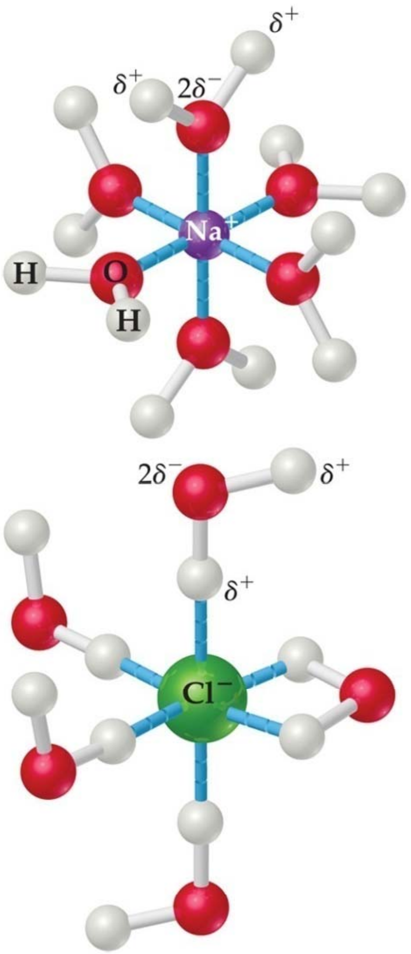


The solute is dissolving



Hydrated ions in solution

How Does a Solution Form



If an ionic salt is soluble in water, it is because the ion-dipole interactions are strong enough to overcome the lattice energy of the salt crystal.

Note: the blue colored bonds represent attraction of water for the ions

Factors Affecting Solubility

- Chemists use the axiom “like dissolves like”:
  - Polar and ionic substances tend to dissolve in polar solvents.
  - Nonpolar substances tend to dissolve in nonpolar solvents.

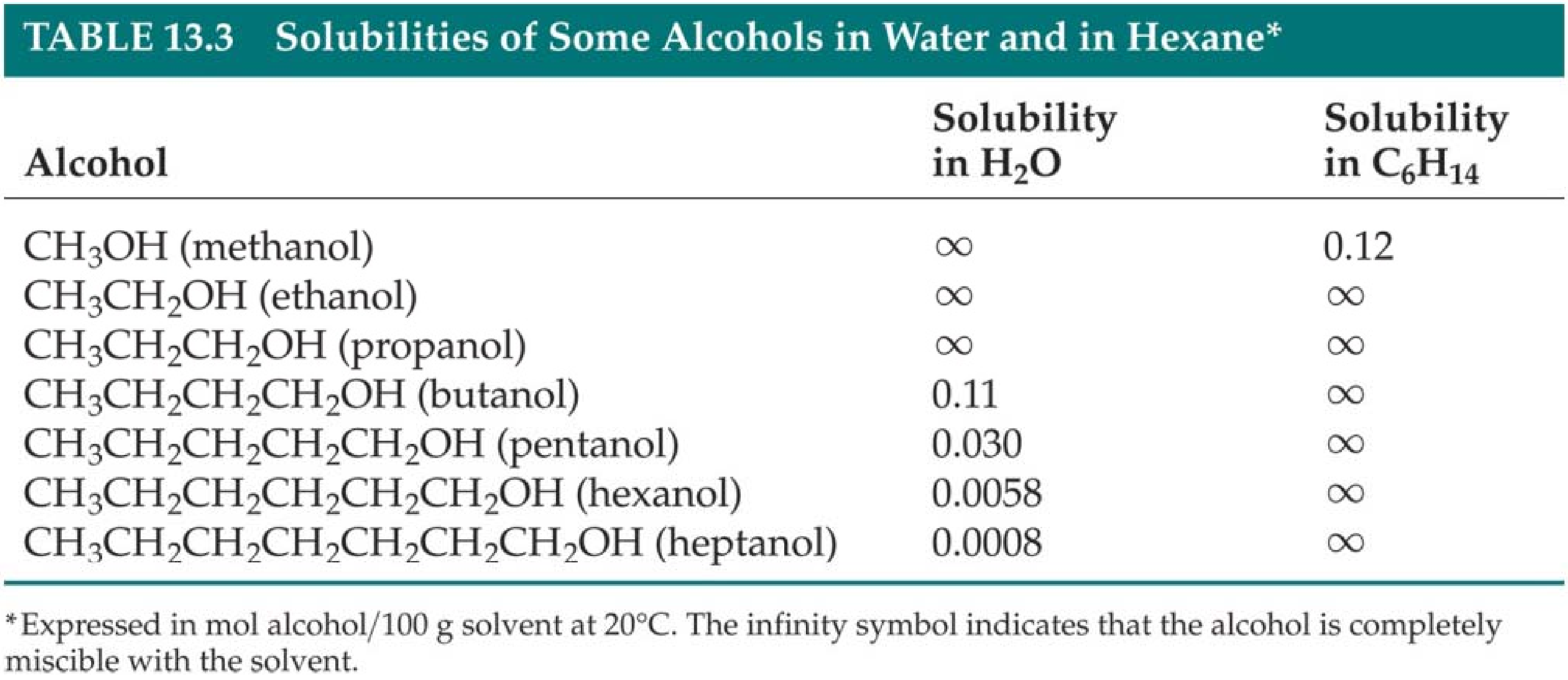


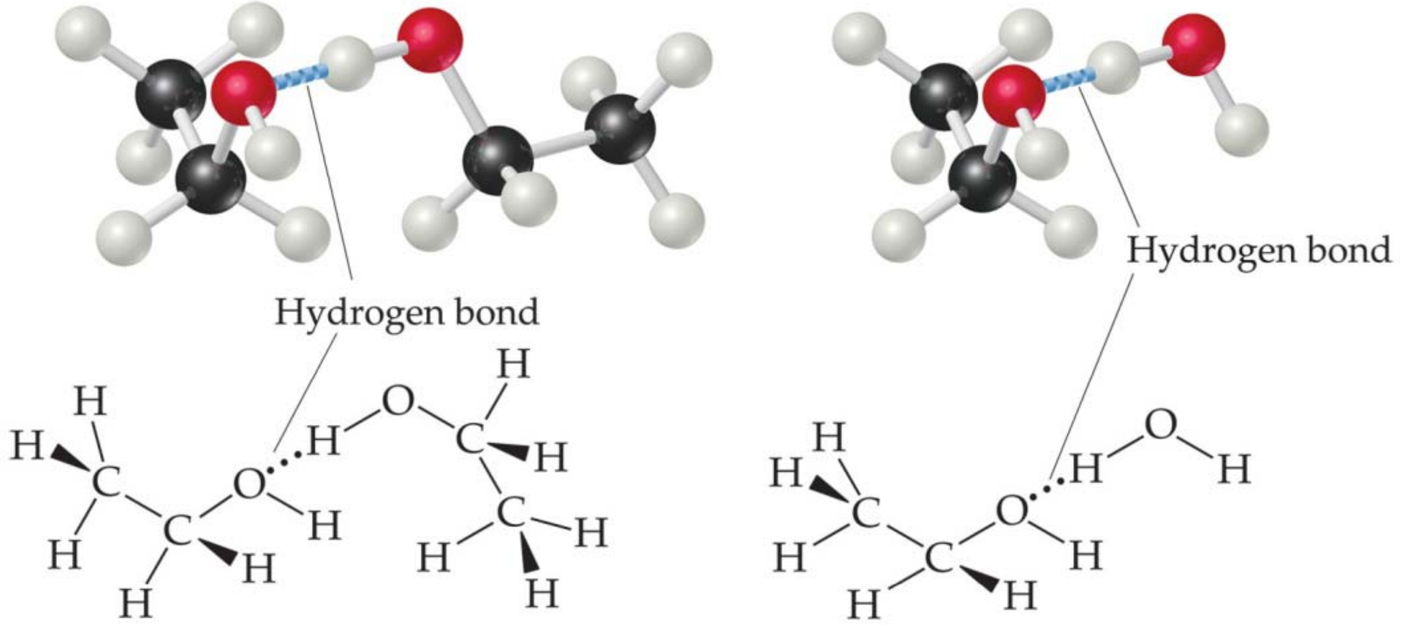
TABLE 13.3 Solubilities of Some Alcohols in Water and in Hexane*

Alcohol	Solubility in H_2O	Solubility in C_6H_{14}
CH_3OH (methanol)	∞	0.12
CH_3CH_2OH (ethanol)	∞	∞
$CH_3CH_2CH_2OH$ (propanol)	∞	∞
$CH_3CH_2CH_2CH_2OH$ (butanol)	0.11	∞
$CH_3CH_2CH_2CH_2CH_2OH$ (pentanol)	0.030	∞
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexanol)	0.0058	∞
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$ (heptanol)	0.0008	∞

*Expressed in mol alcohol/100 g solvent at 20°C. The infinity symbol indicates that the alcohol is completely miscible with the solvent.

Factors Affecting Solubility

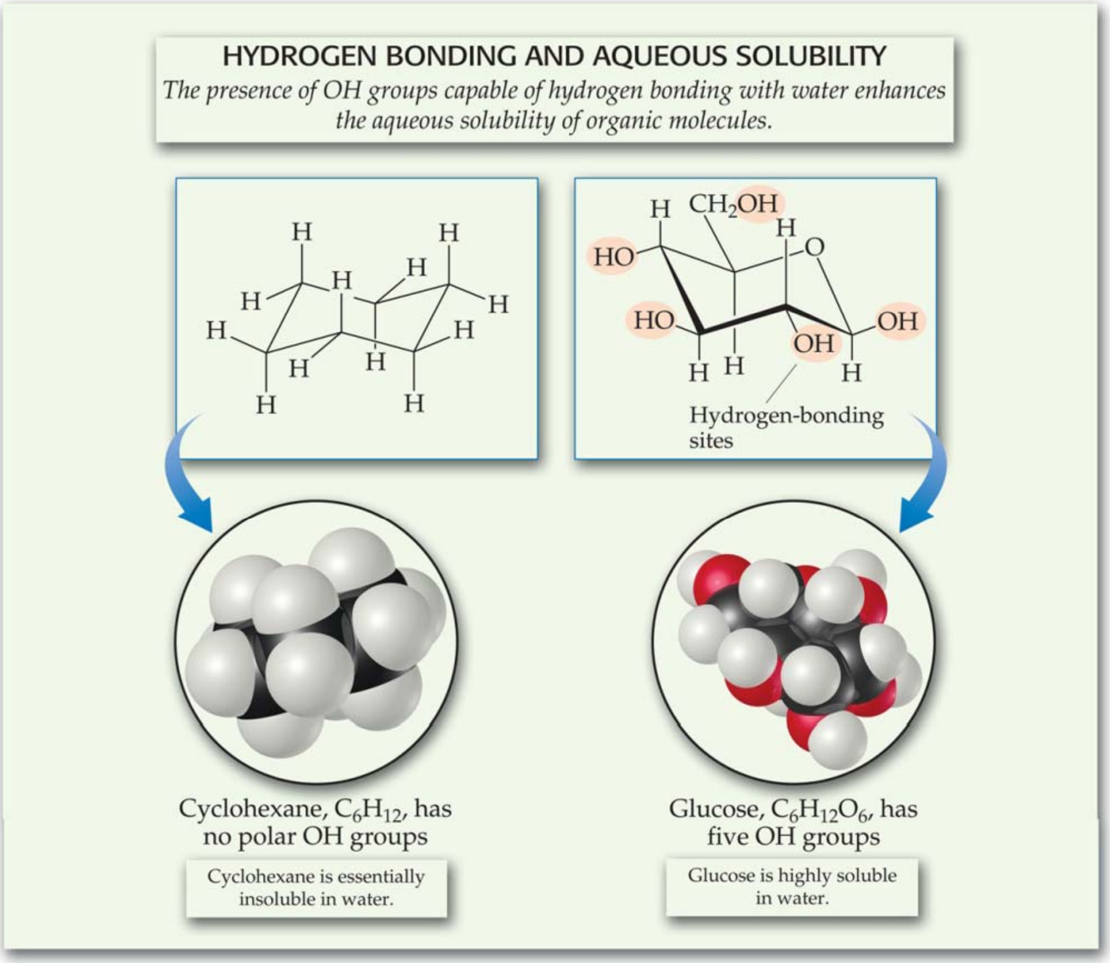
The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.



Factors Affecting Solubility

Glucose (which has hydrogen bonding) is very soluble in water, while

Cyclohexane (which only has dispersion forces) is not.



HYDROGEN BONDING AND AQUEOUS SOLUBILITY

The presence of OH groups capable of hydrogen bonding with water enhances the aqueous solubility of organic molecules.

Cyclohexane, C_6H_{12}, has no polar OH groups

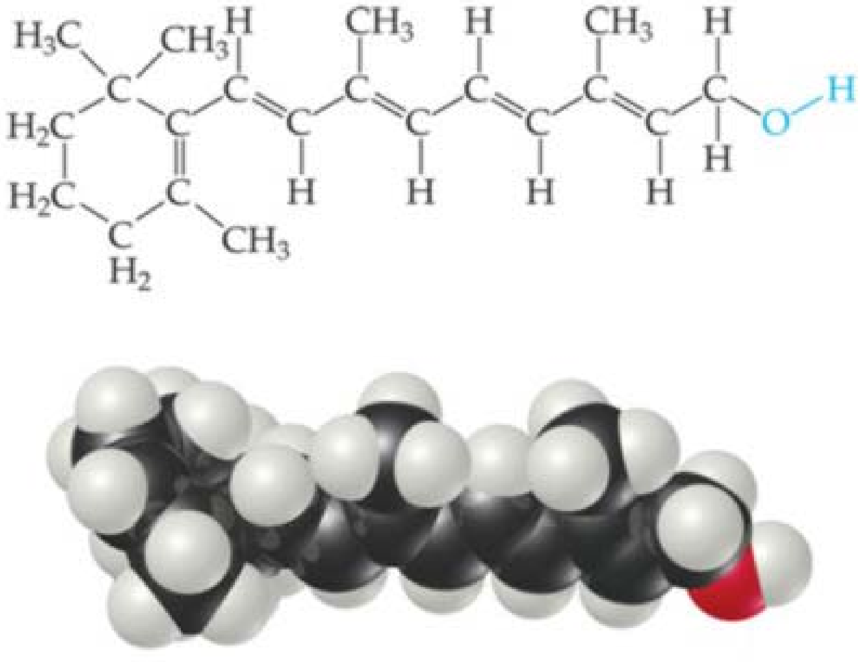
Cyclohexane is essentially insoluble in water.

Glucose, $C_6H_{12}O_6$, has five OH groups

Glucose is highly soluble in water.

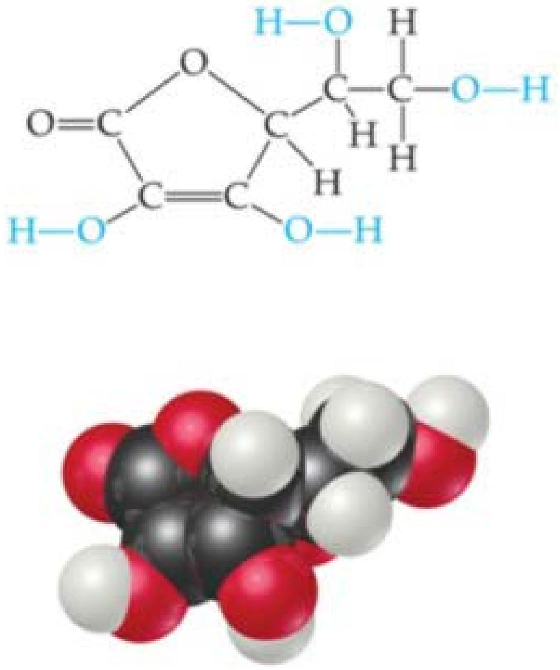
Factors Affecting Solubility

- Vitamin A is soluble in nonpolar compounds (like fats).
- Vitamin C is soluble in water.



Vitamin A

(a)

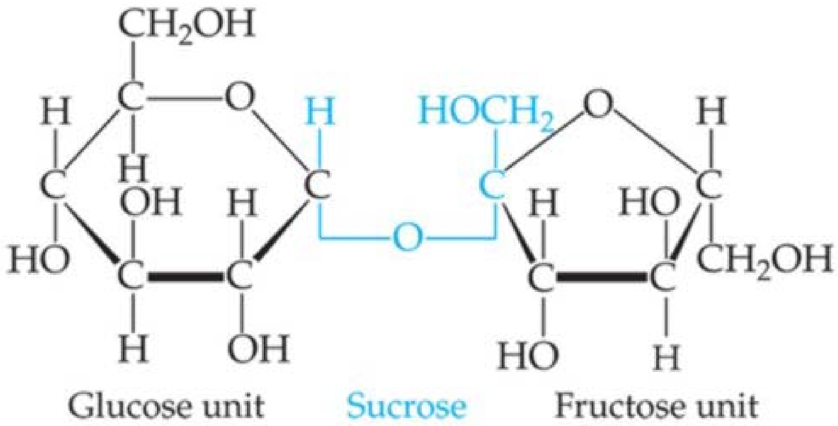


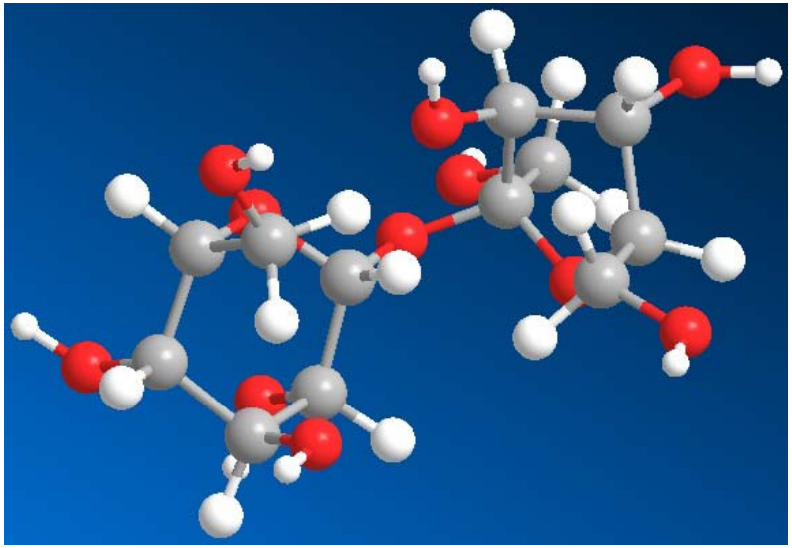
Vitamin C

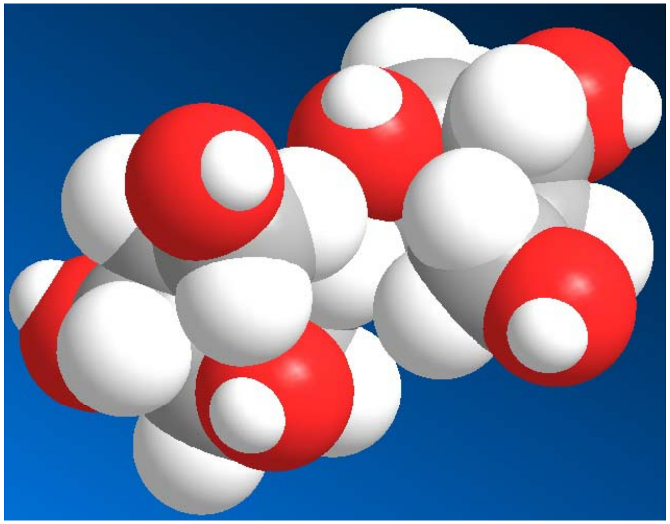
(b)

Intermolecular Forces

Why does a substance dissolve?



