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# Chapter 12

## Physical Properties of Solutions


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# 12.1
# Types of solutions

A **solution** is a homogeneous mixture of two or more substances.

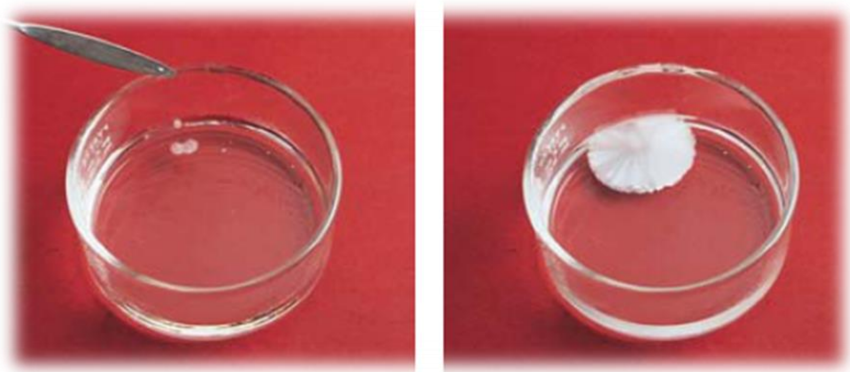
In a solution, the **solute** is dispersed uniformly throughout the **solvent**.

A saturated solution contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.

An unsaturated solution contains less solute than it has the capacity to dissolve.

A supersaturated solution, contains more solute than is present in a saturated solution. Supersaturated solutions are not very stable. In time, some of the solute will come out of a supersaturated solution as crystals.

Crystallization is the process in which dissolved solute comes out of solution and forms crystals.



*In a supersaturated sodium acetate solution, sodium acetate crystals rapidly form when a small seed crystal is added.*

# Types of Solutions

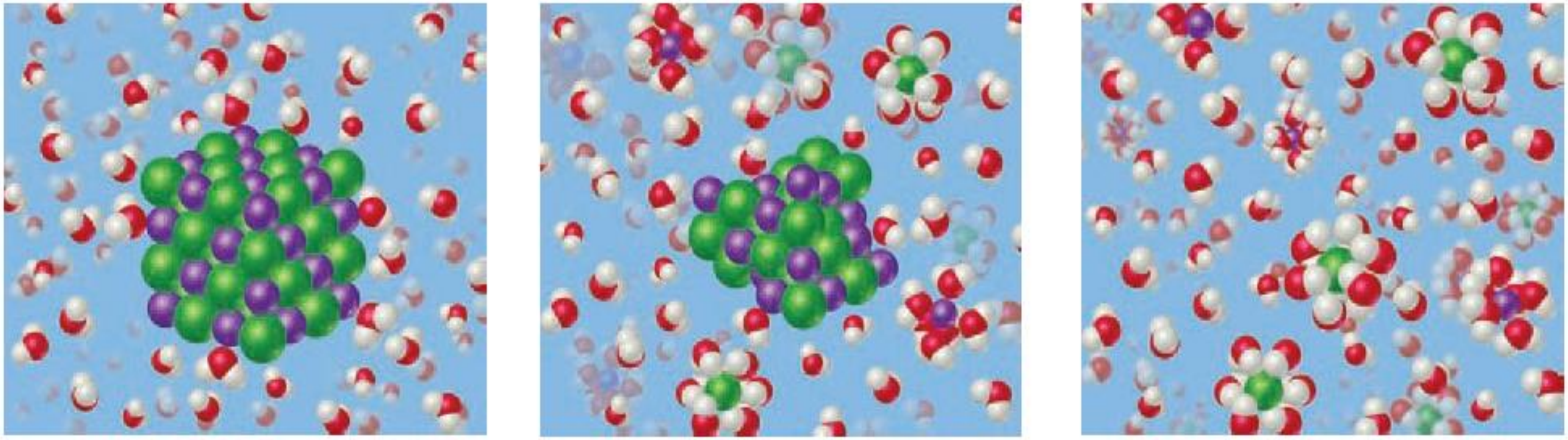
| Component 1 | Component 2 | State of Resulting solution | Examples |
|---|---|---|---|
| Gas | Gas | Gas | Air |
| Gas | Liquid | Liquid | Soda water ($CO_2$ in water) |
| Gas | Solid | Solid | $H_2$ gas in palladium |
| Liquid | Liquid | Liquid | Ethanol in water |
| Solid | Liquid | Liquid | NaCl in water |
| Solid | Solid | Solid | Brass (Cu/Zn), solder (Sn/Pb) |

# 12.2
# A molecular view of the solution process

The intermolecular attractions that hold molecules together in liquids and solids also play a central role in the formation of solutions.