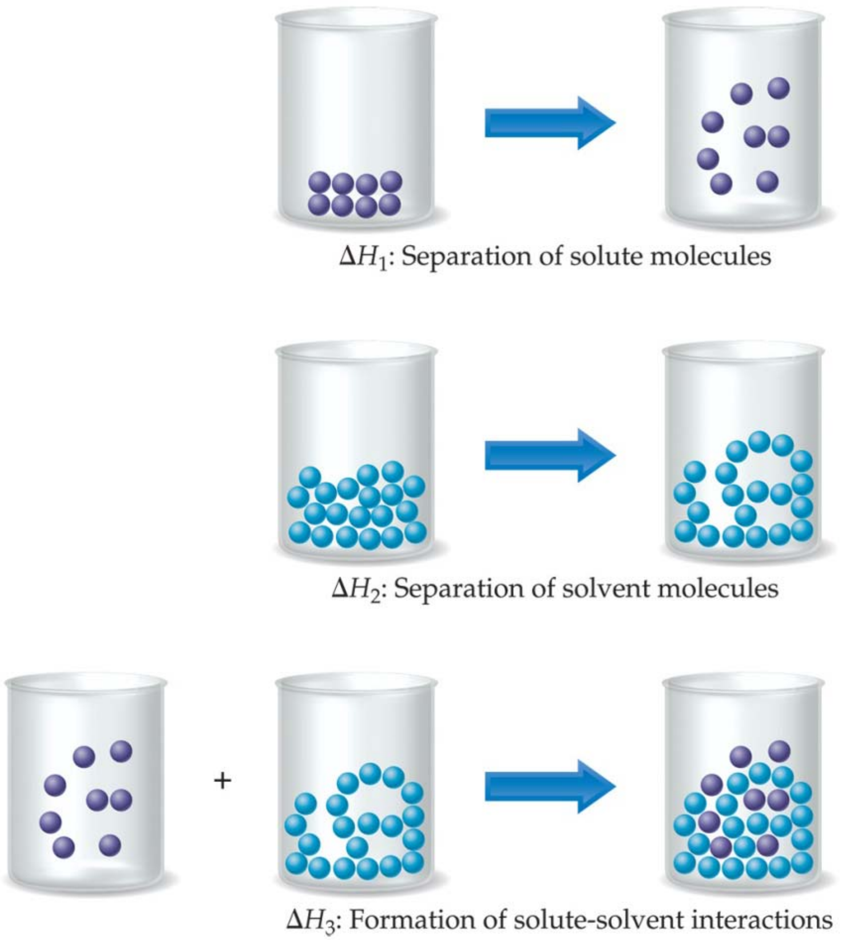




Energy Changes in Solution

- Three processes affect the energetics of the solution process:
  1. Separation of solute particles
  2. Separation of solvent particles
  3. Interactions (attraction) between solute and solvent

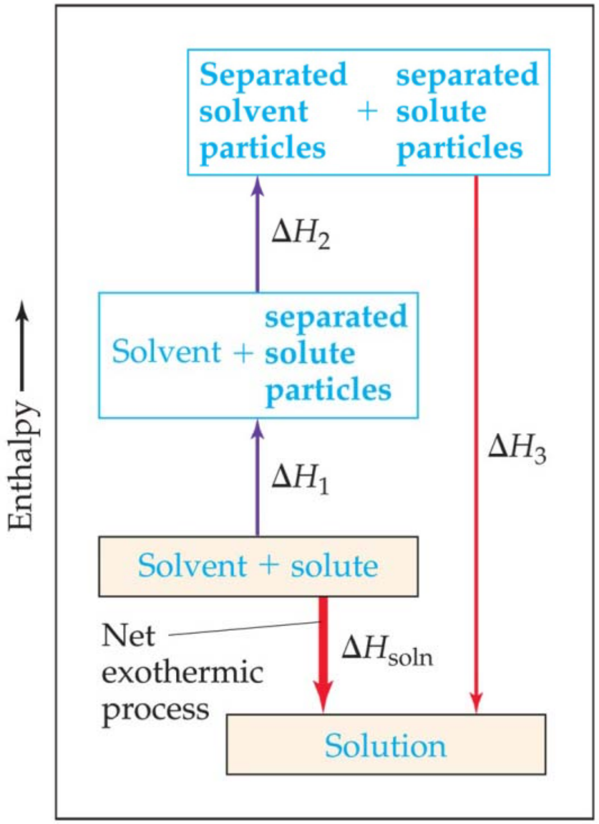
Note: Steps 1 and 2 are sometimes combined as a single step


ΔH_1: Separation of solute molecules

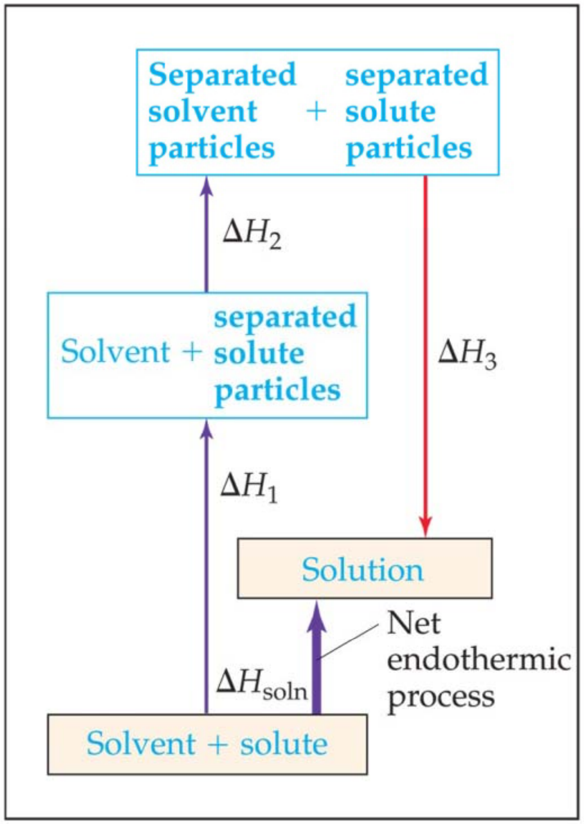
ΔH_2: Separation of solvent molecules

ΔH_3: Formation of solute-solvent interactions

Energy Changes in Solution



Exothermic



Endothermic

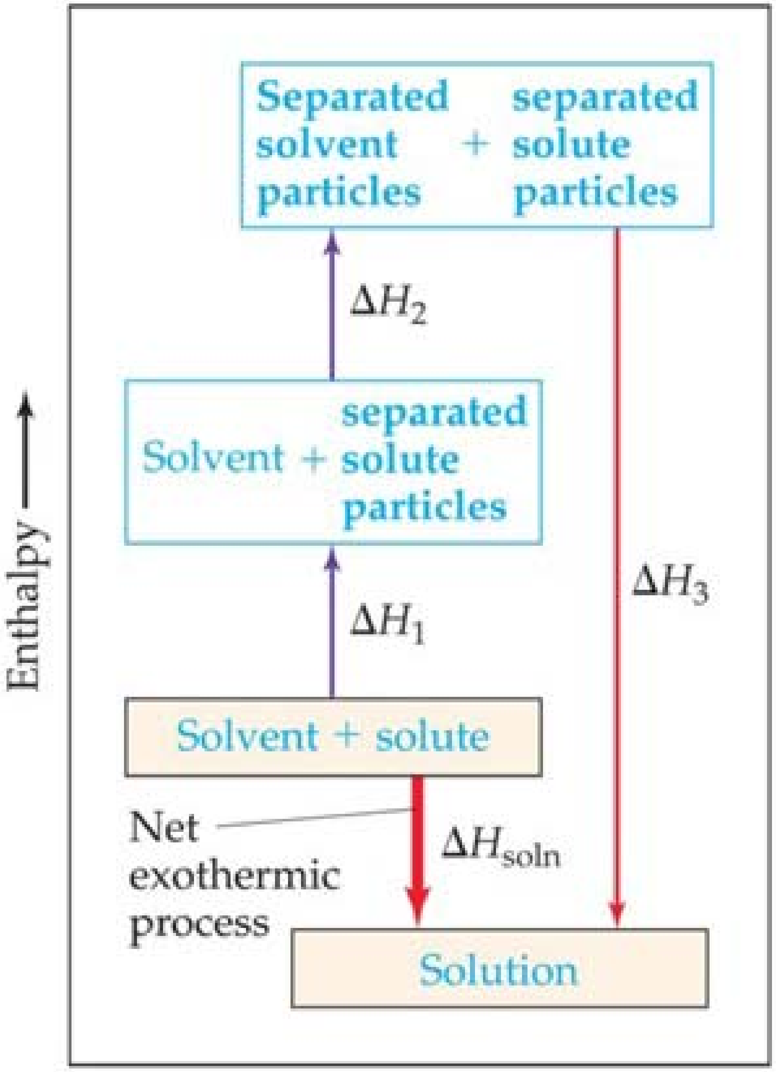
The enthalpy change of the solution process depends on ΔH for each of these steps.

The Exothermic Solution Process

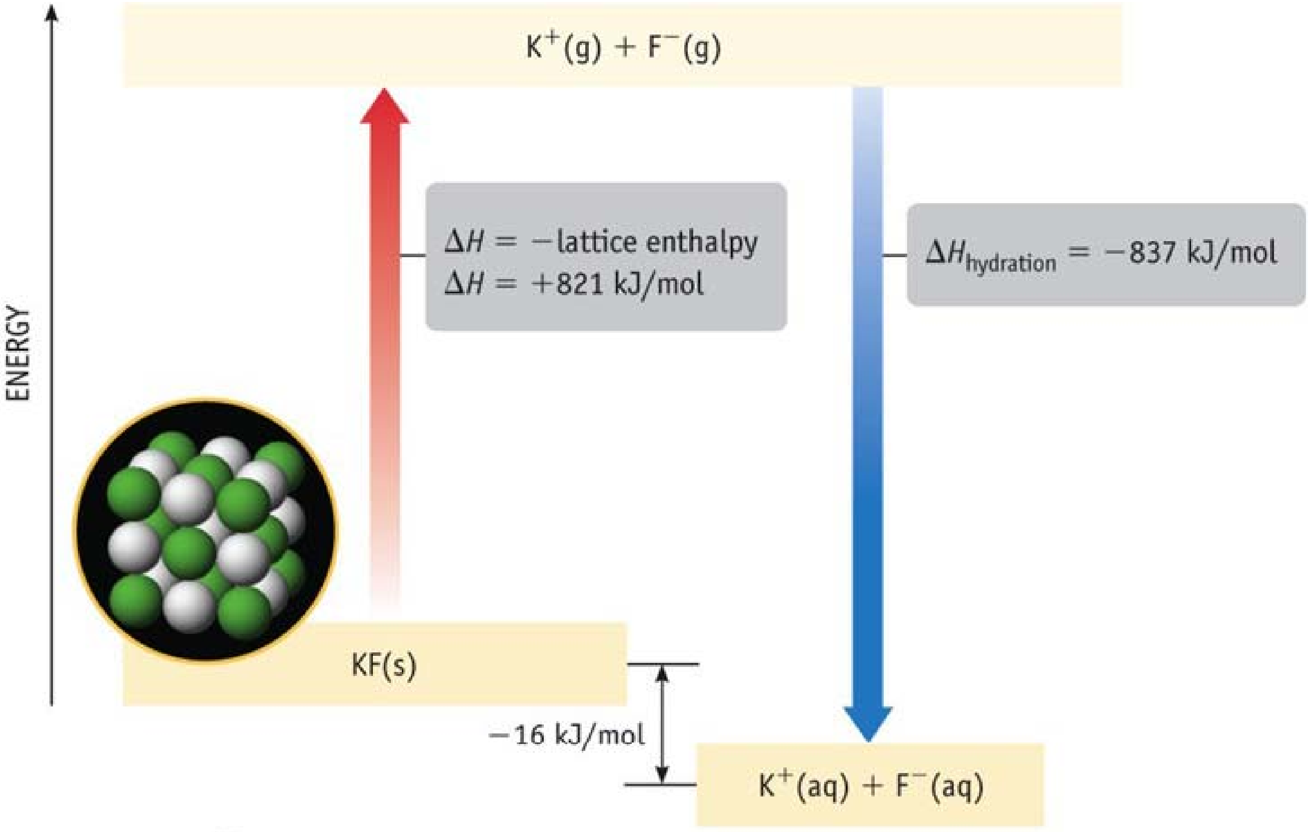
We can break down the process into separate steps:

1. Ions break free from crystal lattice, ΔH_1
2. Intermolecular forces between solvent, ΔH_2 molecules are “broken”
3. Hydration (solvation) of the ions by water molecules, ΔH_3

$\Delta H_3 > \Delta H_1 + \Delta H_2$



Calculating the Enthalpy of an Exothermic Solution



In this example, KF is dissolved in water. Step 2, the separation of solvent molecules, is incorporated into the lattice energy

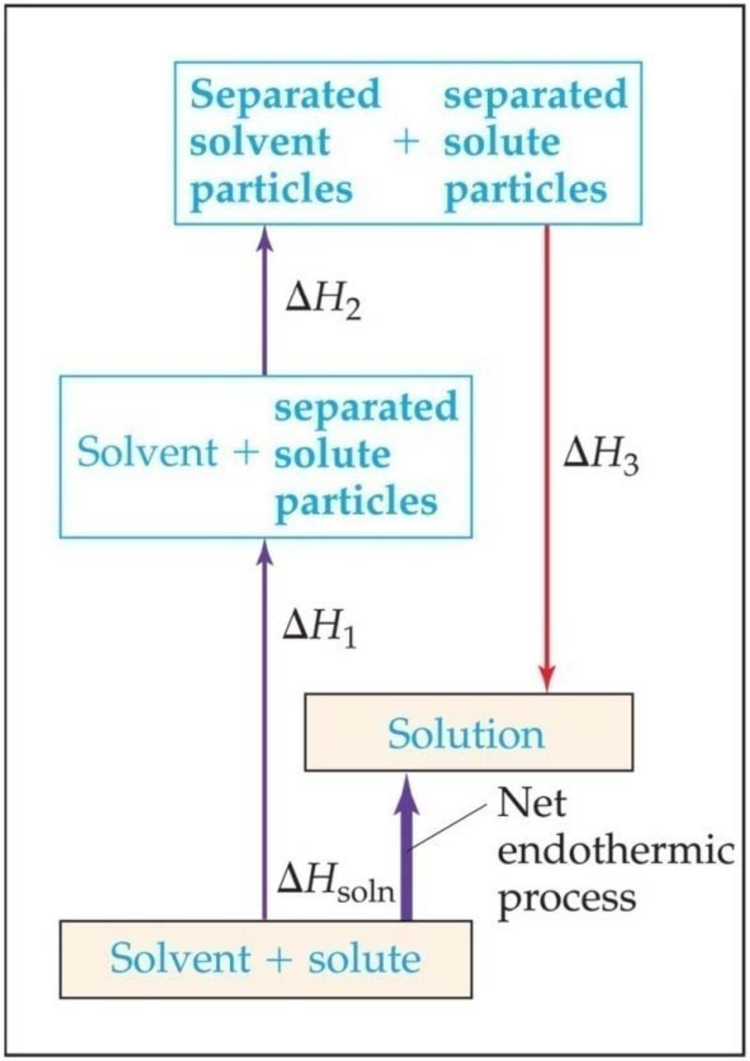
The Endothermic Solution Process

The process occurs in the same steps as an exothermic process

The energies are different:

$\Delta H_3 < \Delta H_1 + \Delta H_2$

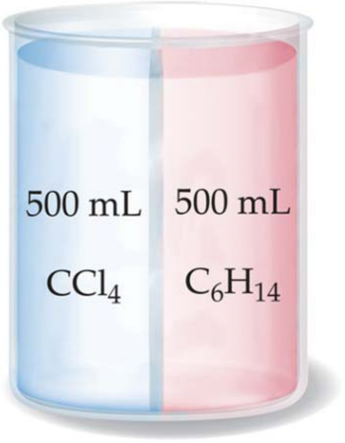
.



Enthalpy Is Only Part of the Picture

The reason is that increasing the disorder or randomness (known as **entropy**) of a system tends to lower the energy of the system.

So even though enthalpy may increase, the overall energy of the system can still decrease if the system becomes more disordered.



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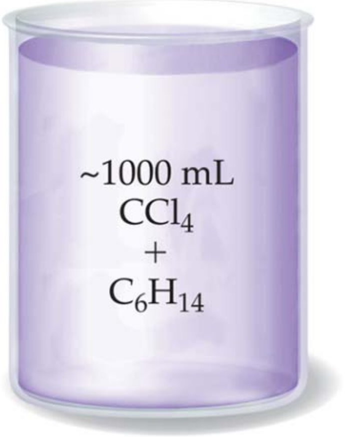
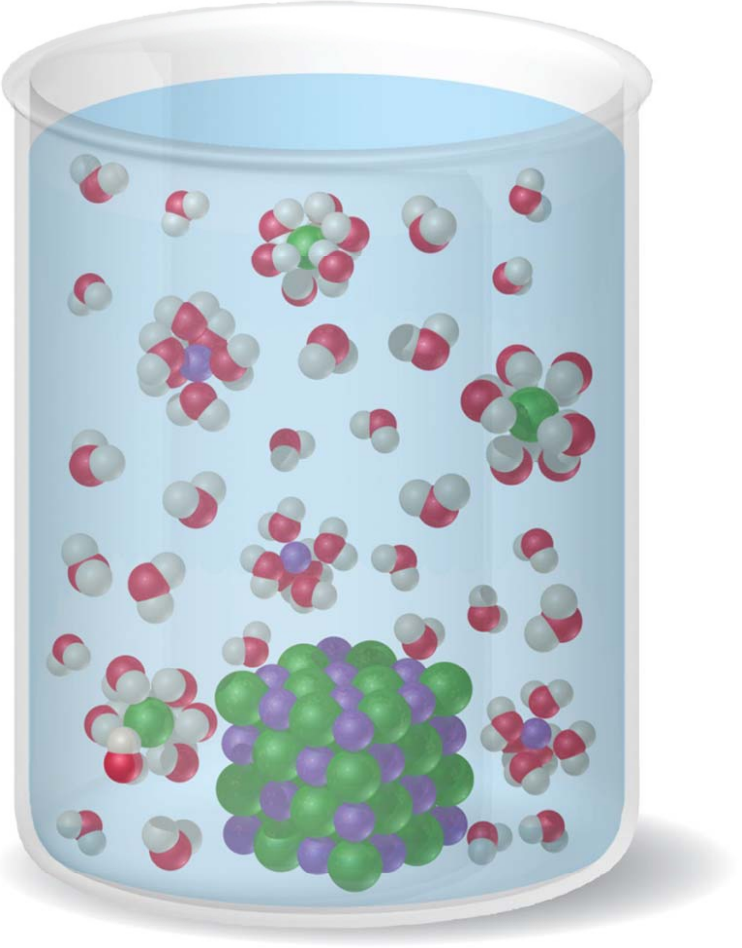


(b)

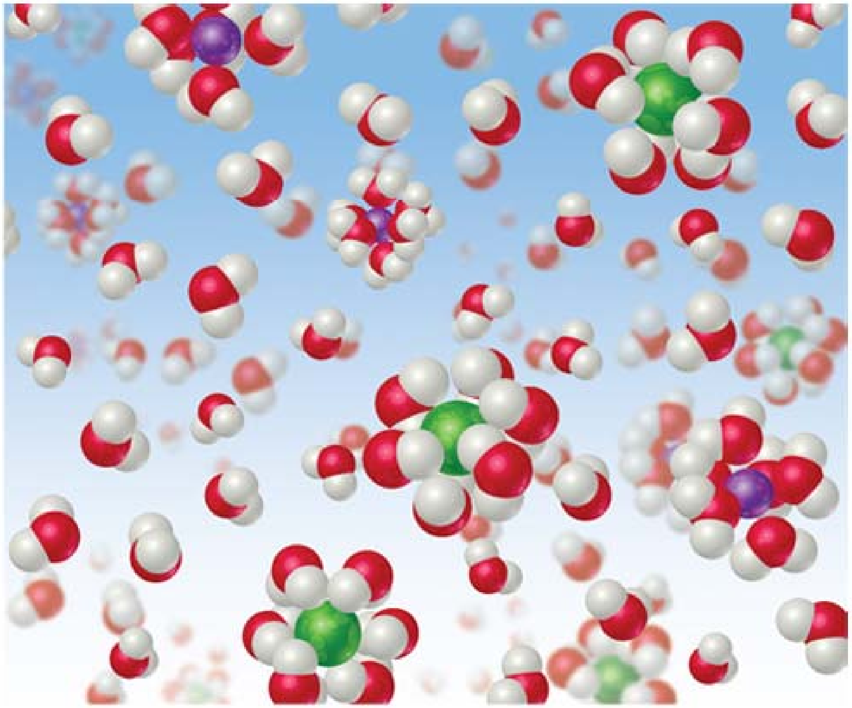
Types of Solutions



- Saturated
  - Solvent holds as much solute as is possible at that temperature.
  - To insure saturation, a small amount of solute remains undissolved on the bottom of the container
  - Dissolved solute is in dynamic equilibrium with solid solute particles.

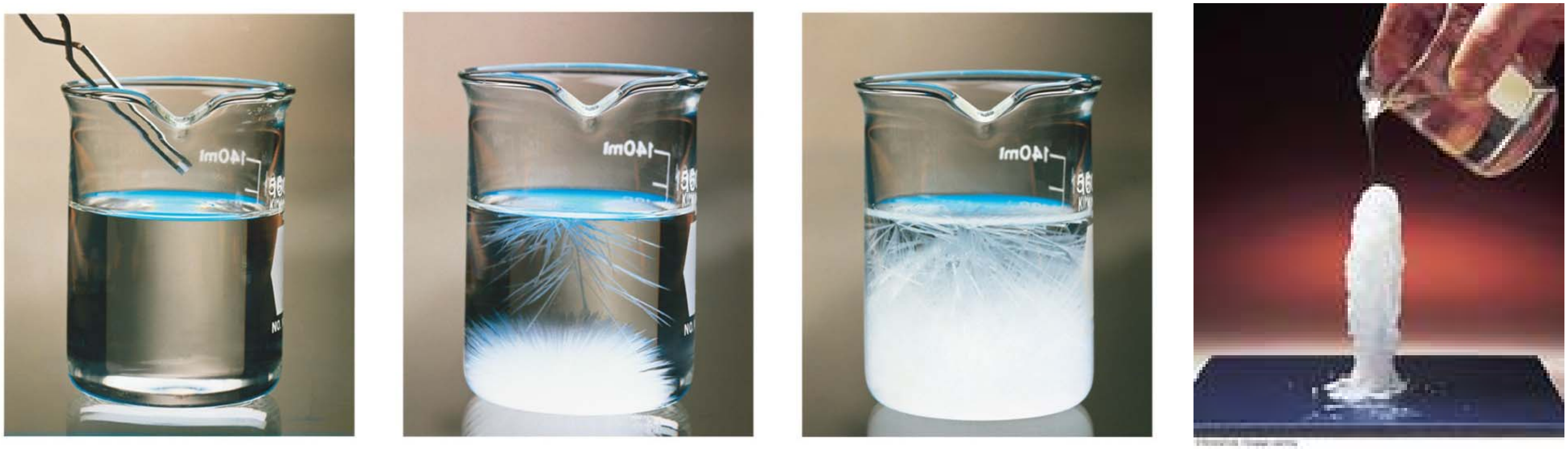
Types of Solutions

- Unsaturated
  - Less than the maximum amount of solute for that temperature is dissolved in the solvent.
  - The amount of solute in the solution can vary from a small amount to almost saturated



Types of Solutions

- **Supersaturated**
  - Solvent holds more solute than is normally possible at that temperature.
  - These solutions are unstable; crystallization can usually be stimulated by adding a “seed crystal” or scratching the side of the flask.



Solutions

- Just because a substance disappears when it comes in contact with a solvent, it doesn't mean the substance dissolved.
- Dissolution is a physical change — you can get back the original solute by evaporating the solvent.
- If you can't, the substance didn't dissolve, it reacted.

Factors Affecting Solubility

- Chemists use the axiom “like dissolves like”:
  - ➢ Polar substances tend to dissolve in polar solvents.
  - ➢ Nonpolar substances tend to dissolve in nonpolar solvents.

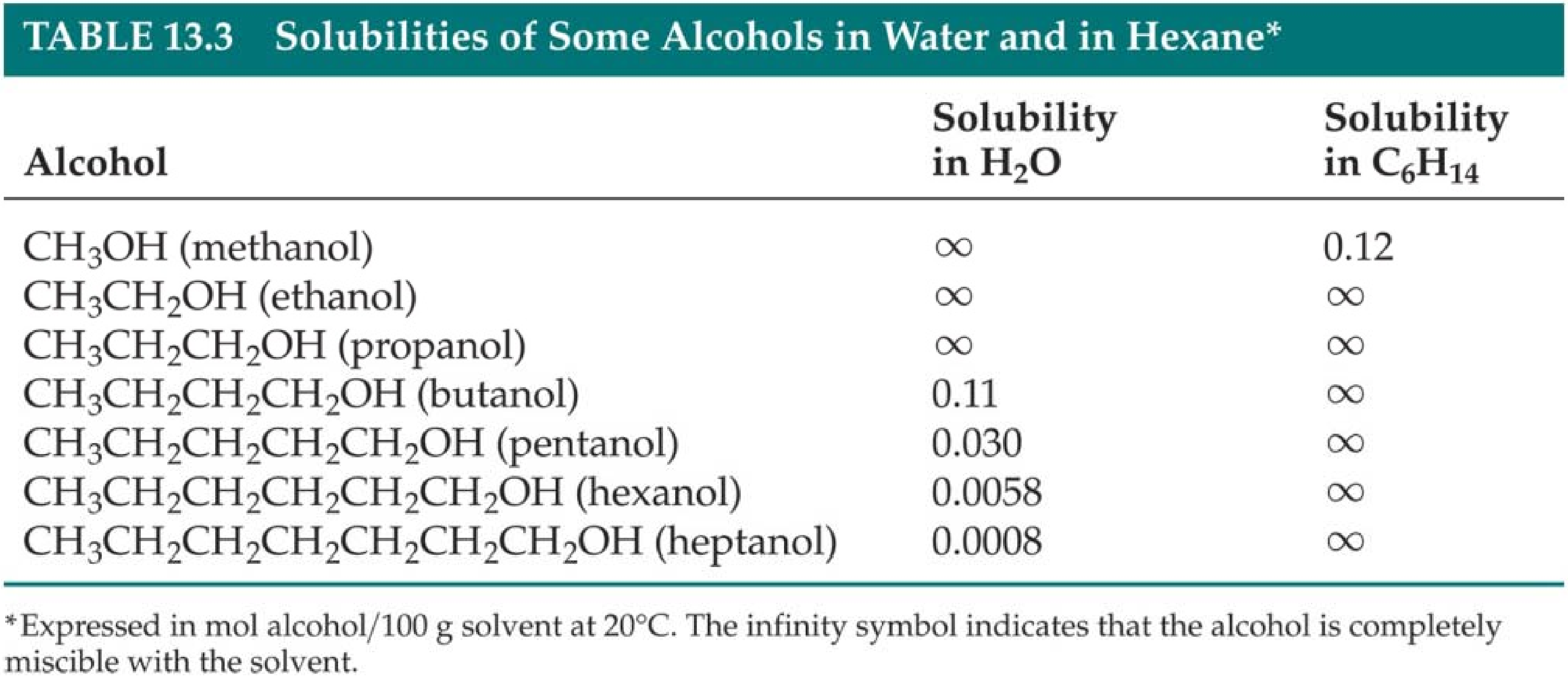


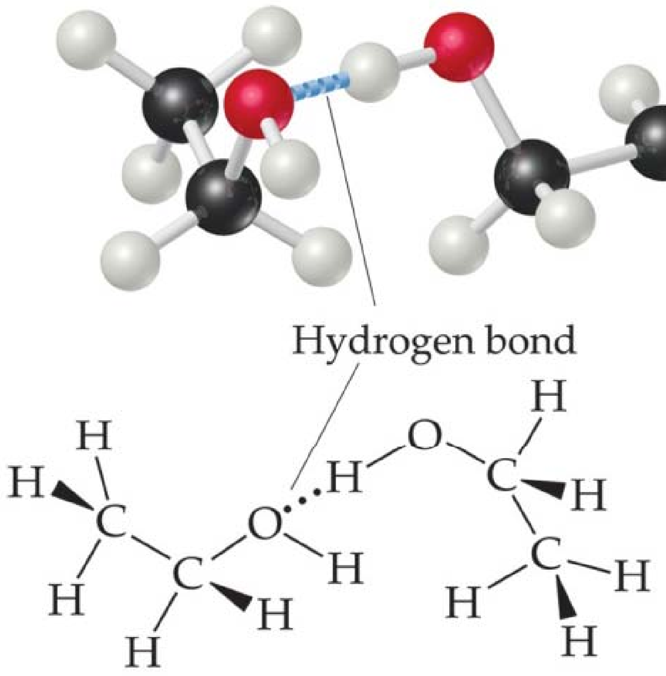
TABLE 13.3 Solubilities of Some Alcohols in Water and in Hexane*

Alcohol	Solubility in H_2O	Solubility in C_6H_{14}
CH_3OH (methanol)	∞	0.12
CH_3CH_2OH (ethanol)	∞	∞
$CH_3CH_2CH_2OH$ (propanol)	∞	∞
$CH_3CH_2CH_2CH_2OH$ (butanol)	0.11	∞
$CH_3CH_2CH_2CH_2CH_2OH$ (pentanol)	0.030	∞
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexanol)	0.0058	∞
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$ (heptanol)	0.0008	∞

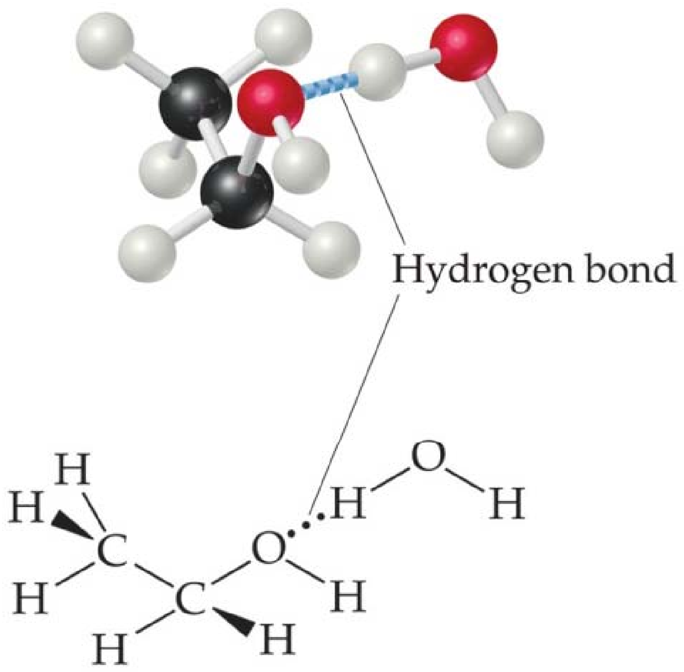
*Expressed in mol alcohol/100 g solvent at 20°C. The infinity symbol indicates that the alcohol is completely miscible with the solvent.

Factors Affecting Solubility

The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.



Ethanol

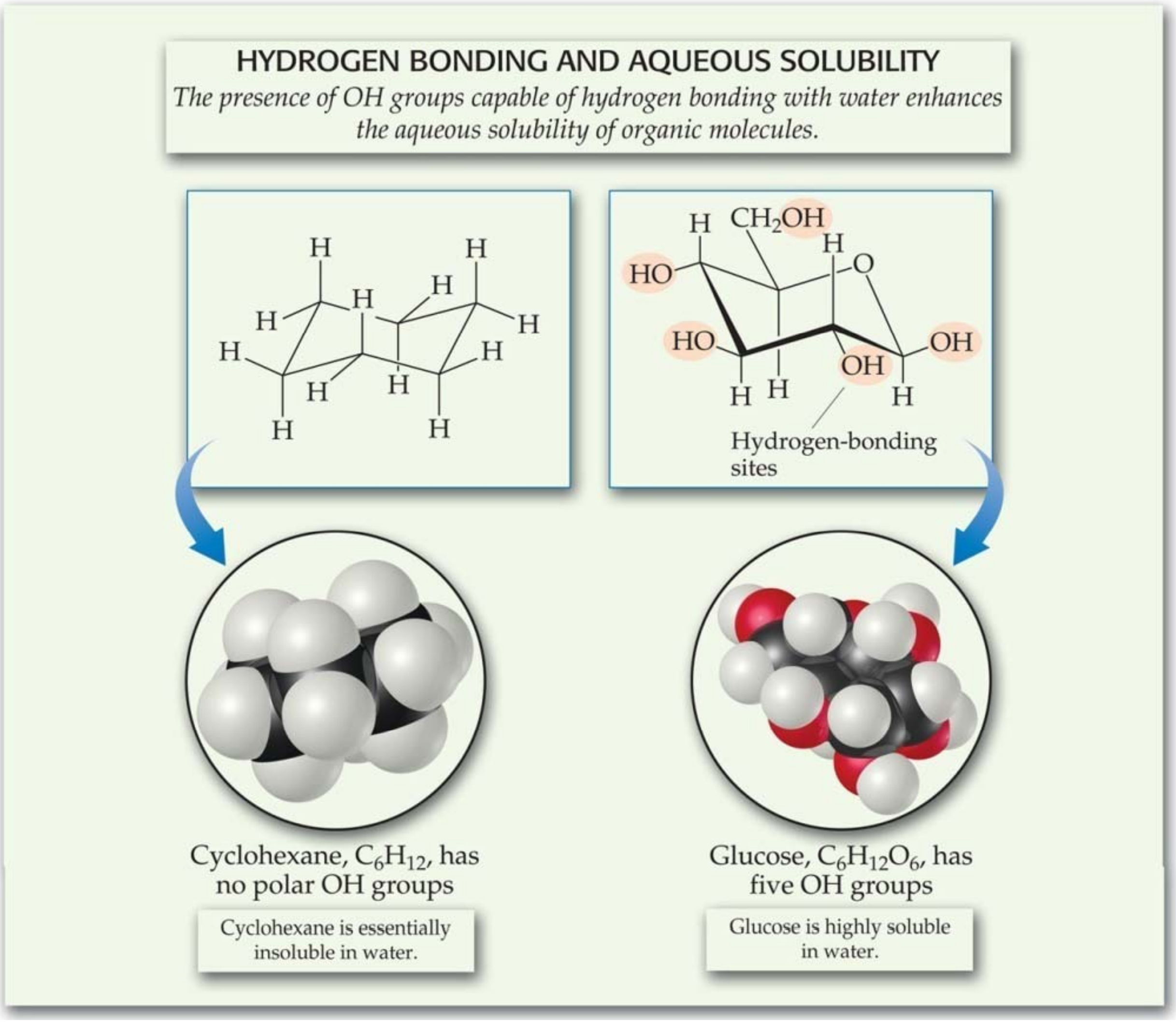


Ethanol-water

Factors Affecting Solubility

Glucose (which has hydrogen bonding) is very soluble in water

Cyclohexane (which only has dispersion forces) is not.



HYDROGEN BONDING AND AQUEOUS SOLUBILITY

The presence of OH groups capable of hydrogen bonding with water enhances the aqueous solubility of organic molecules.

Cyclohexane, C_6H_{12}, has no polar OH groups

Cyclohexane is essentially insoluble in water.

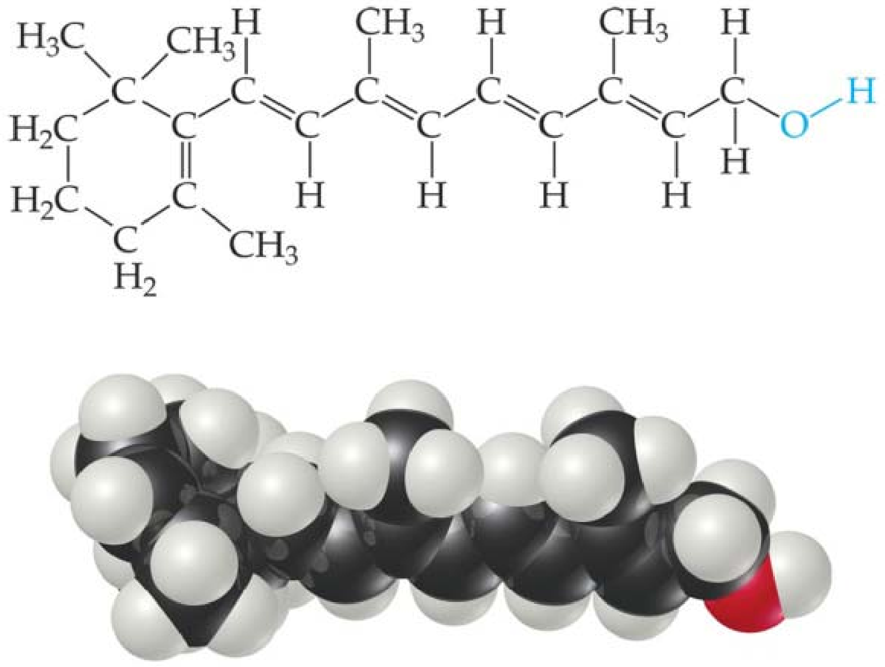
Glucose, $C_6H_{12}O_6$, has five OH groups

Glucose is highly soluble in water.

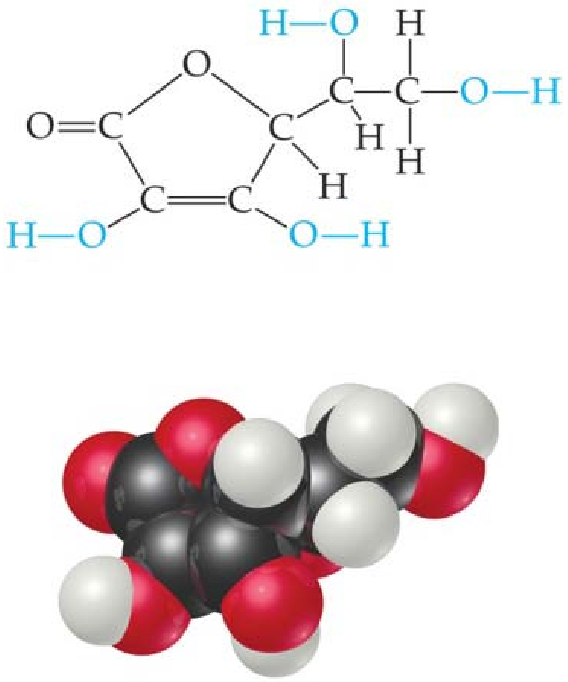
Factors Affecting Solubility

- Vitamin A is soluble in nonpolar compounds (like fats).
- Vitamin C is soluble in water.

Question: In what kinds of foods are these substances found?



Vitamin A



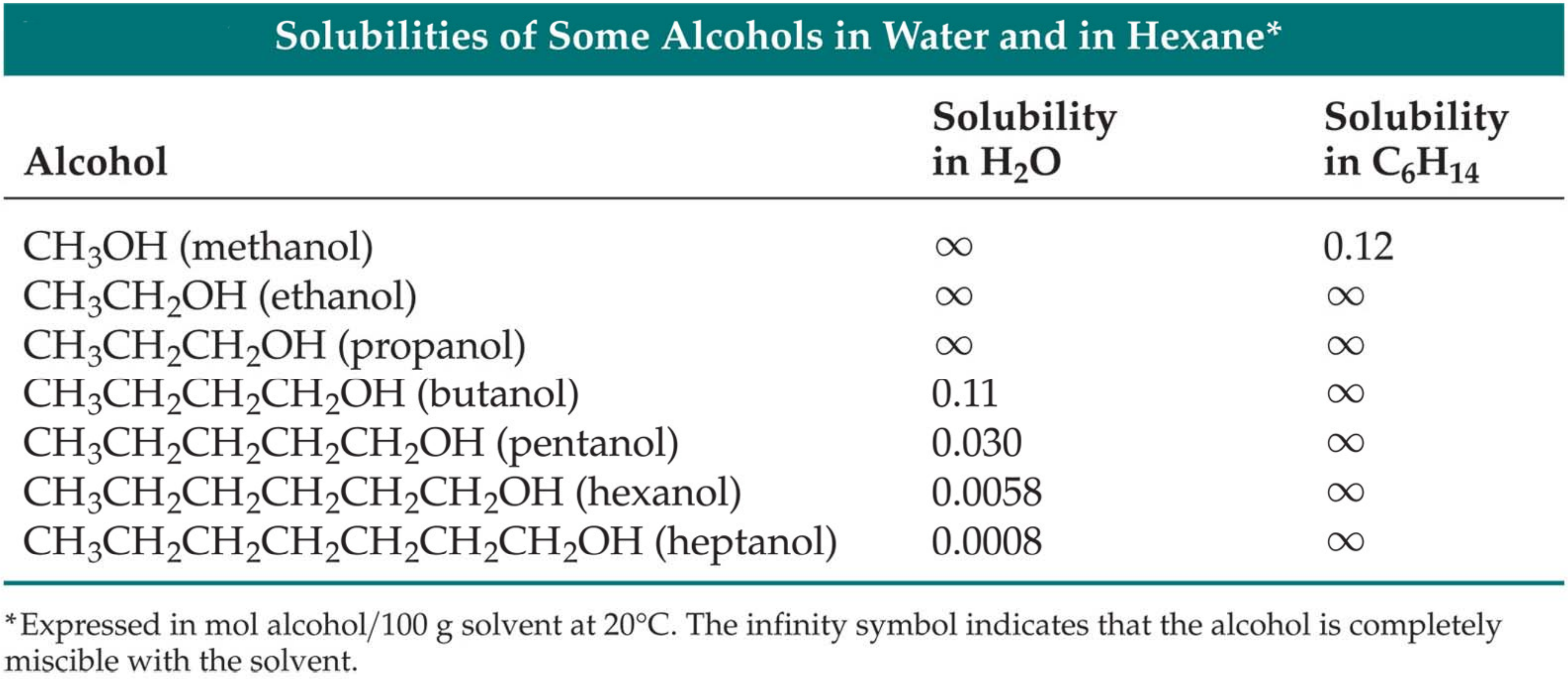
Vitamin C

Water as a Solvent

- How water dissolves molecular compounds:
  - When the nonpolar part of an organic molecule is considerably larger than the polar part, the molecule no longer dissolves in water.

For example ethanol, CH_3CH_2OH is soluble in water but butanol $CH_3CH_2CH_2CH_2OH$ is not

Water as a Solvent



Solubilities of Some Alcohols in Water and in Hexane*

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*Expressed in mol alcohol/100 g solvent at 20°C. The infinity symbol indicates that the alcohol is completely miscible with the solvent.

Gases in Solution

- In general, the solubility of gases in water increases with increasing mass.
- Larger molecules have stronger dispersion forces.