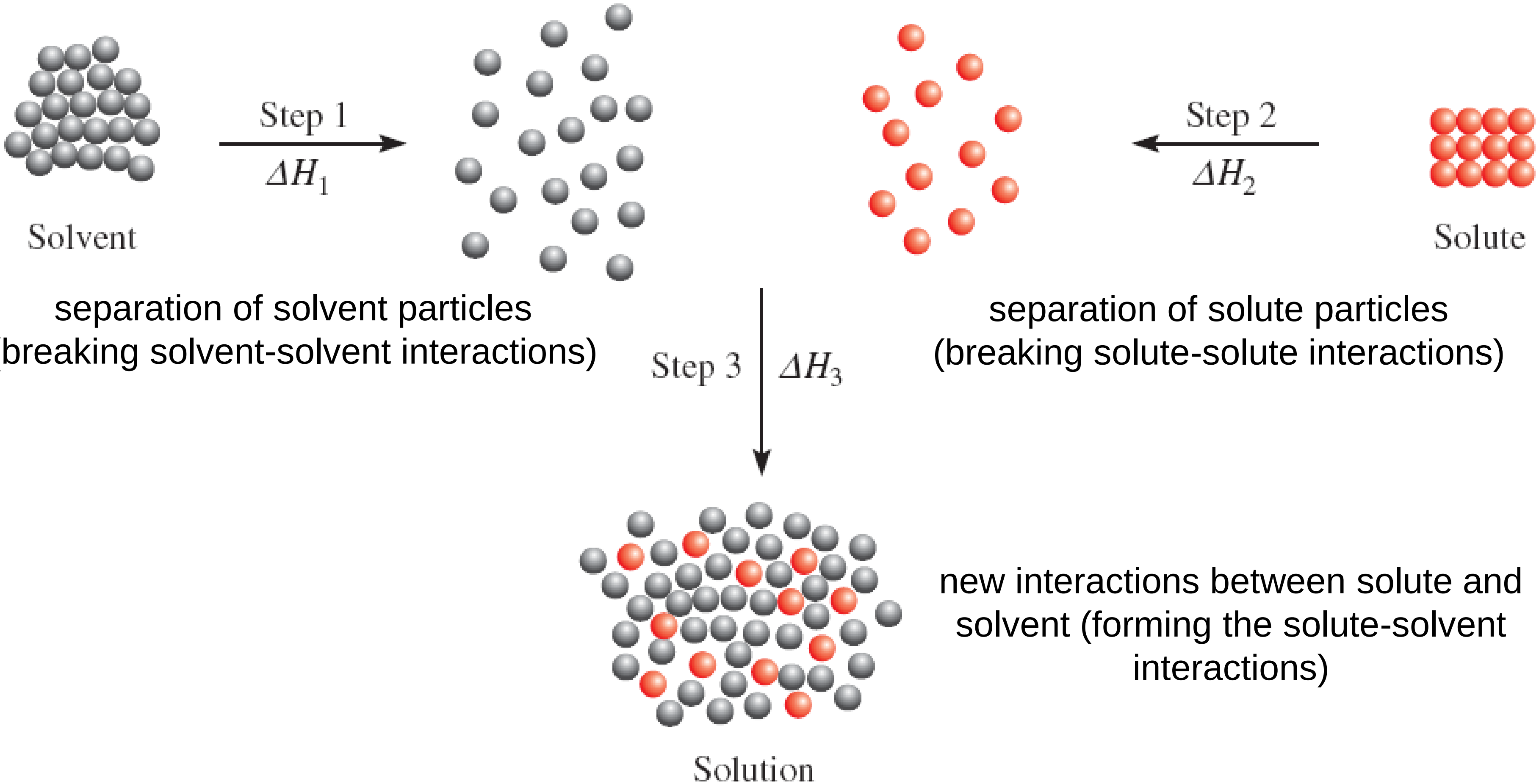
The ease with which a solute particle replaces a solvent molecule depends on the relative strengths of three types of interactions:

- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction



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

Three processes affect the energetics of solution:




separation of solvent particles (breaking solvent-solvent interactions)

separation of solute particles (breaking solute-solute interactions)

new interactions between solute and solvent (forming the solute-solvent interactions)

The overall enthalpy change in forming a solution, $\Delta H_{soln}$, is the sum of the three associated processes:

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

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

-If the solute-solvent attraction is stronger than the solvent-solvent attraction and solute-solute attraction, the solution process is favorable, or exothermic ($\Delta H_{soln} < 0$).

-If the solute-solvent interaction is weaker than the solvent-solvent and solute-solute interactions, then the solution process is endothermic ($\Delta H_{soln} > 0$).

Solubility is a measure of how much solute will dissolve in a solvent at a specific temperature.

Chemists use the axiom "**like dissolves like**".

-Polar substances tend to dissolve in polar solvents.
-Nonpolar substances tend to dissolve in nonpolar solvents.

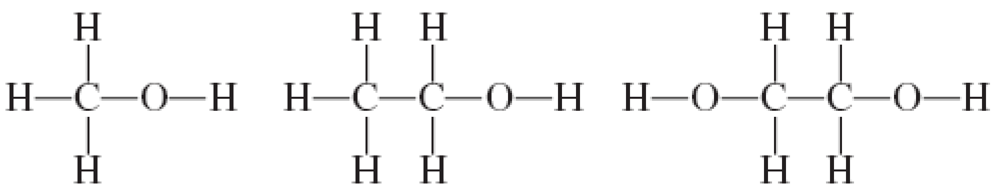
The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.

The stronger the intermolecular attractions between solute and solvent, the more likely the solute will dissolve.

## Examples,,,

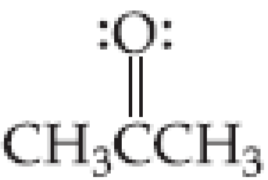
Carbon tetrachloride ($\mathbf{CCl_4}$) and benzene ($\mathbf{C_6H_6}$) are readily dissolve in each other. Both $\mathbf{CCl_4}$ and $\mathbf{C_6H_6}$ are nonpolar liquids. The only intermolecular forces present in these substances are dispersion forces.
Nonpolar hydrocarbons such as hexane ($\mathbf{C_6H_{14}}$) and octane ($\mathbf{C_8H_{18}}$) dissolve in another nonpolar one like $\mathbf{CCl_4}$.

Alcohols such as methanol, ethanol, and 1,2-ethylene glycol are miscible with water because they can form hydrogen bonds with water molecules:



methanol ethanol 1,2-ethylene glycol

Acetone has a strongly polar **C=O** bond and pairs of nonbonding electrons on the **O** atom that can form hydrogen bonds with water.

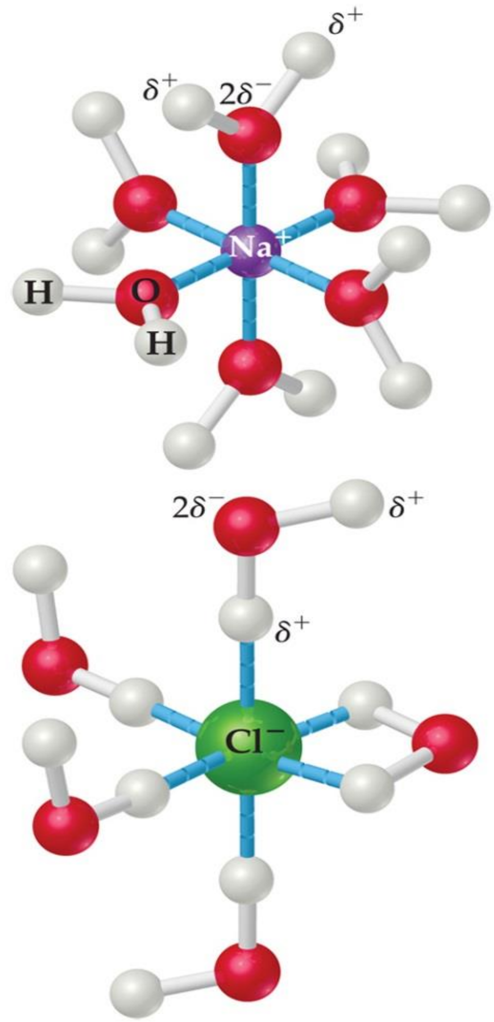


Sodium chloride (**NaCl**) dissolves in water, the ions are stabilized in solution by hydration, which involves ion-dipole interaction. In general, ionic compounds should be much more soluble in polar solvents, such as water, liquid ammonia, and liquid hydrogen fluoride, than in nonpolar solvents, such as benzene and $\mathbf{CCl_4}$.