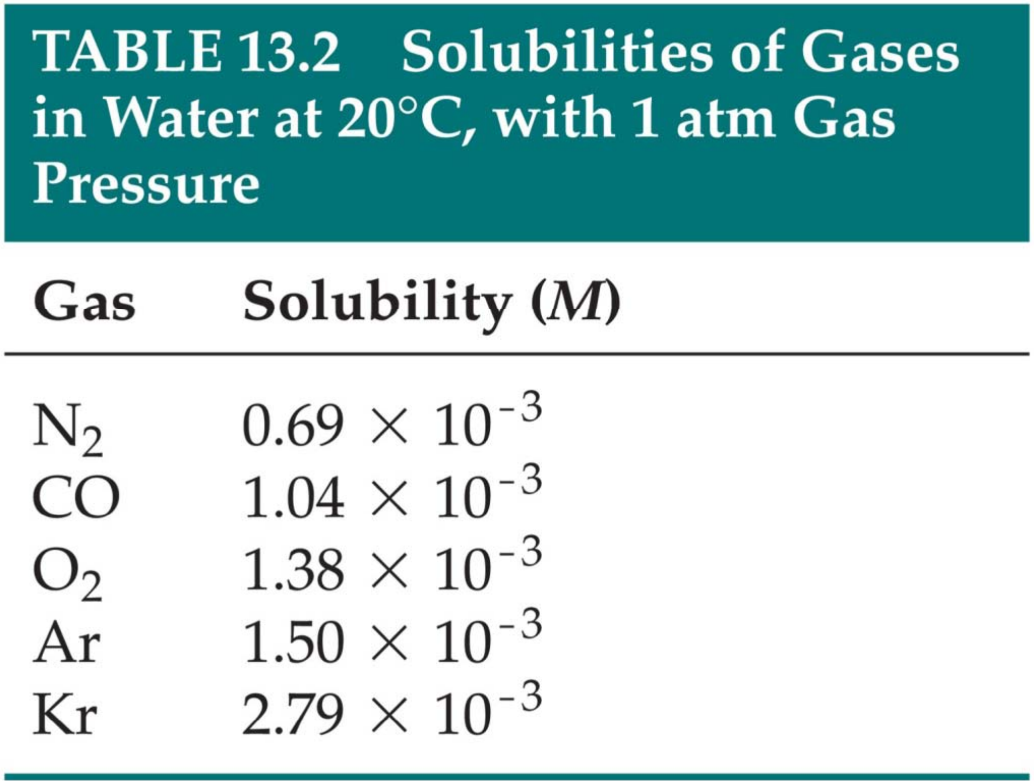
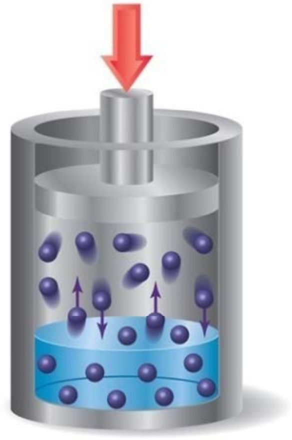


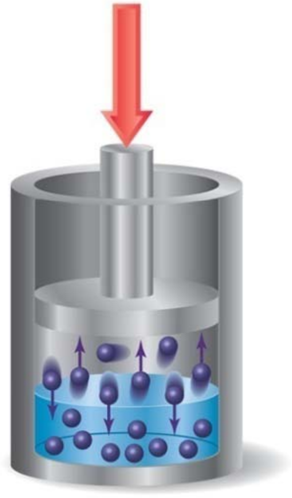
TABLE 13.2 Solubilities of Gases in Water at 20°C, with 1 atm Gas Pressure

Gas	Solubility (*M*)
N_2	0.69×10^{-3}
CO	1.04×10^{-3}
O_2	1.38×10^{-3}
Ar	1.50×10^{-3}
Kr	2.79×10^{-3}

Gases in Solution



(a)



(b)

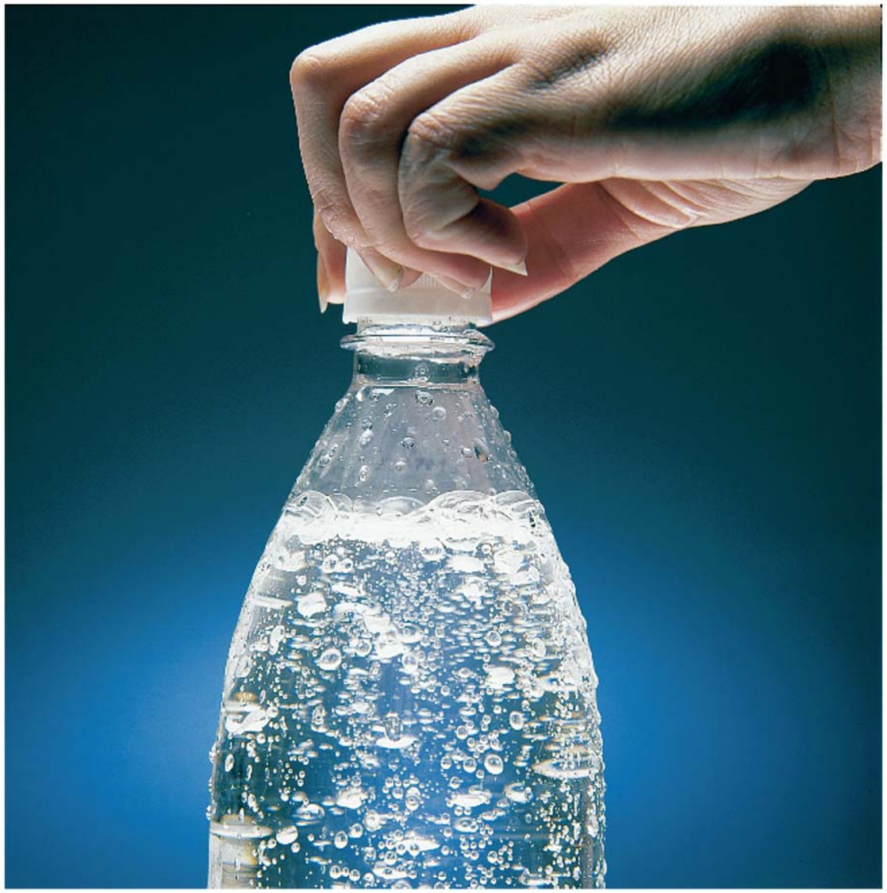
- The solubility of liquids and solids does not change appreciably with pressure.
- The solubility of a gas in a liquid is directly proportional to its pressure in contact with the liquid.

Henry's Law

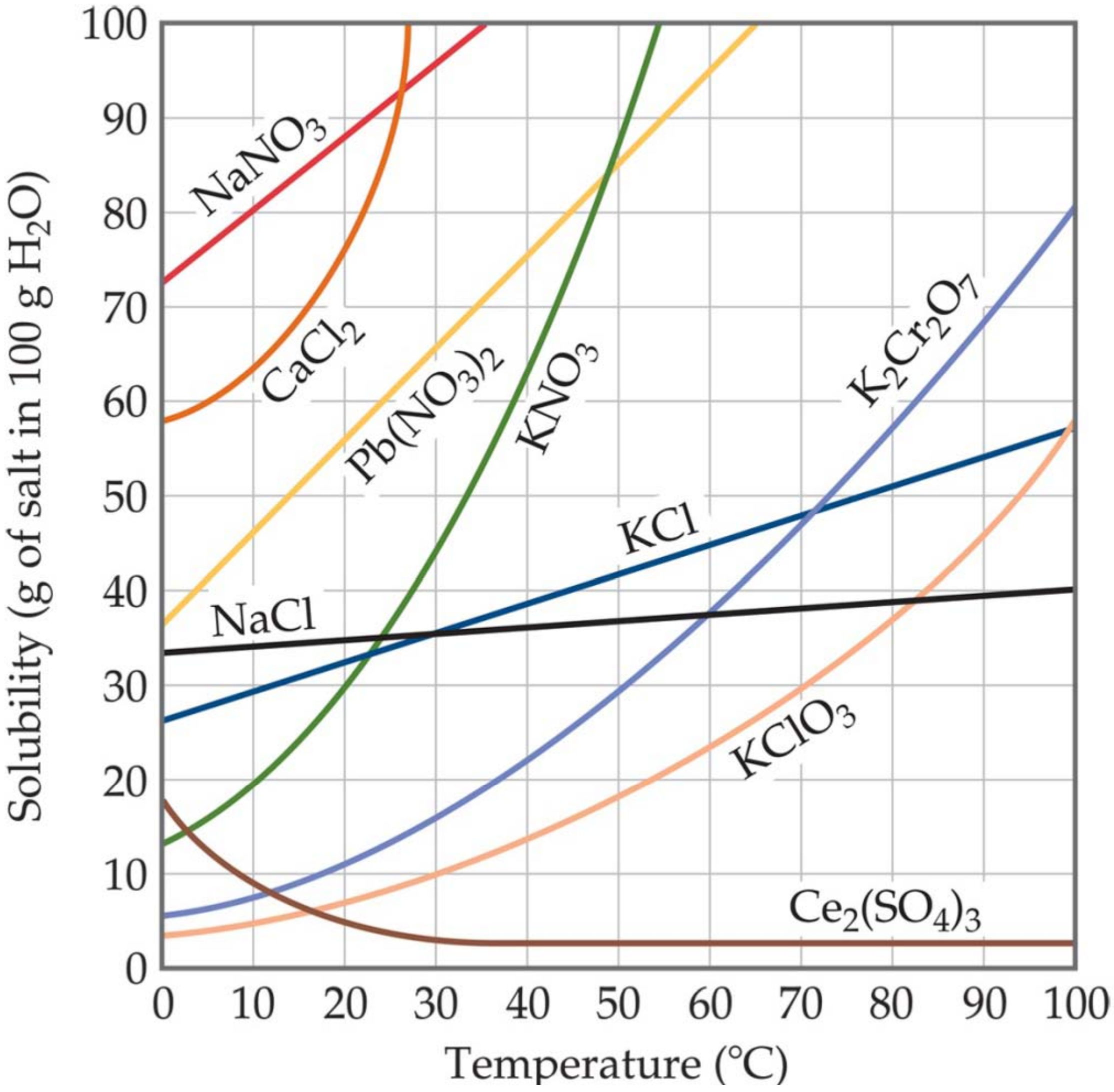
$$S_g = kP_g$$

where

- S_g is the solubility of the gas;
- k is the Henry's law constant for that gas in that solvent;
- P_g is the partial pressure of the gas above the liquid.



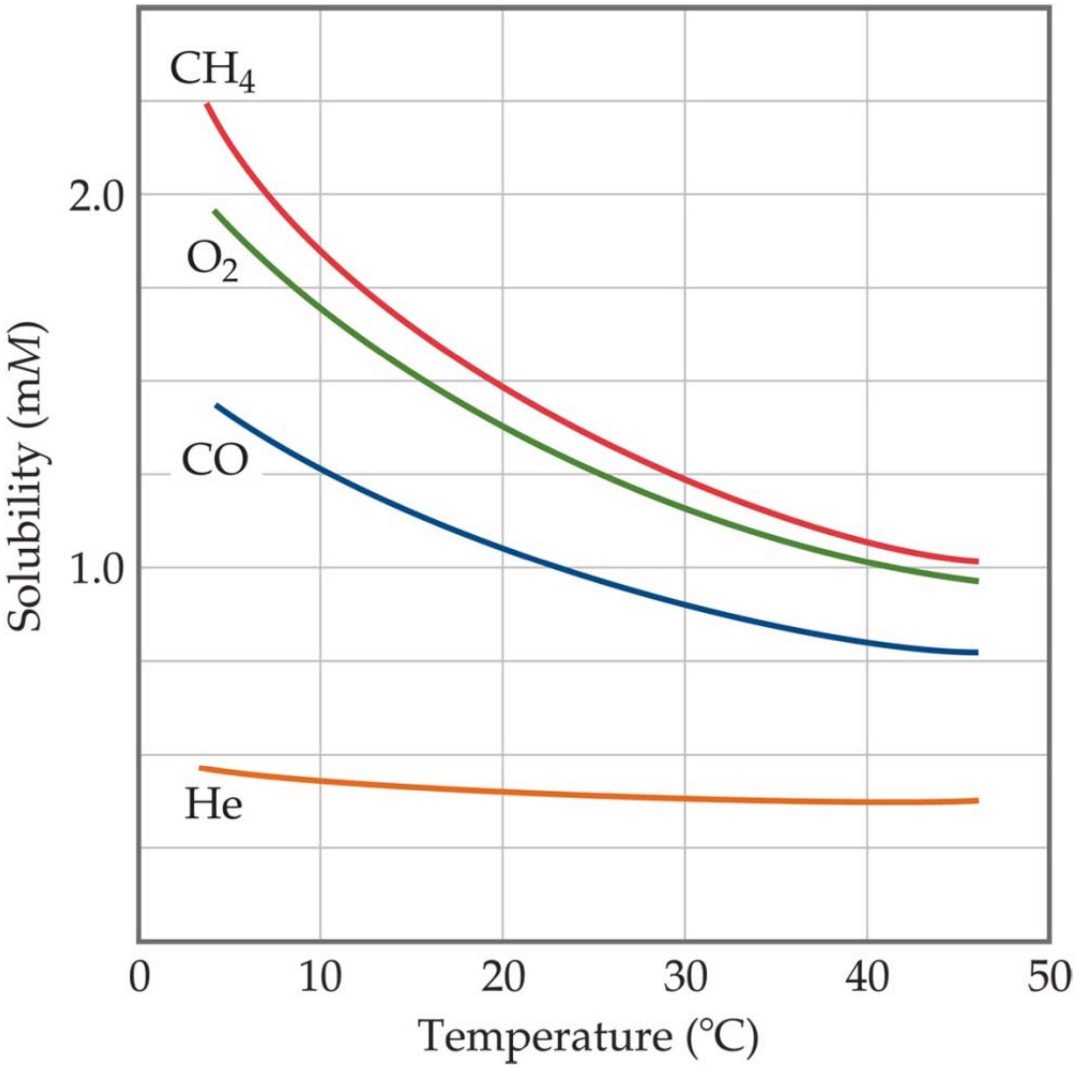
Temperature



Generally, the solubility of solid solutes in liquid solvents increases with increasing temperature.

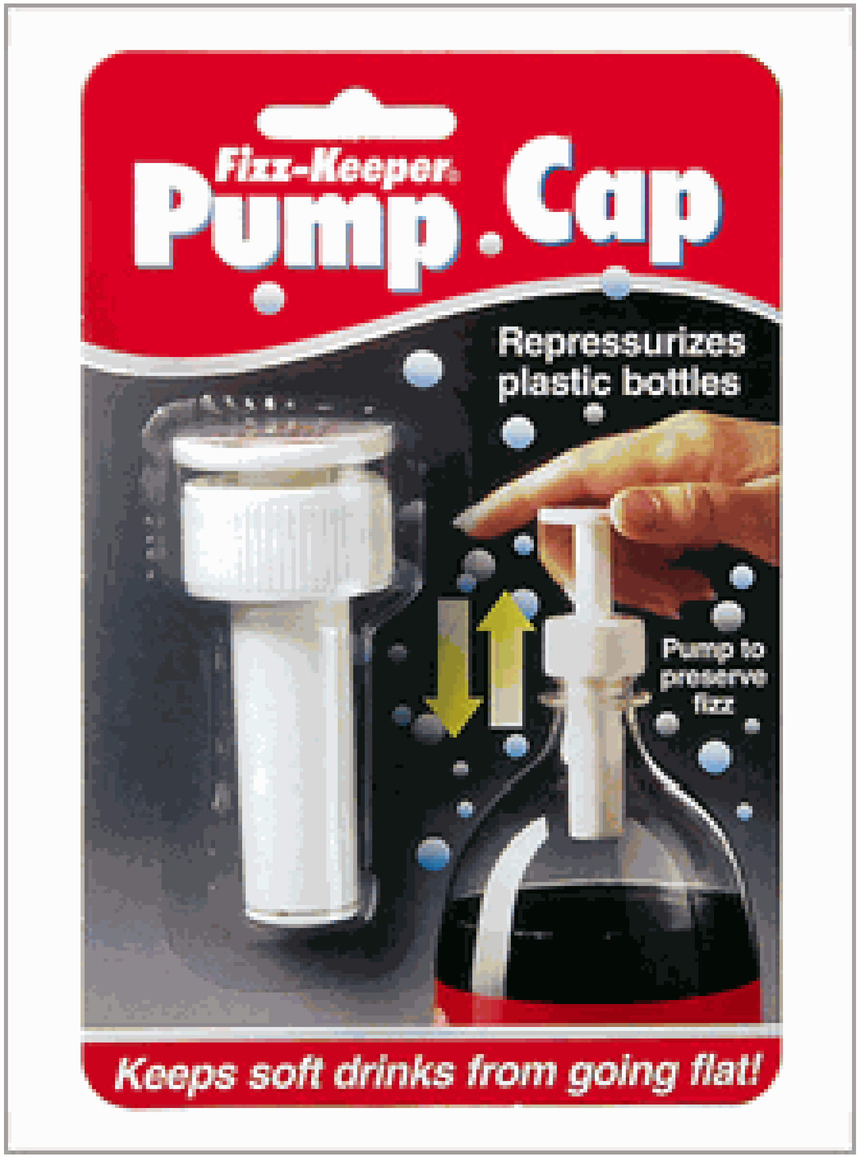
Temperature

- The opposite is true of gases:
  - Carbonated soft drinks are more “bubbly” if stored in the refrigerator.
  - Warm lakes have less O_2 dissolved in them than cool lakes.



Gases in Solution

- The Fizz-Keeper
  - Claims to keep “soft drinks from going flat!”
  - Does it work?
    - Why?
    - Why not?



Expressing Concentrations of Solutions

Percent, %

Can be expressed as:

- Percent by mass, $\%_{(m/m)}$
- Percent by volume, $\%_{(v/v)}$ for solutions of liquids
- Percent mass-volume, $\%_{(m/v)}$ for solids in liquids

$$\% \text{ of A} = \frac{\text{amount of A in solution}}{\text{total amount of solution}} \times 100$$

Most commonly, we use percent by mass

Parts per Million and Parts per Billion

Parts per Million (ppm)

$$\text{ppm} = \frac{\text{mass of A in solution}}{\text{total mass of solution}} \times 10^6$$

Parts per Billion (ppb)

$$\text{ppb} = \frac{\text{mass of A in solution}}{\text{total mass of solution}} \times 10^9$$

Molarity (*M*)

$$M = \frac{\text{mol of solute}}{\text{L of solution}}$$

An alternate equation is

$$M = \frac{g_{solute} \times 1000\,{}^{mL}\!/_{L}}{MW_{solute} \times mL_{solution}}$$

- Note: Because volume is temperature dependent, Molarity can change with temperature.

Mole Fraction (*X*)

$$X_A = \frac{\text{moles of A}}{\text{total moles in solution}}$$

For a solution of two or more components, A, B, etc…

$$X_A + X_B + \cdots = 1$$

Molality (*m*)

$$m = \frac{\text{mol of solute}}{\text{kg of solvent}}$$

An alternate equation is

$$m = \frac{g_{solute} \times 1000\, {}^{g}\!/_{kg}}{MW_{solute} \times g_{solvent}}$$

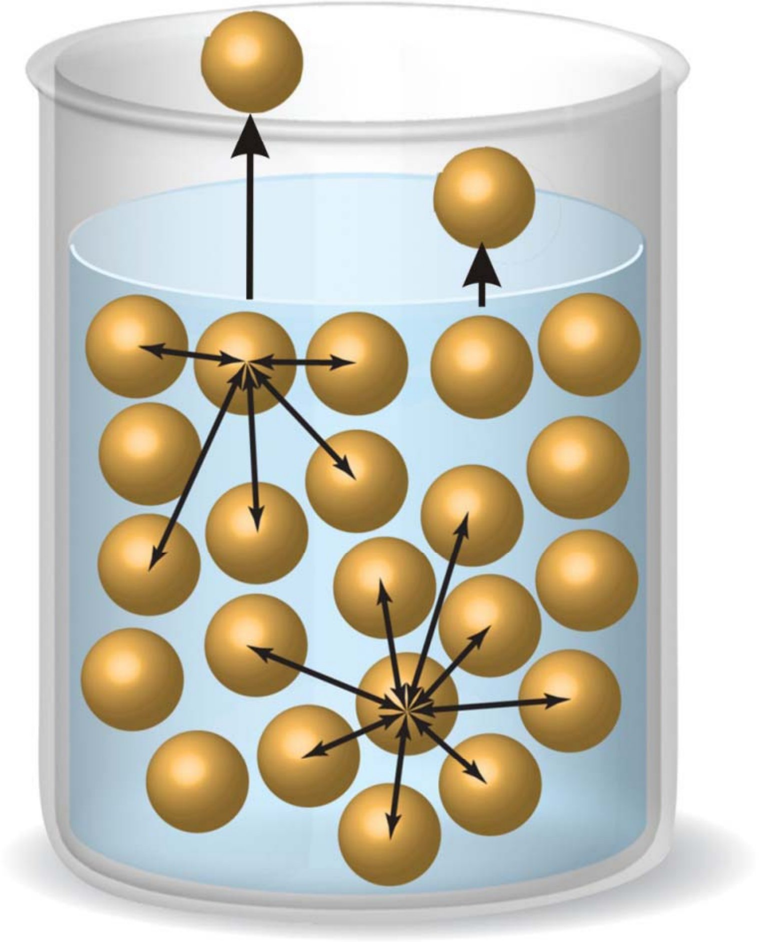
Note: Because both moles and mass do not change with temperature, molality (unlike molarity) is *not* temperature dependent.

Colligative Properties

- Changes in **colligative properties** depend only on the *number* of solute particles present, not on the *identity* of the solute particles.
- Among colligative properties are
  - Vapor pressure lowering
  - Boiling point elevation
  - Melting point depression
  - Osmotic pressure

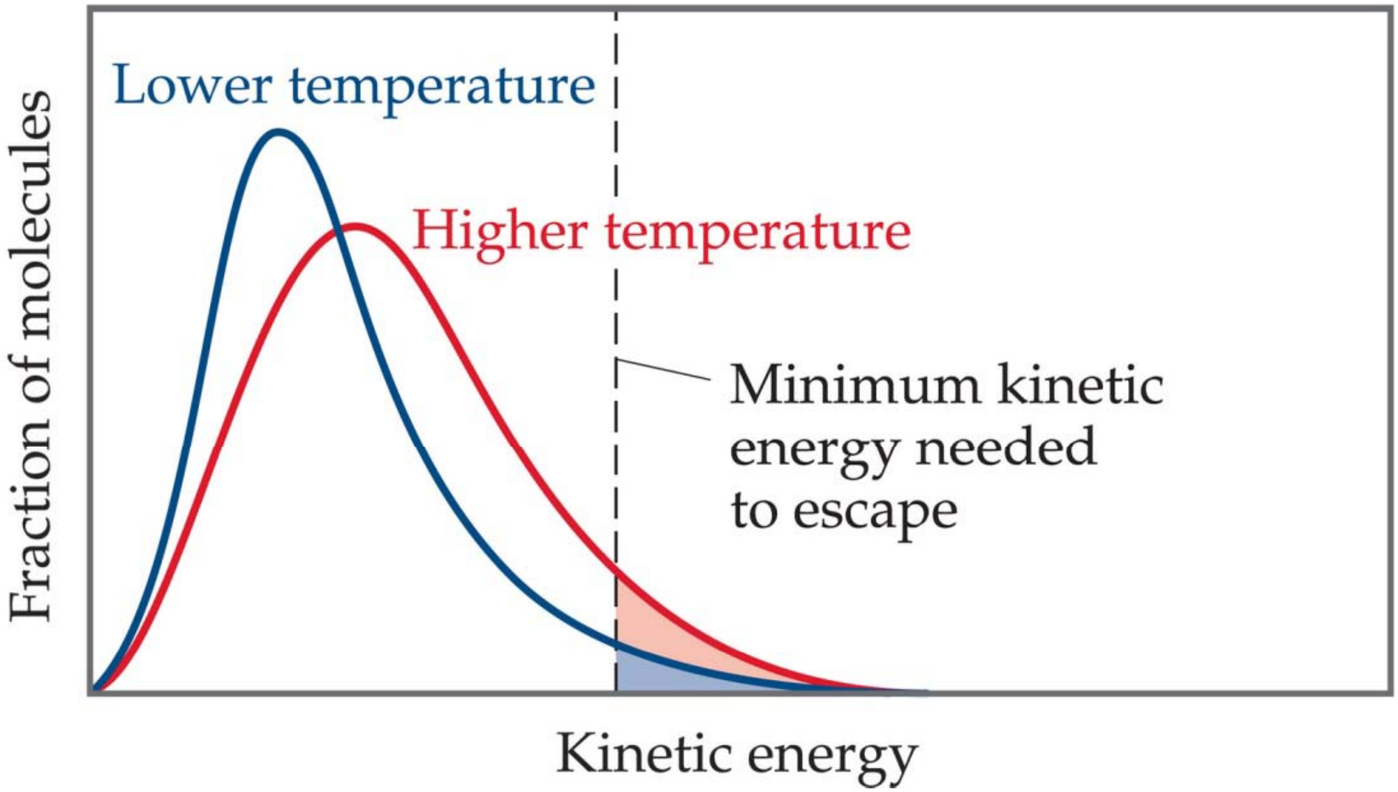
Vapor Pressure

Due to both temperature effects and energy transfers from collisions, molecules on the surface of a liquid are able to gain sufficient kinetic energy to escape into the atmosphere



Vapor Pressure

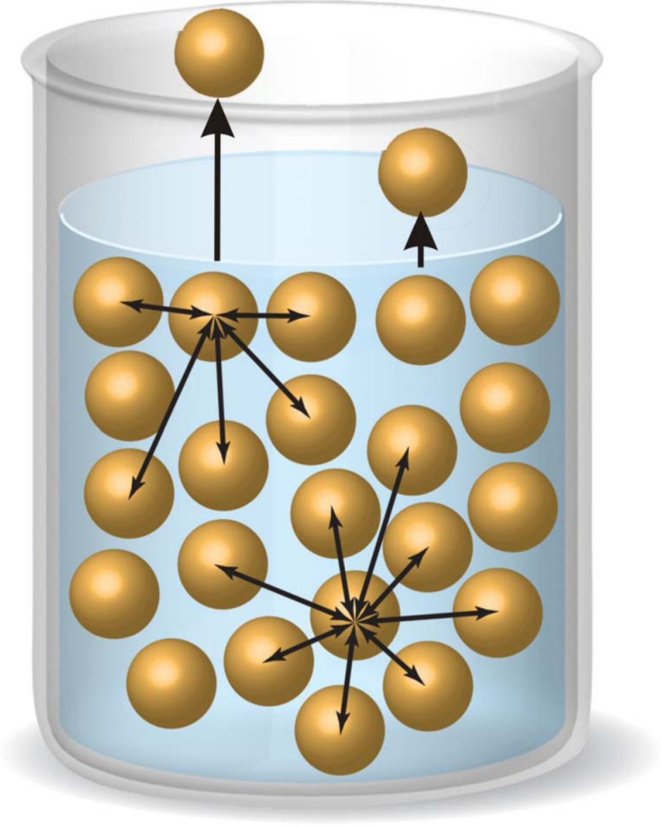
- **At any temperature, some molecules in a liquid have enough energy to escape.**
- **As the temperature rises, the fraction of molecules that have enough energy to escape increases.**



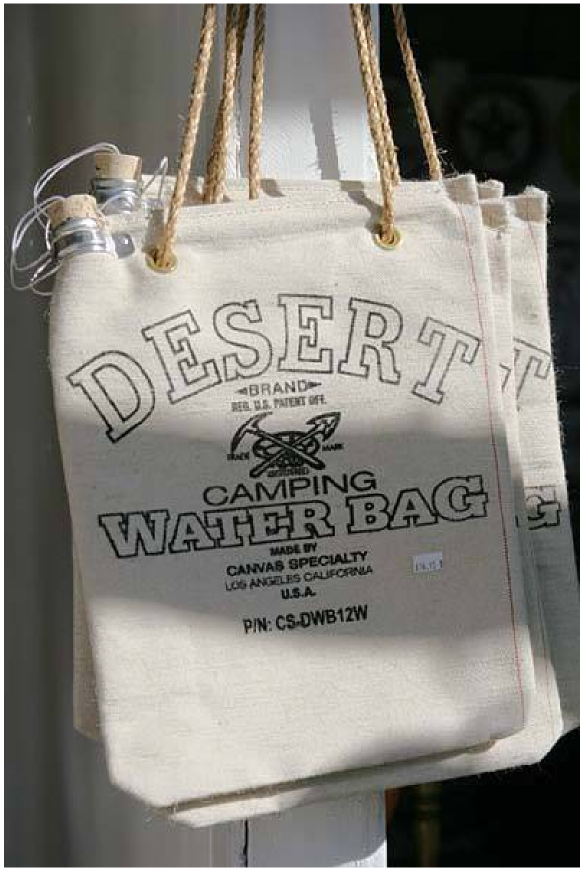
Vapor Pressure

If the container is open to the atmosphere, the molecules simply escape. This process is called **evaporation**.

As molecules escape from the surface, they take energy with them resulting in a cooling effect on the liquid.



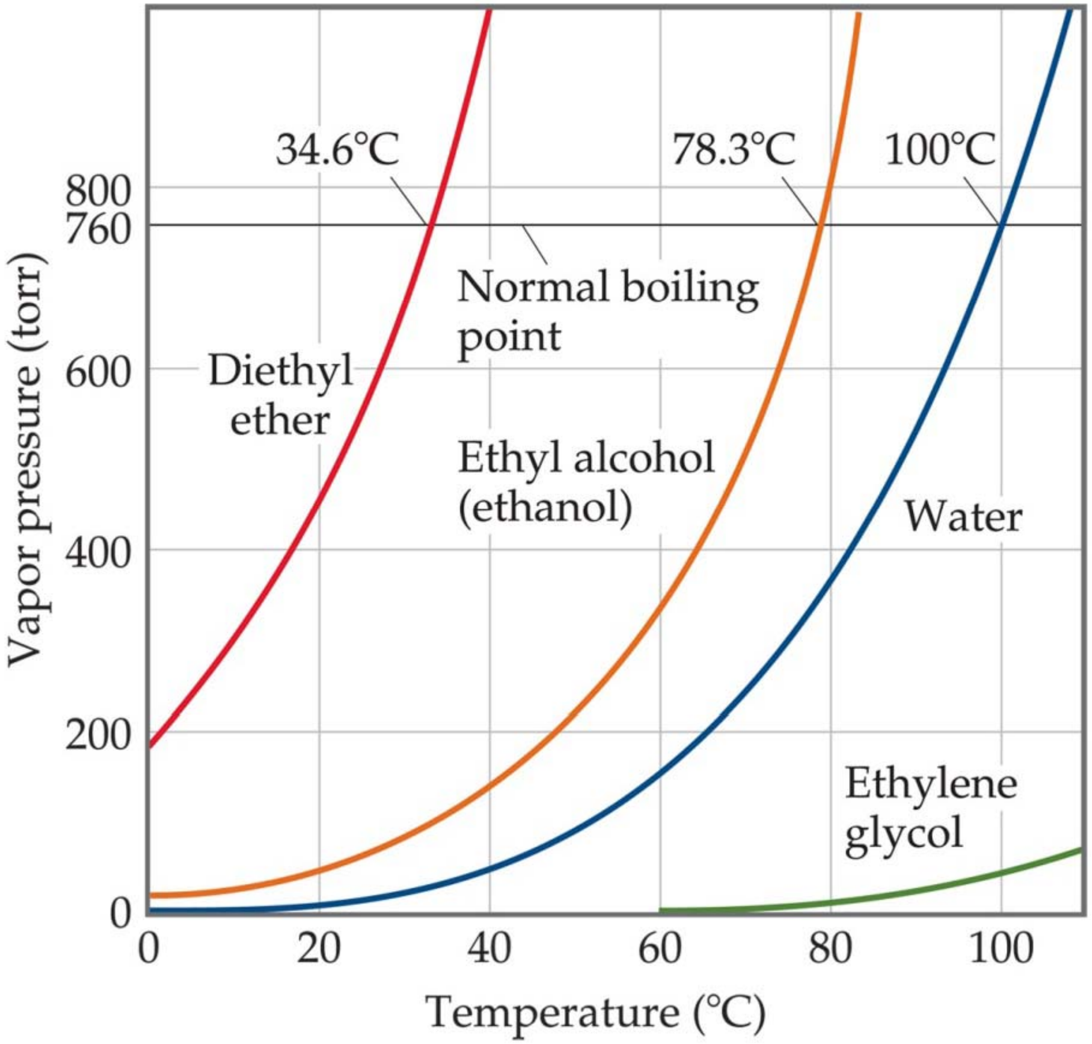
Vapor Pressure



A desert water bag (left)
A desert canteen (center)
An Army canteen (right)

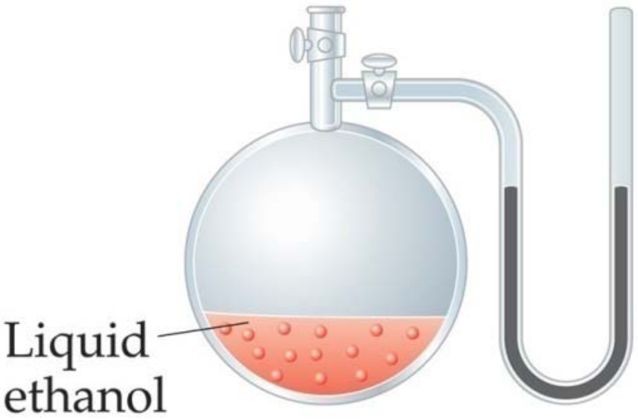
Vapor Pressure

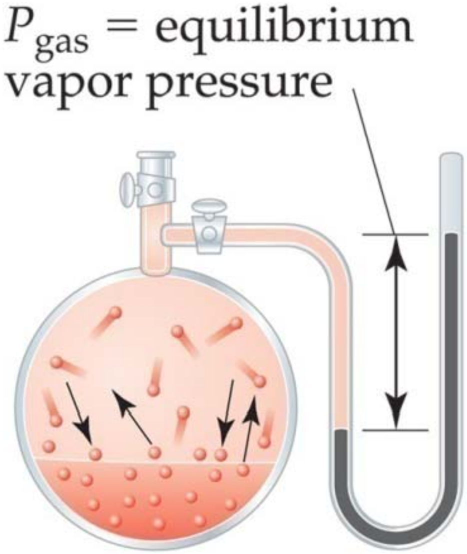
- Vapor pressure increases with temperature.
- When the vapor pressure of a liquid equals the atmospheric pressure, the liquid boils.
- The **normal boiling point** of a liquid is the temperature at which its vapor pressure is 760 torr.



Vapor Pressure

If the container is closed to the atmosphere, as more molecules escape the liquid, the pressure they exert increases.

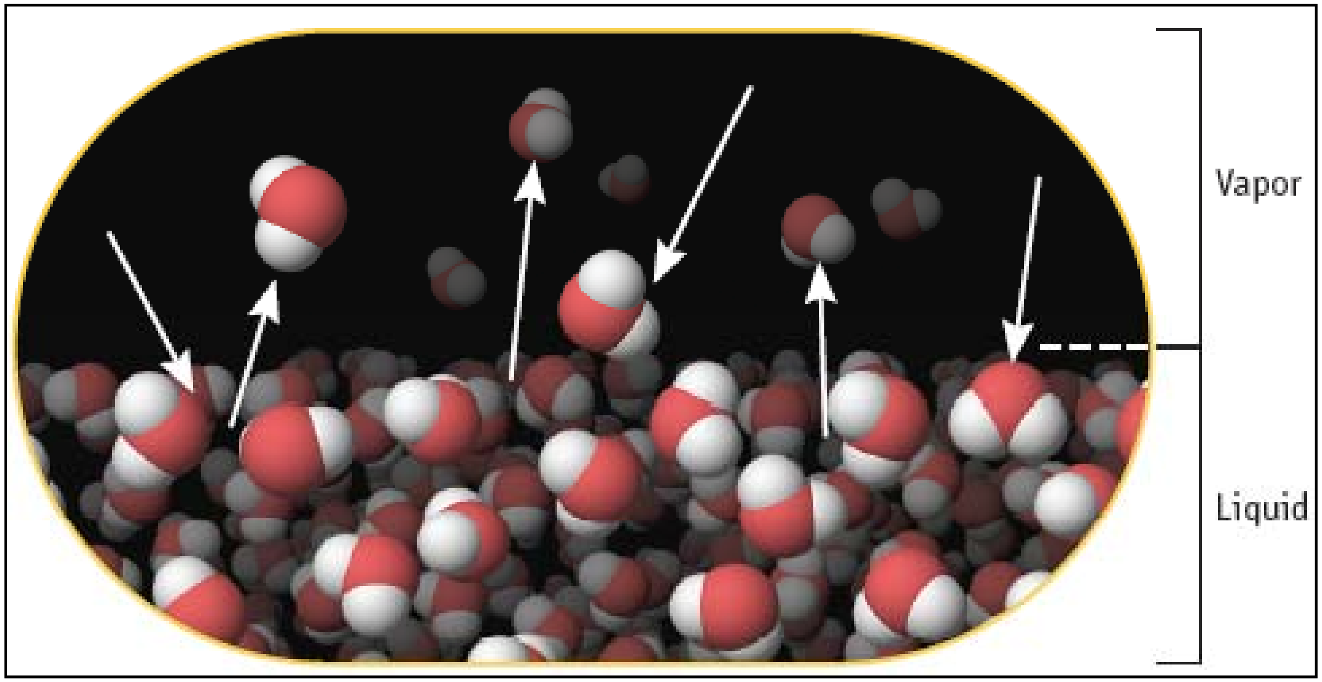




Vapor Pressure

In a sealed container, eventually, the air space in the container becomes saturated with vapor molecules.

The liquid and vapor reach a state of dynamic equilibrium: as liquid molecules evaporate, vapor molecules condense at the same rate. This is called the vapor pressure equilibrium



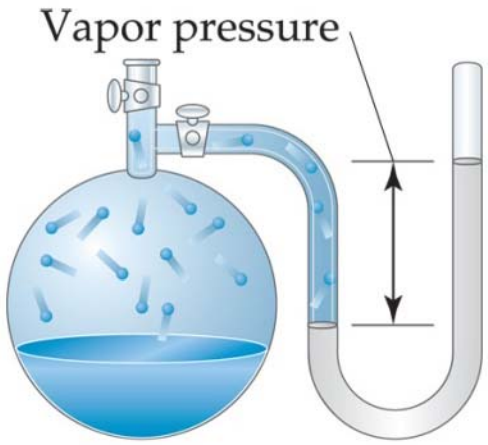
Vapor pressure of water at various temperatures

Temperature °C	Pressure mm Hg	Temperature °C	Pressure mm Hg	Temperature °C	Pressure mm Hg	Temperature °C	Pressure mm Hg
0	4.6	26	25.2	52	102.1	78	327.3
1	4.9	27	26.7	53	107.2	79	341.0
2	5.3	28	28.3	54	112.5	80	355.1
3	5.7	29	30.0	55	118.0	81	369.7
4	6.1	30	31.8	56	123.8	82	384.9
5	6.5	31	33.7	57	129.8	83	400.6
6	7.0	32	35.7	58	136.1	84	416.8
7	7.5	33	37.7	59	142.6	85	433.6
8	8.0	34	39.9	60	149.4	86	450.9
9	8.6	35	42.2	61	156.4	87	468.7
10	9.2	36	44.6	62	163.8	88	487.1
11	9.8	37	47.1	63	171.4	89	506.1
12	10.5	38	49.7	64	179.3	90	525.8
13	11.2	39	52.4	65	187.5	91	546.0
14	12.0	40	55.3	66	196.1	92	567.0
15	12.8	41	58.3	67	205.0	93	588.6
16	13.6	42	61.5	68	214.2	94	610.9
17	14.5	43	64.8	69	223.7	95	633.9
18	15.5	44	68.3	70	233.7	96	657.6
19	16.5	45	71.9	71	243.9	97	682.1
20	17.5	46	75.7	72	254.6	98	707.3
21	18.7	47	79.6	73	265.7	99	733.2
22	19.8	48	83.7	74	277.2	100	760
23	21.1	49	88.0	75	289.1		
24	22.4	50	92.5	76	301.4		

Vapor Pressure

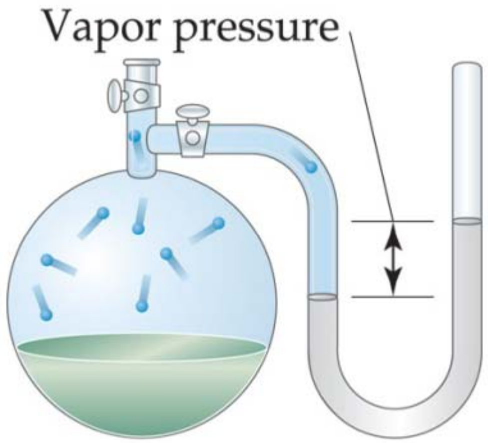
Because of solute-solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase.

Therefore, the vapor pressure of a solution is lower than that of the pure solvent.



Solvent alone

(a)

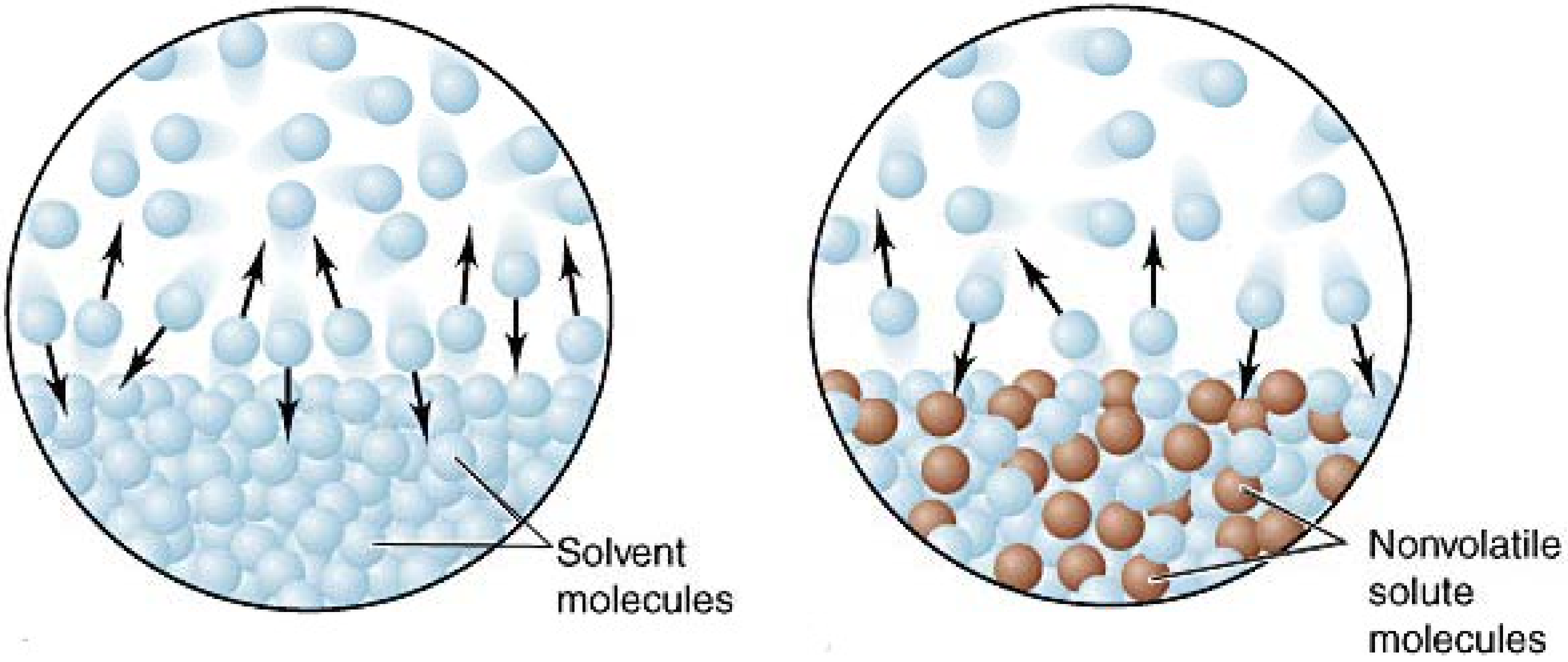


Solvent + solute

(b)

Vapor Pressure

There are less molecules of the solvent in the vapor phase above the solution



Raoult's Law

The VP of H_2O (or the solvent) over a solution depends on the number of H_2O molecules per solute molecule.

P_{solvent} *is proportional to* X_{solvent}

$$P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

where

- X_{solvent} is the mole fraction of the solvent
- $P^{\circ}_{\text{solvent}}$ is the normal vapor pressure of the solvent at that temperature

This equation is known as Raoult's Law

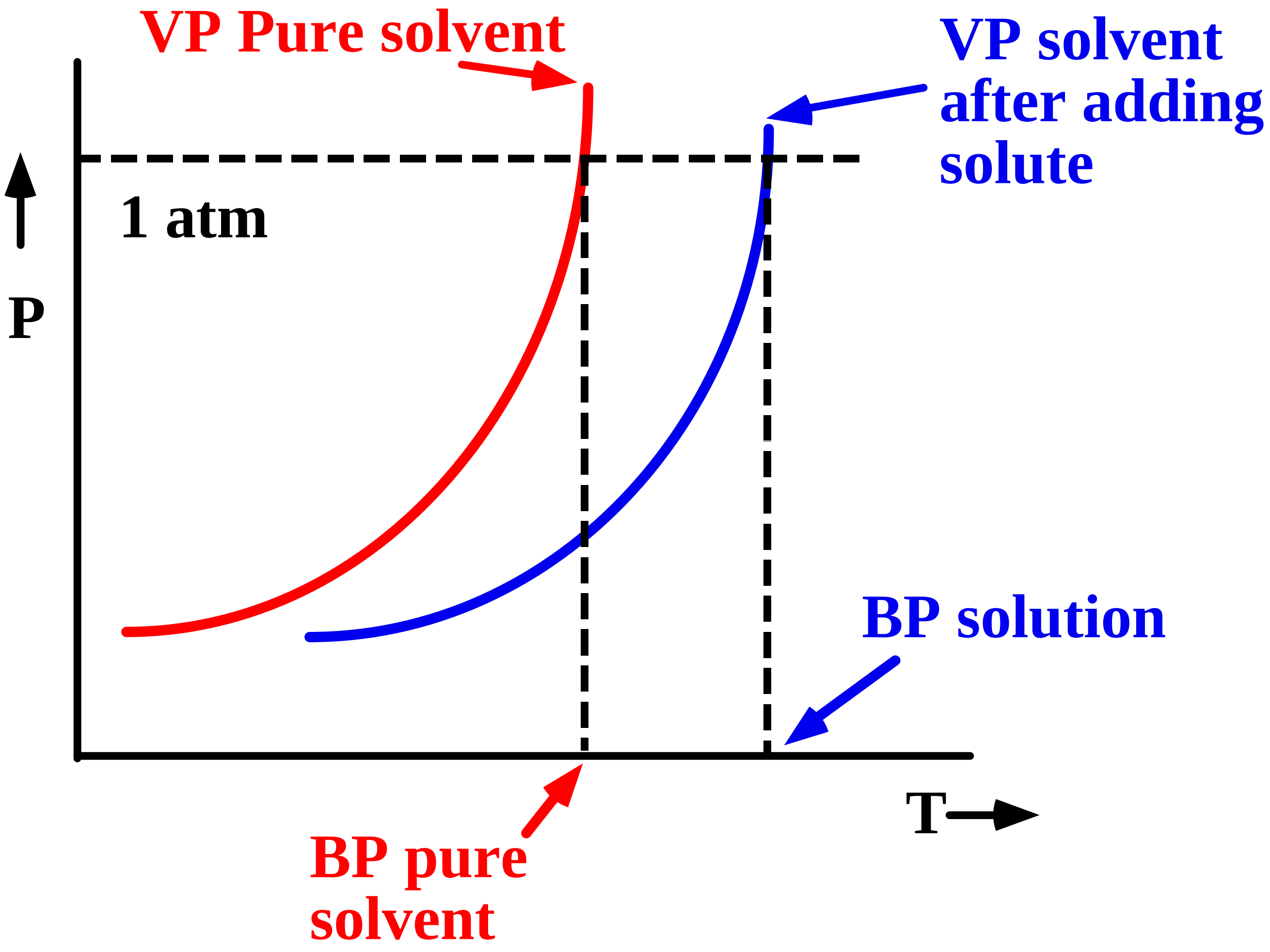
Raoult's Law

An ideal solution is one that obeys Raoult's law.

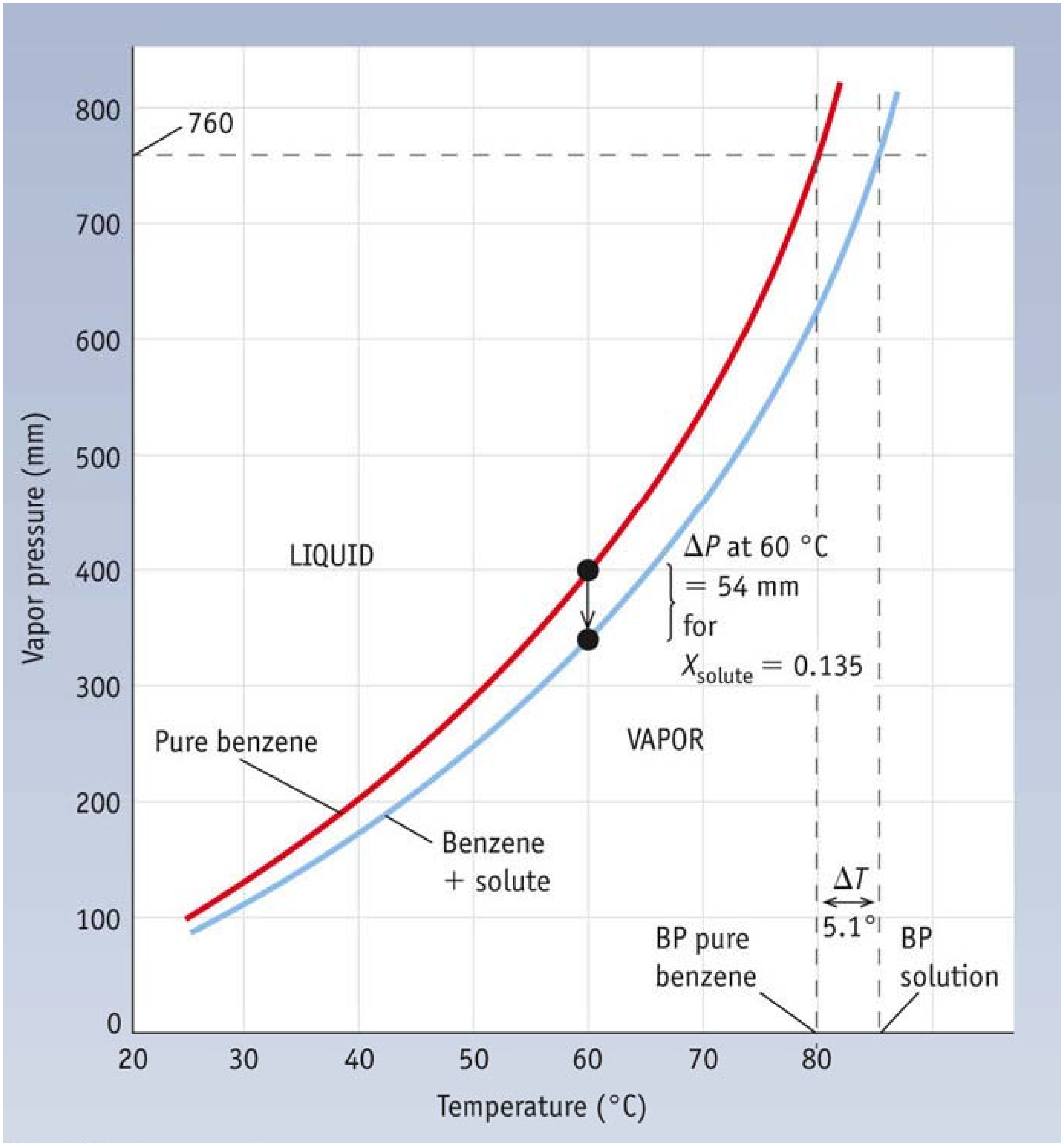
$$P_A = X_A P°_A$$

- Because mole fraction of solvent, X_A, is always less than 1, then P_A is always less than P^o_A.
- The vapor pressure of solvent over a solution is always **LOWERED!**

Changes in Freezing and Boiling Points of Solvent

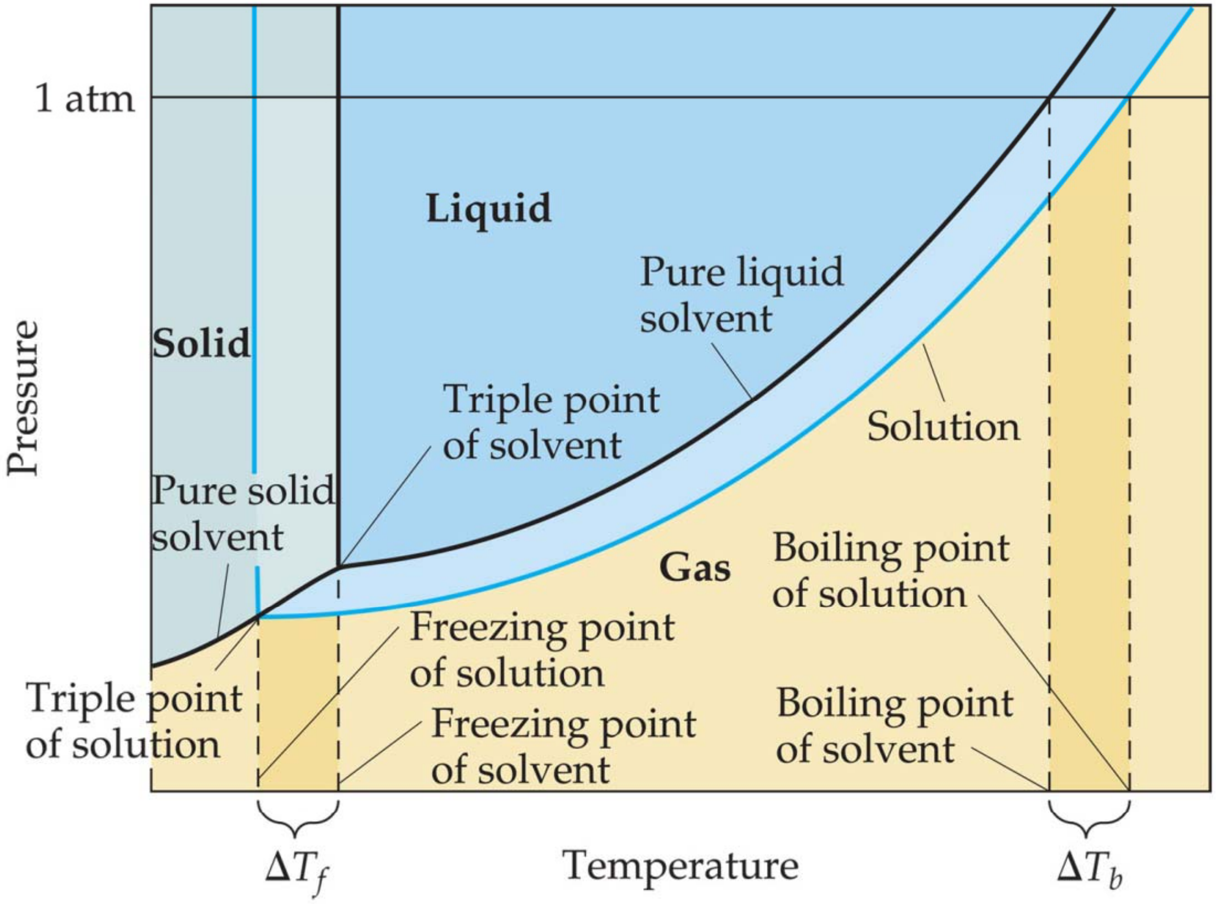


Vapor Pressure Lowering



Boiling Point Elevation and Freezing Point Depression

Nonvolatile solute-solvent interactions cause solutions to have higher boiling points and lower freezing points than the pure solvent.



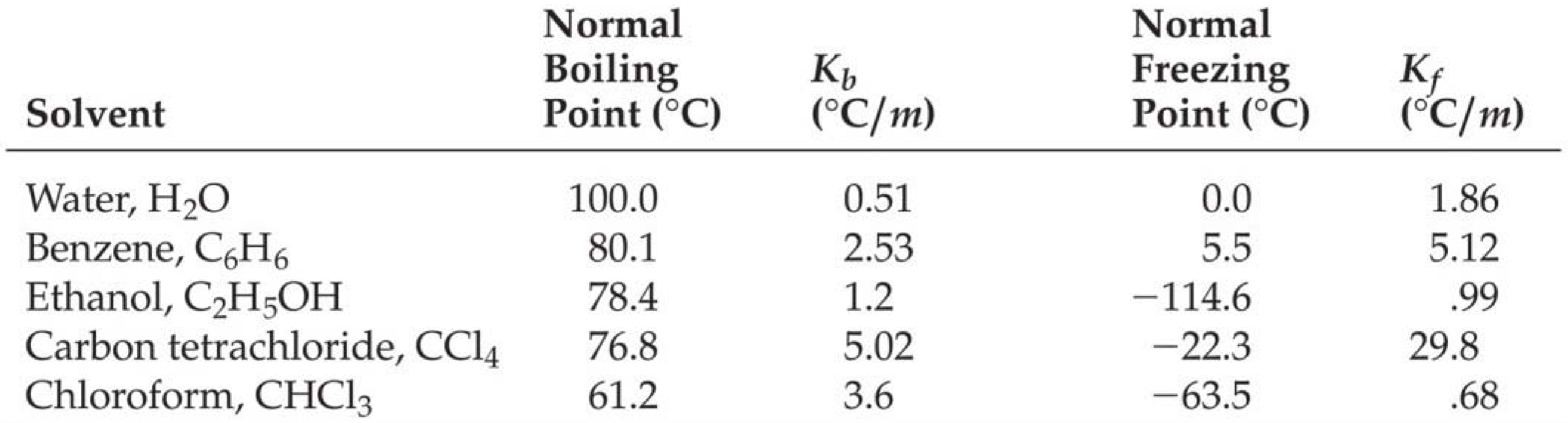
Boiling Point Elevation

The change in boiling point is proportional to the molality of the solution:

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

where:

K_b is the molal boiling point elevation constant, a property of the solvent.



Solvent	Normal Boiling Point (°C)	K_b (°C/m)	Normal Freezing Point (°C)	K_f (°C/m)
Water, H_2O	100.0	0.51	0.0	1.86
Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, C_2H_5OH	78.4	1.2	−114.6	.99
Carbon tetrachloride, CCl_4	76.8	5.02	−22.3	29.8
Chloroform, $CHCl_3$	61.2	3.6	−63.5	.68

ΔT_b is *added to* the normal boiling point of the solvent.

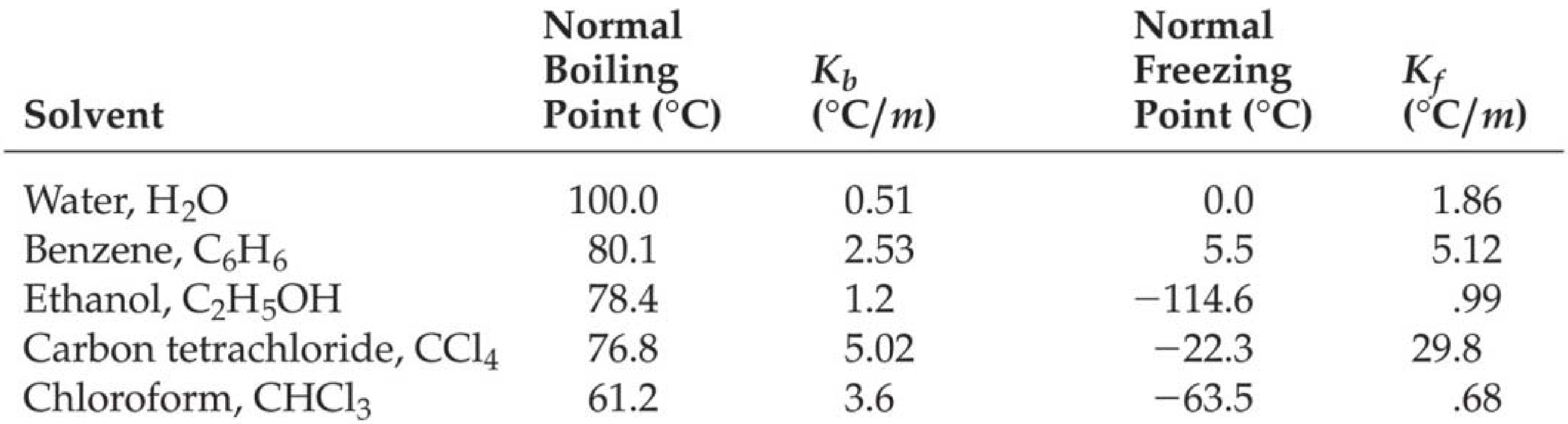
Freezing Point Depression

- The change in freezing point can be found similarly:

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

Where:

K_f is the molal freezing point depression constant of the solvent.



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Carbon tetrachloride, CCl_4	76.8	5.02	−22.3	29.8
Chloroform, $CHCl_3$	61.2	3.6	−63.5	.68

ΔT_f is *subtracted from* the normal freezing point of the solvent.

Boiling Point Elevation and Freezing Point Depression

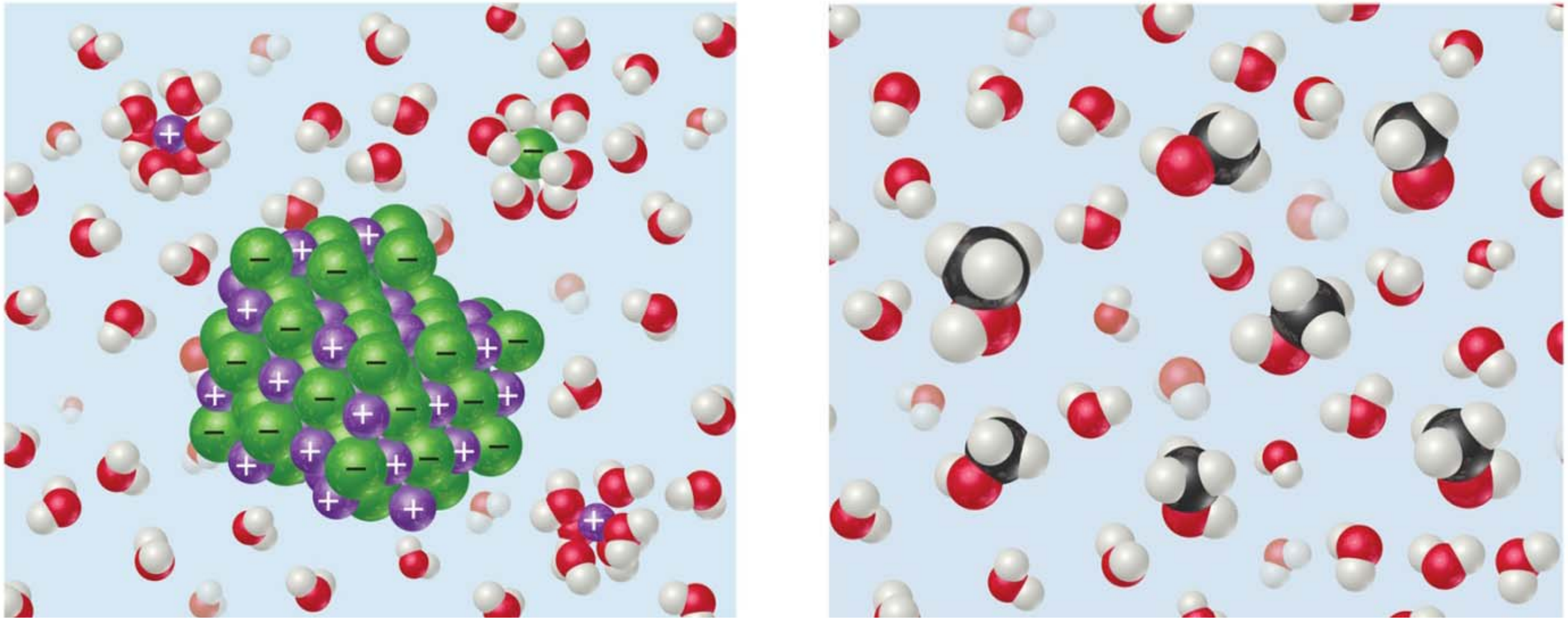
Note that in both equations, ΔT does not depend on *what the solute is*, but only on *how many particles* are dissolved.

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

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

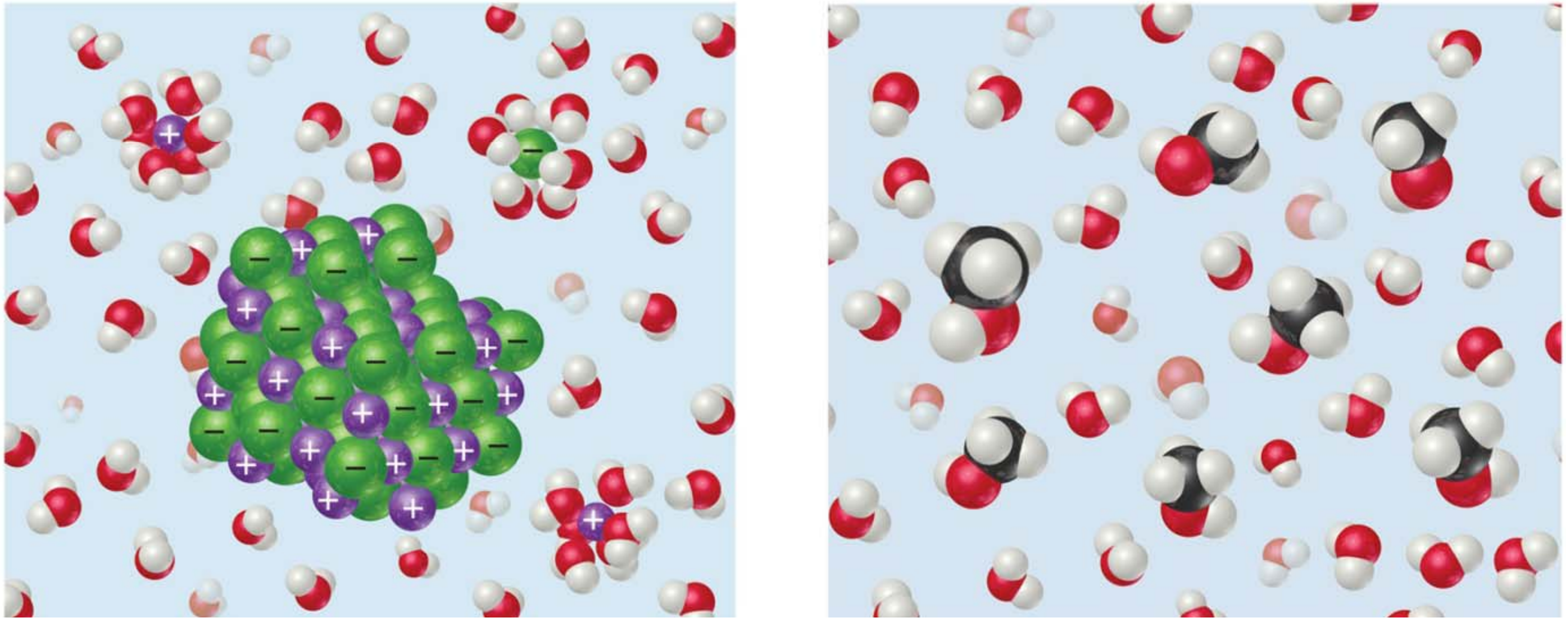
Colligative Properties of Electrolytes

Since colligative properties depend on the number of particles dissolved, solutions of electrolytes (which dissociate in solution) should show greater changes than those of nonelectrolytes.

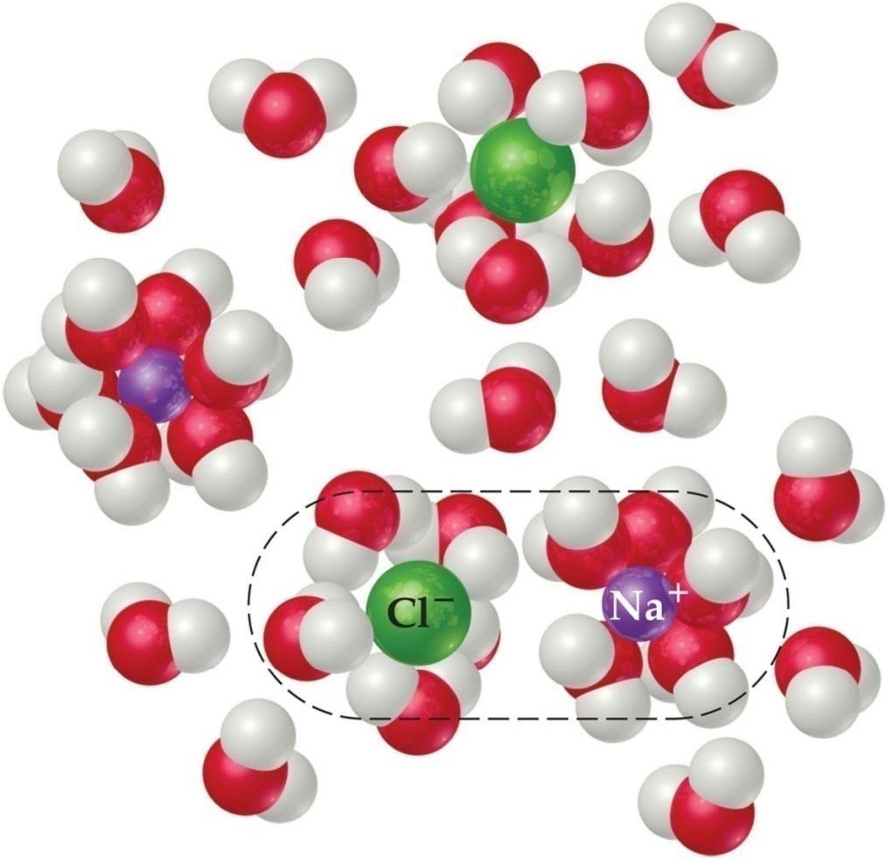


Colligative Properties of Electrolytes

However, a 1 *M* solution of NaCl does not show twice the change in freezing point that a 1 *M* solution of methanol does.

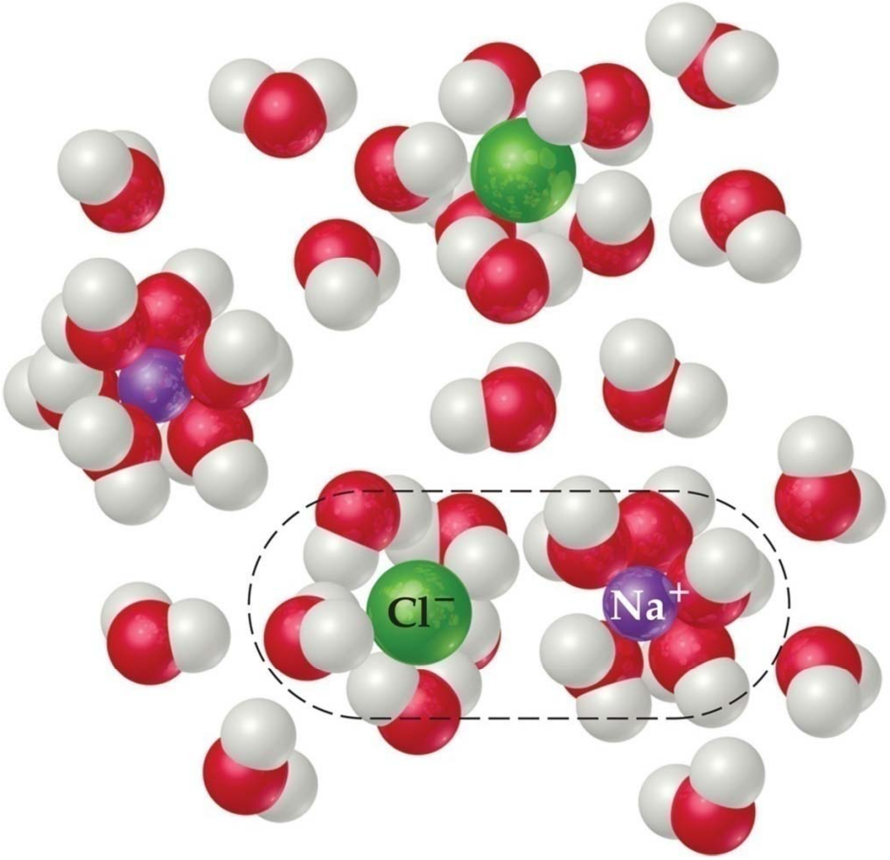


The van’t Hoff Factor



One mole of NaCl in water does not really give rise to two moles of ions.

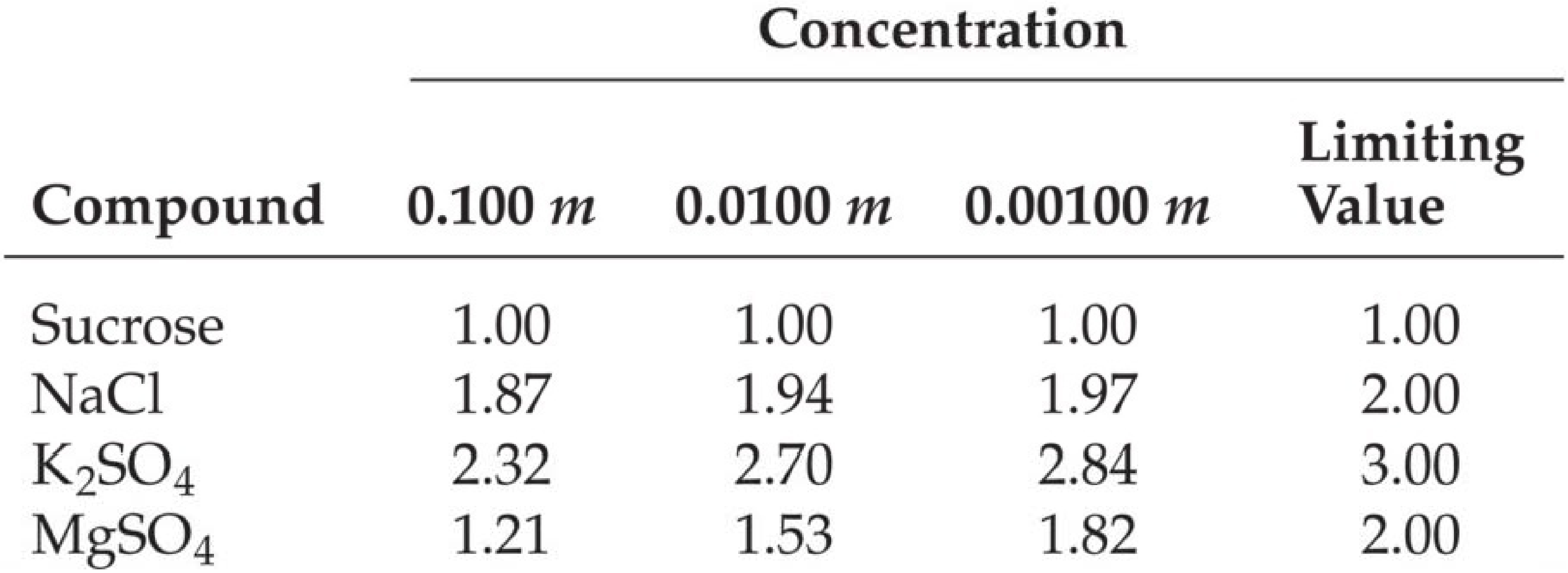
The van’t Hoff Factor



Some Na^+ and Cl^- reassociate for a short time, so the true concentration of particles is somewhat less than two times the concentration of NaCl.

The van’t Hoff Factor

- Reassociation is more likely at higher concentration.
- Therefore, the number of particles present is concentration dependent.

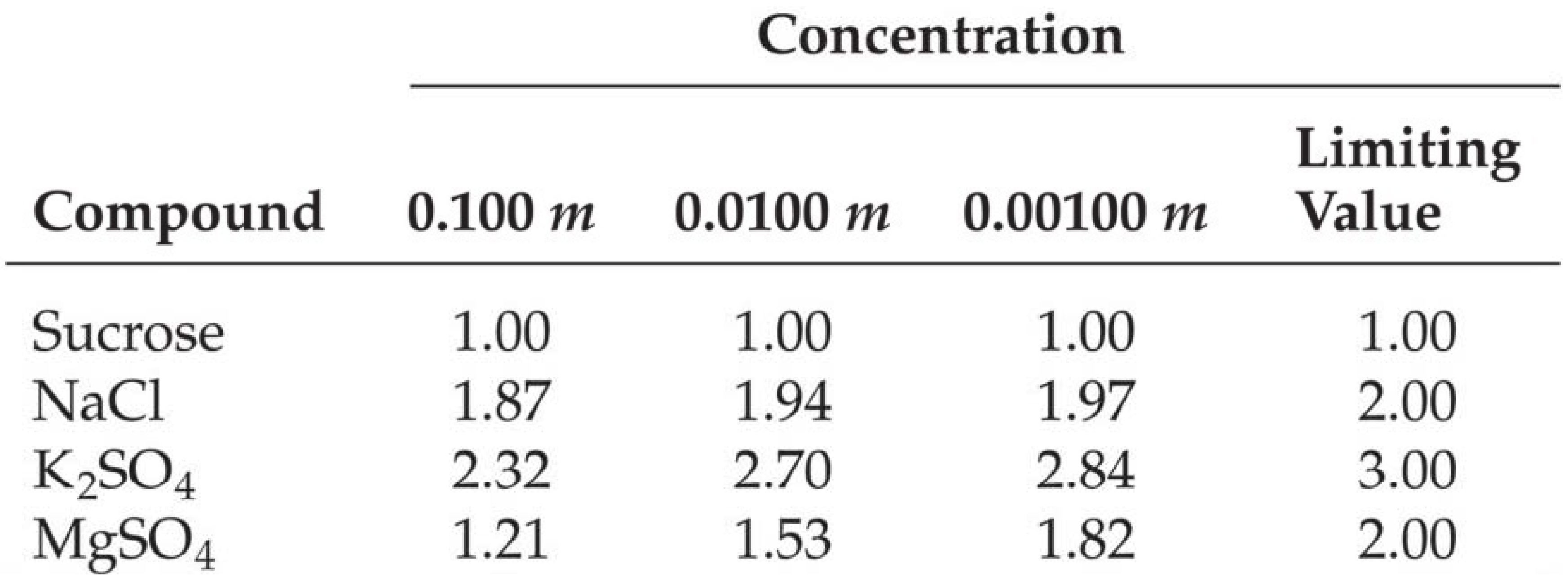


	Concentration			
Compound	0.100 m	0.0100 m	0.00100 m	Limiting Value
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

The van’t Hoff Factor

We modify the previous equations by multiplying by the van’t Hoff factor, *I*

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



	Concentration			
Compound	**0.100 *m***	**0.0100 *m***	**0.00100 *m***	**Limiting Value**
Sucrose	1.00	1.00	1.00	1.00
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K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

Electrolytes

Strong electrolyte: a compound that dissociates completely to ions in an aqueous solution.

Compound	Dissociates to	No. of ions per formula unit
NaCl	Na^+ and Cl^-	2
$CaCl_2$	Ca^{2+} and 2 Cl^-	3
K_2SO_4	2 K^+ and SO_4^{2-}	3
$Mg_3(PO_4)_2$	3 Mg^{2+} and 2 PO_4^{3-}	5

Ionic substances dissociate into the ions and polyatomic ions used in writing the chemical formulas of the compounds

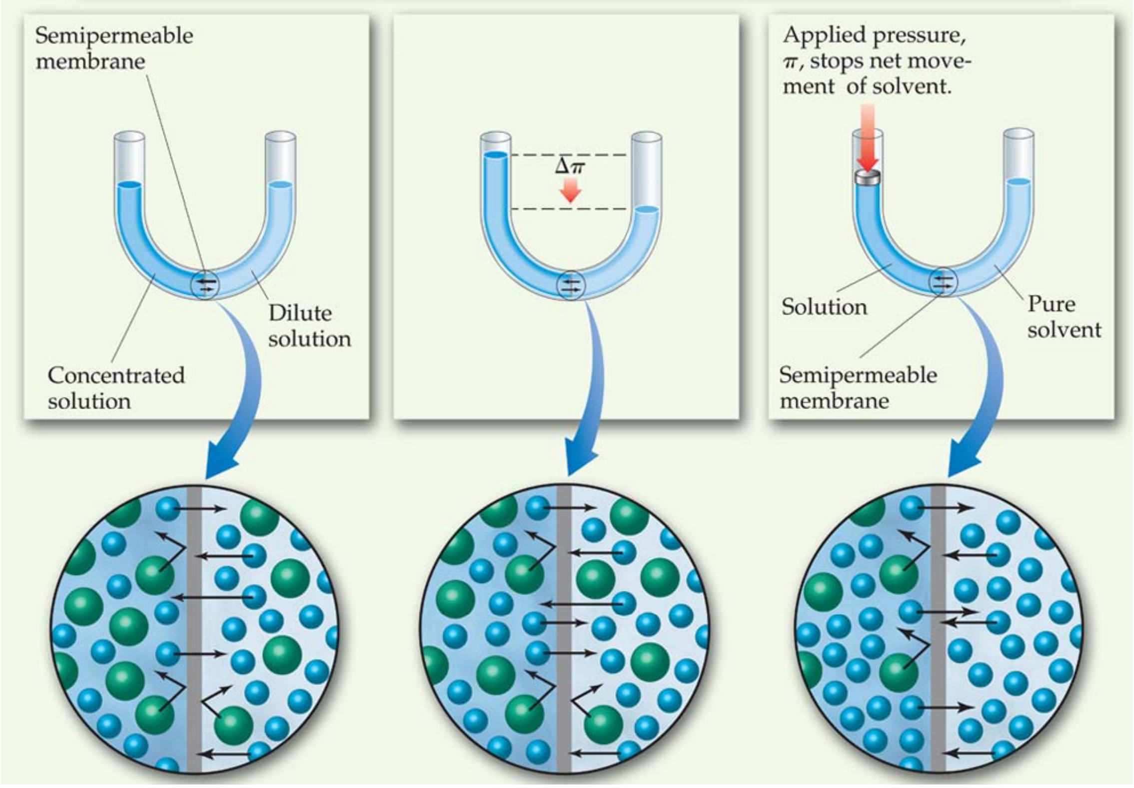
Weak electrolyte: a compound that only partially dissociates to ions in an aqueous solution.

An example is acetic acid, $HC_2H_3O_2$, which exists as $HC_2H_3O_2$ molecules, H^+ and $C_2H_3O_2^-$ in water solution

Osmosis

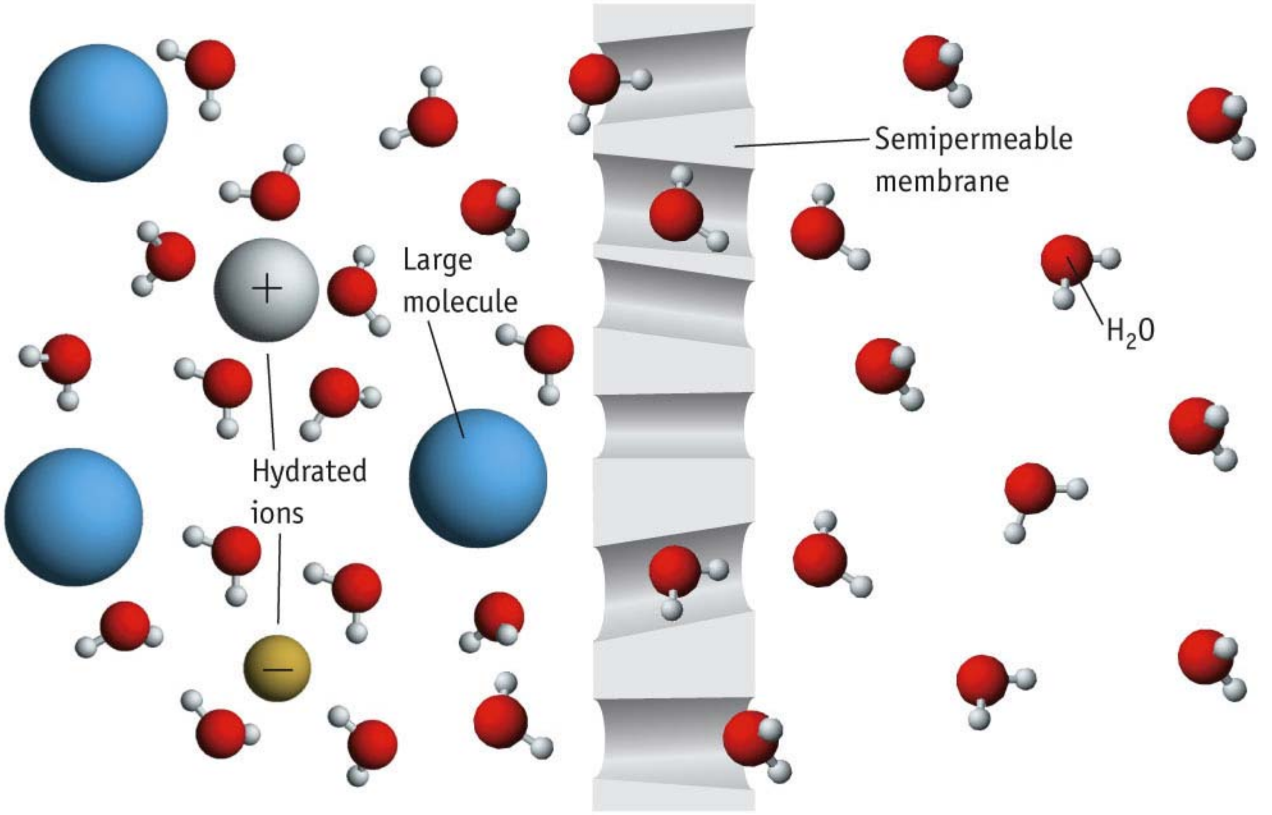
- Some substances form **semipermeable membranes**, allowing some smaller particles to pass through, but blocking other larger particles.
- In biological systems, most semipermeable membranes allow water to pass through, but solutes are not free to do so.

Osmosis



In osmosis, there is net movement of solvent from the area of higher solvent concentration (*lower solute concentration*) to the area of lower solvent concentration (*higher solute concentration*).

Osmosis



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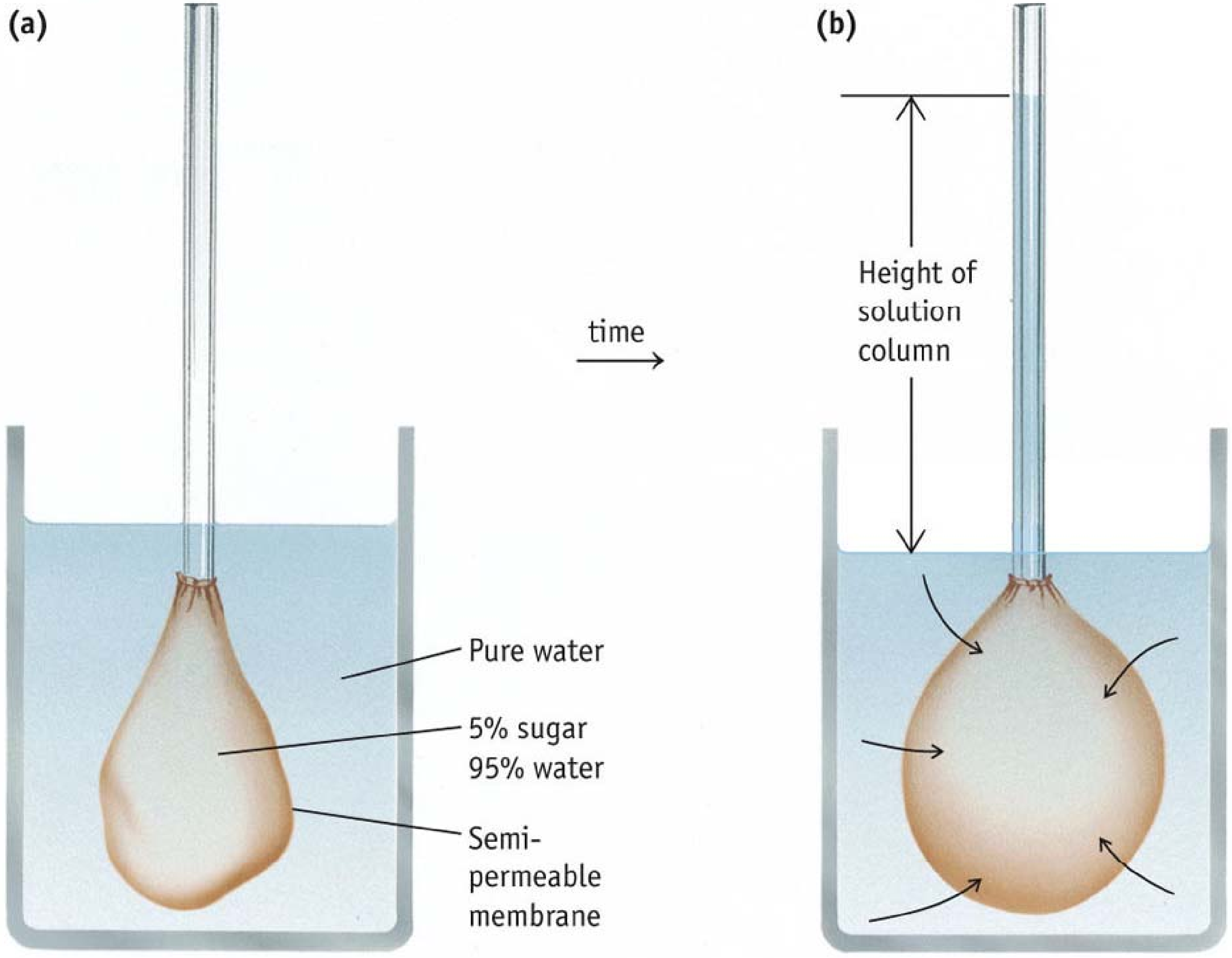
The semipermeable membrane allows only the movement of solvent molecules.
Solvent molecules move from pure solvent to solution in an attempt to make both have the same concentration of solute.

The driving force is entropy

Process of Osmosis



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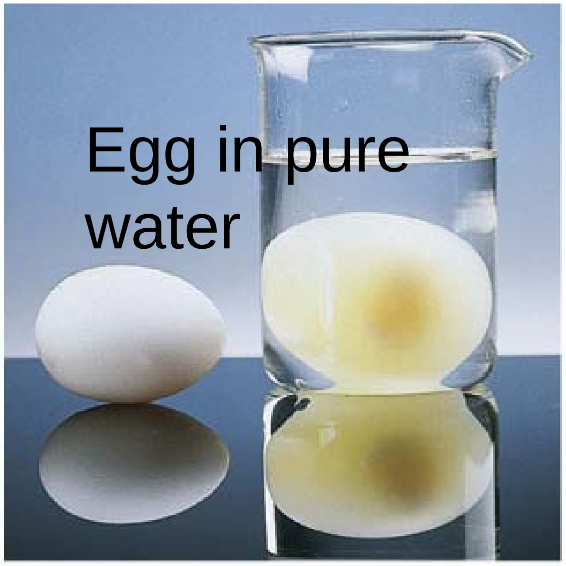
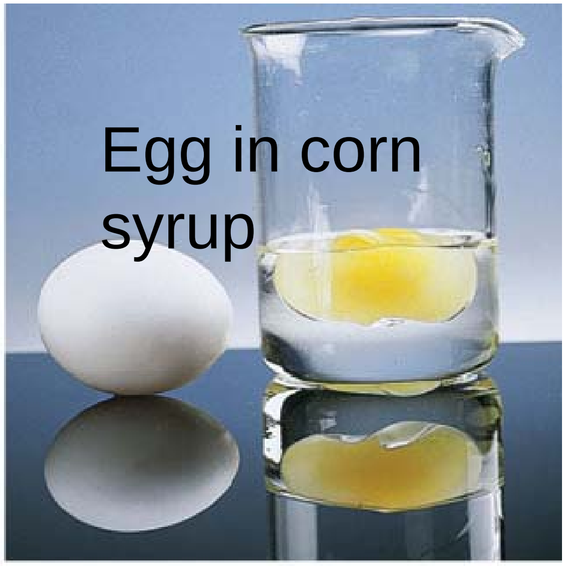
Osmosis


Dissolving the shell in vinegar

(a) A fresh egg is placed in dilute acetic acid. The acid reacts with the $CaCO_3$ of the shell but leaves the egg membrane intact.


Egg in pure water

(b) If the egg, with its shell removed, is placed in pure water, the egg swells.


Egg in corn syrup

(c) If the egg, with its shell removed, is placed in a concentrated sugar solution, the egg shrivels.

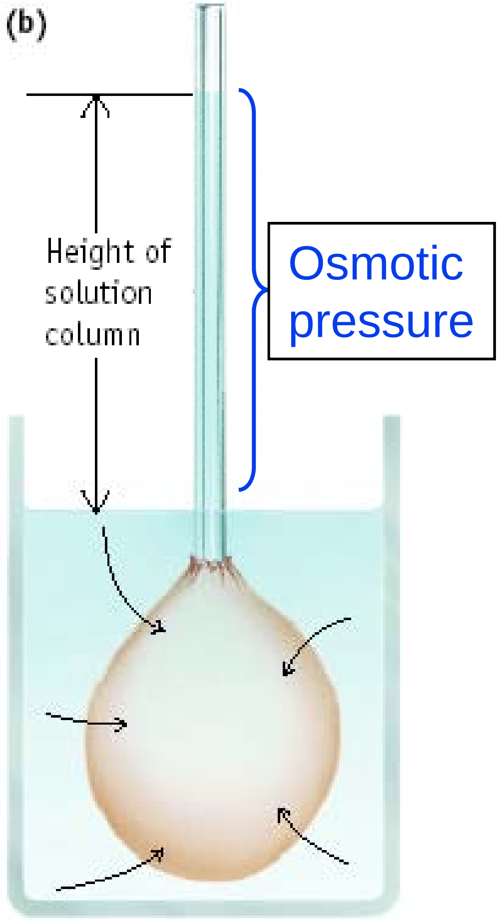
Osmotic Pressure

- The pressure required to stop osmosis, known as **osmotic pressure**, Π, is

$$\Pi = \left(\frac{n}{V}\right)RT = MRT$$

where M is the molarity of the solution

If the osmotic pressure is the same on both sides of a membrane (i.e., the concentrations are the same), the solutions are **isotonic**.



Osmosis

- Osmosis of solvent from one solution to another can continue until the solutions are **ISOTONIC** — they have the same concentration.

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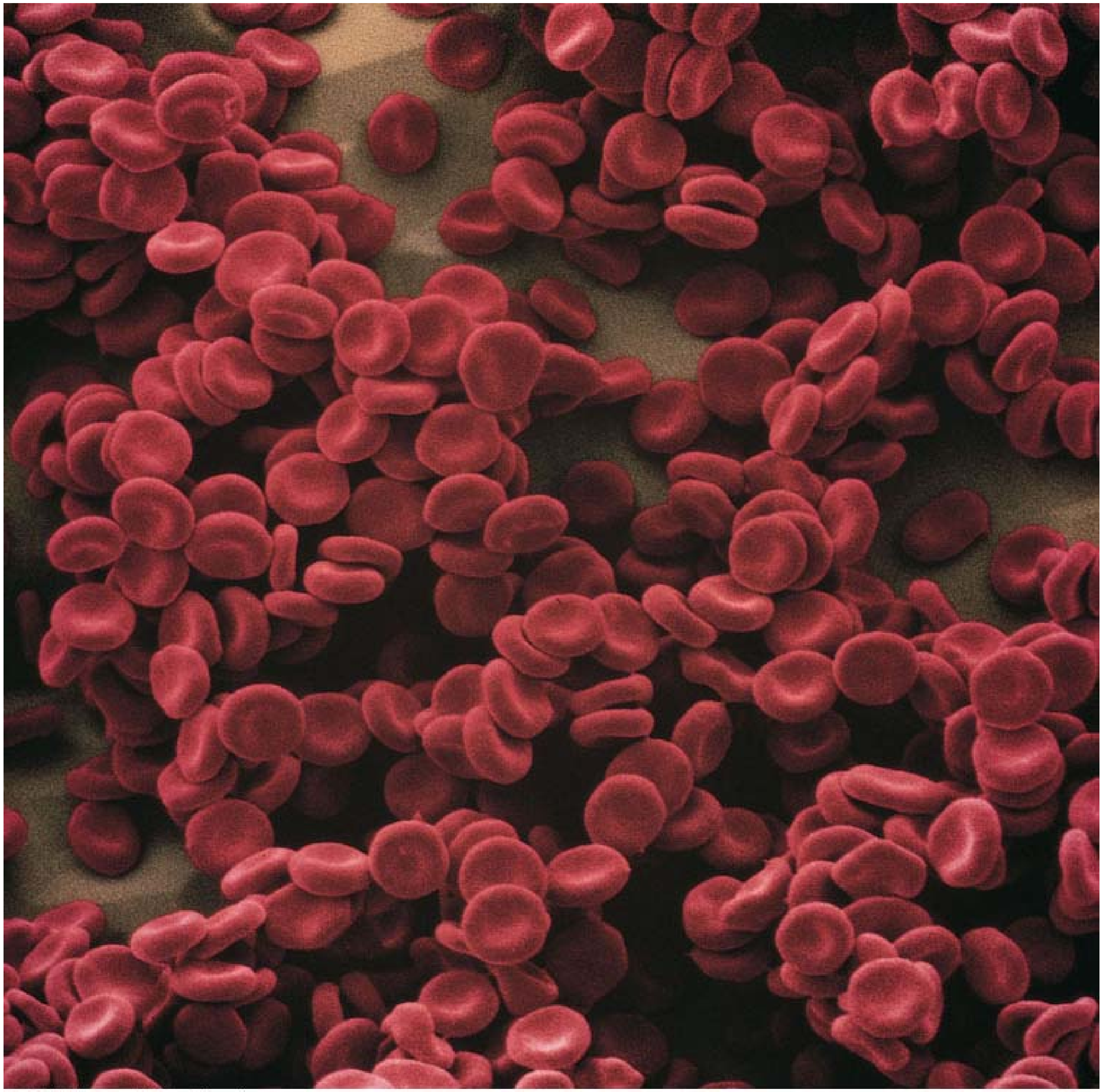
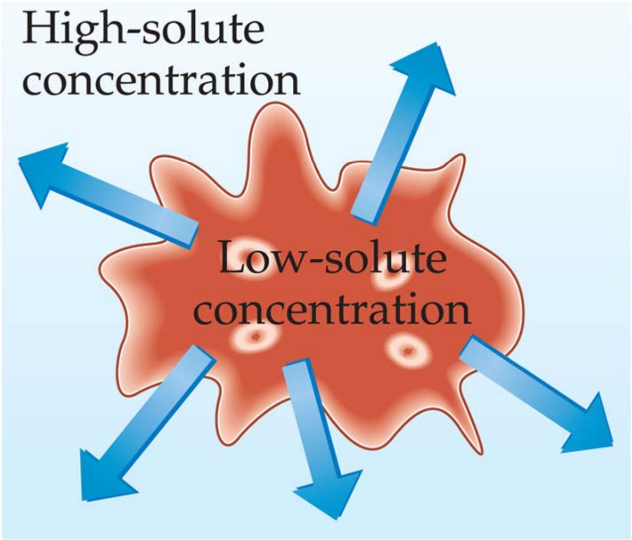
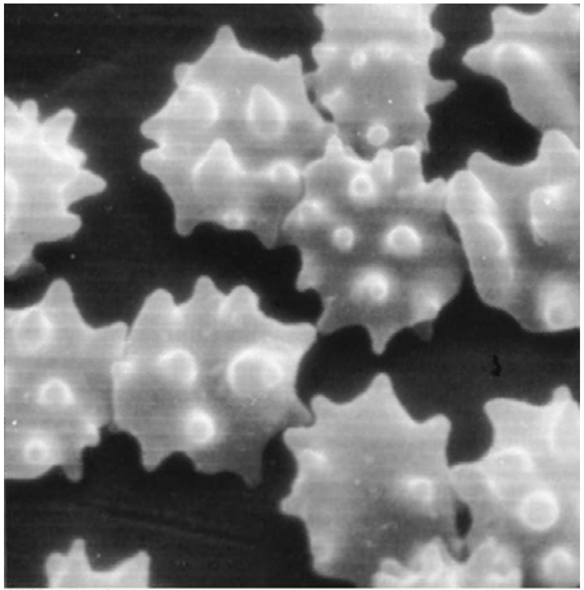


Normal red blood cells

Osmosis in Blood Cells

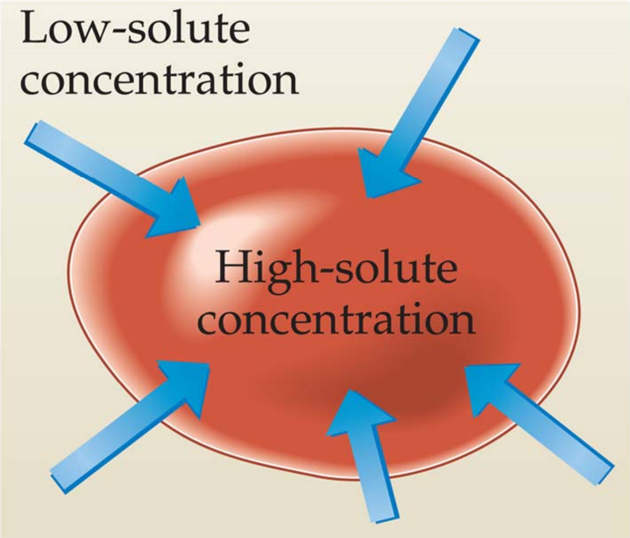
- If the solute concentration outside the cell is greater than that inside the cell, the solution is **hypertonic**.
- Water will flow out of the cell, and **crenation** results.

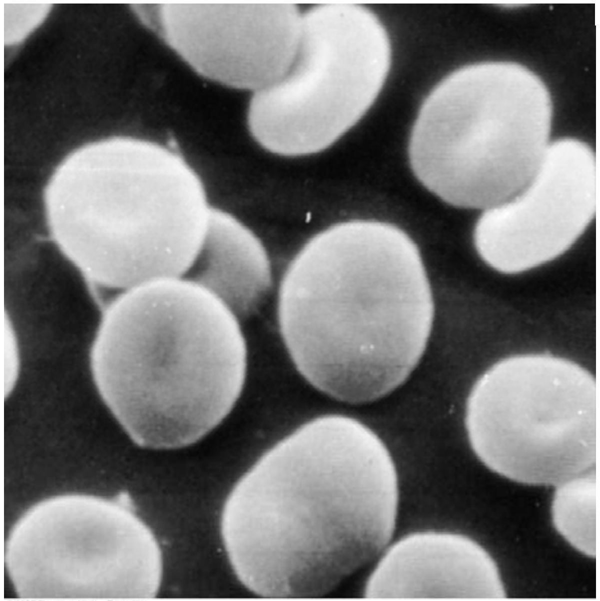




Osmosis in Cells

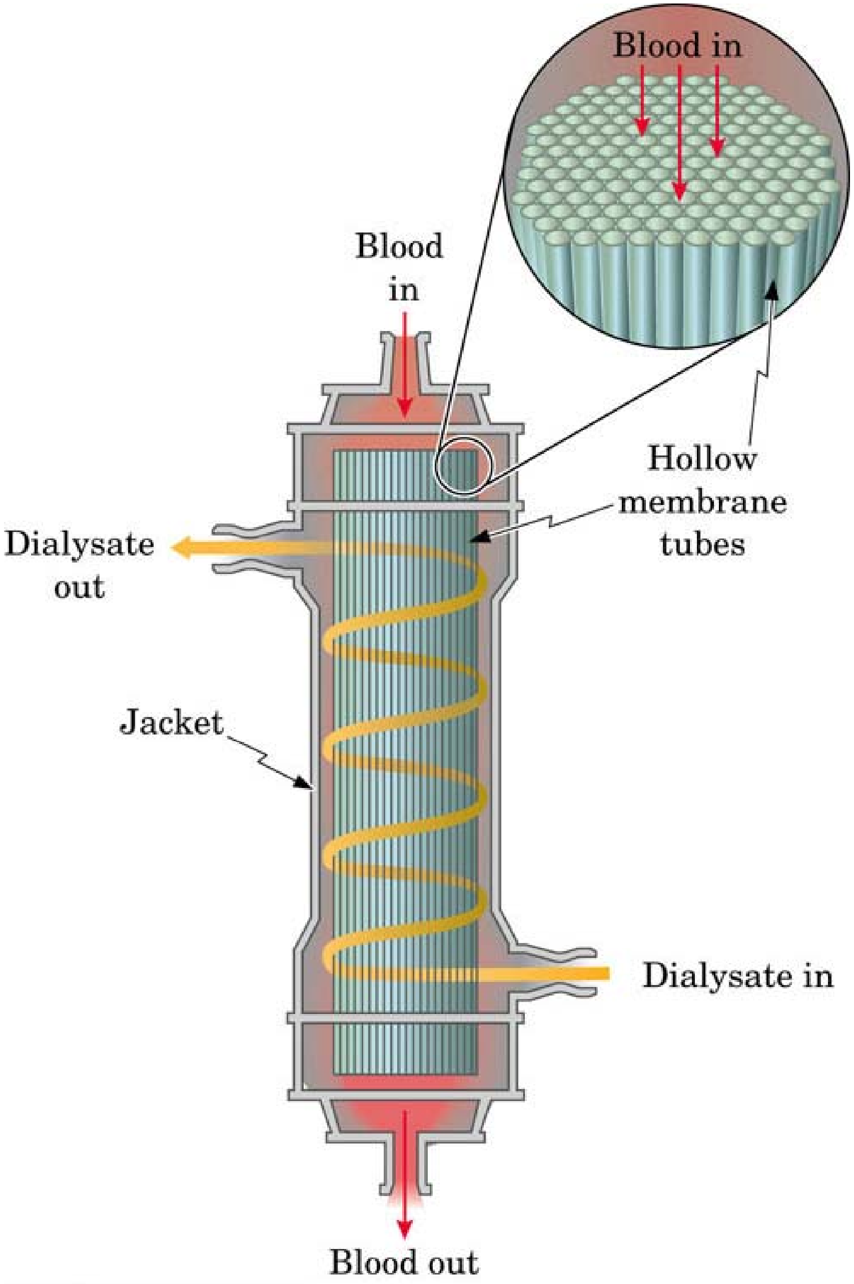
- If the solute concentration outside the cell is less than that inside the cell, the solution is **hypotonic**.
- Water will flow into the cell, and **hemolysis** results.





Dialysis

Dialysis: the separation of larger molecules, dissolved substances, or colloidal particles from smaller molecules, substances, or colloidal particles by a semipermeable membrane.



Reverse Osmosis
Water Desalination

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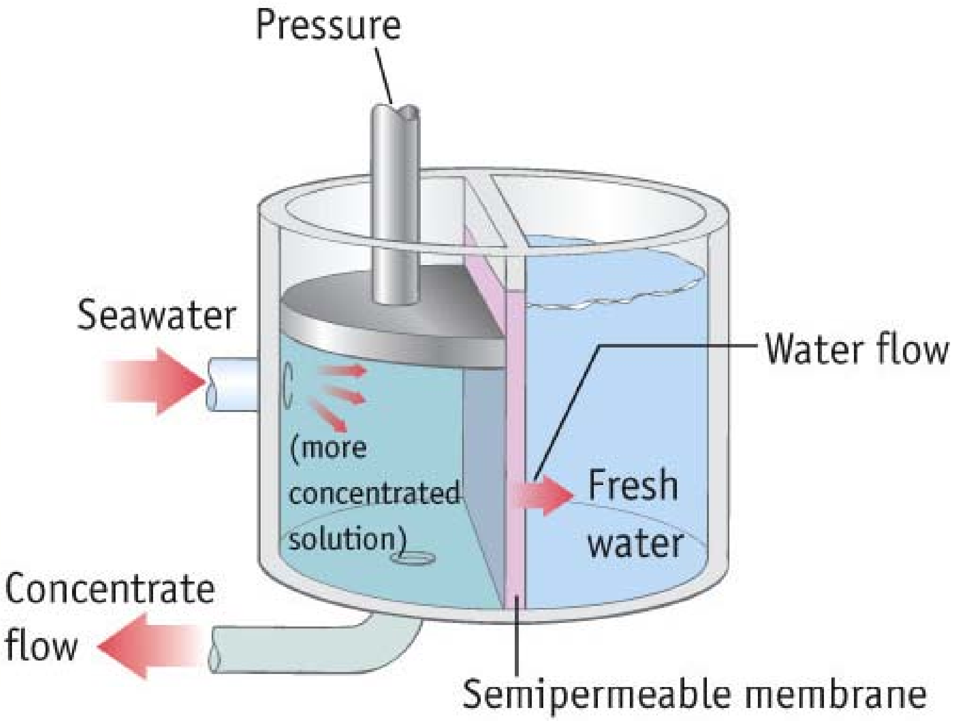

Water desalination plant in Tampa