Two liquids are said to be **miscible** if they are completely soluble in each other in all proportions.

When **NaCl** is added to $\mathbf{H_2O}$, $\mathbf{H_2O}$ molecules orient themselves on the surface of the **NaCl** crystals.

The +ve end of $\mathbf{H_2O}$ dipole is oriented toward the $\mathbf{Cl^-}$ ions, and the –ve end of the $\mathbf{H_2O}$ dipole is oriented toward the $Na^+$ ions. The attractions are strong enough to pull the ions from their positions in the crystal. Once separated from the crystal, the $\mathbf{Na^+}$ and $\mathbf{Cl^-}$ ion are surrounded by $\mathbf{H_2O}$ molecules.




**Solvation** is the process in which an ion or a molecule is surrounded by solvent molecules arranged in a specific manner. The process is called **hydration** when the solvent is water.

## EXAMPLE

Predict the relative solubilities in the following cases:
(a) Bromine (**$Br_2$**) in benzene **$C_6H_6$** (*$\mu$ = 0 D*) and in water (*$\mu$ = 1.87 D*),
(b) **KCl** in **$CCl_4$** (*$\mu$ = 0 D*) and in liquid ammonia, **$NH_3$** (*$\mu$ = 1.46 D*),
(c) formaldehyde (**$CH_2O$**) in carbon disulfide (**$CS_2$**, *$\mu$ = 0 D*) and in water.

(a) **$Br_2$** is a nonpolar molecule and therefore should be more soluble in **$C_6H_6$**, which is also nonpolar, than in water.

(b) **KCl** is an ionic compound. For it to dissolve, the individual **$K^+$** and **$Cl^-$** ions must be stabilized by ion-dipole interaction. Because **$CCl_4$** has no dipole moment, **KCl** should be more soluble in liquid **$NH_3$**, a polar molecule with a large dipole moment.

(c) Because **$CH_2O$** is a polar molecule and **$CS_2$** (a linear molecule) is nonpolar, the forces between molecules of **$CH_2O$** and **$CS_2$** are dipole-induced dipole and dispersion. On the other hand, **$CH_2O$** can form hydrogen bonds with water, so it should be more soluble in that solvent.

## Example

Predict whether each of the following substances is more likely to dissolve in the nonpolar solvent carbon tetrachloride ($CCl_4$) or in water:
(a) $C_7H_{16}$, (b) $Na_2SO_4$, (c) HCl, and (d) $I_2$.

## Solution

- $C_7H_{16}$: hydrocarbon, so it is molecular and nonpolar.
- $Na_2SO_4$: compound containing a metal and nonmetals, is ionic.
- HCl: containing two nonmetals that differ in electronegativity, is polar.
- $I_2$: diatomic molecule with atoms of equal electronegativity, is nonpolar.

Therefore,
$C_7H_{16}$ and $I_2$ (the nonpolar solutes) would be more soluble in the nonpolar $CCl_4$ than in polar $H_2O$
Whereas water would be the better solvent for $Na_2SO_4$ and HCl (the ionic and polar covalent solutes).

# 12.3
# Concentration units

**Quantitative** study of a solution requires knowing its concentration.

**Concentration** is the amount of solute present in a given amount of solvent or solution.

Chemists use several different concentration units, each of which has advantages as well as limitations.

The most four common units of concentration:

- **percent by mass**,
- **mole fraction**,
- **molarity**,
- **molality**.

## Percent by Mass

The **percent by mass** (also called percent by weight or weight percent) is the ratio of the mass of a solute to the mass of the solution, multiplied by 100 percent:

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\%$$

The percent by mass is a unitless.

## EXAMPLE

A sample of 0.892 g of potassium chloride (KCl) is dissolved in 54.6 g of water. What is the percent by mass of KCl in the solution?

$$\begin{aligned}\text{percent by mass of KCl} &= \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\% \\ &= \frac{0.892\text{ g}}{0.892\text{ g} + 54.6\text{ g}} \times 100\% \\ &= \boxed{1.61\%}\end{aligned}$$

## Practice Exercise

A sample of 6.44 g of naphthalene ($C_{10}H_8$) is dissolved in 80.1 g of benzene ($C_6H_6$). Calculate the percent by mass of naphthalene in this solution.

## Mole Fraction (*X*)

The mole fraction of a component of a solution, say, component A, is written $X_A$ and is defined as

$$\text{mole fraction of component A} = X_A = \frac{\text{moles of A}}{\text{sum of moles of all components}}$$

The mole fraction is unitless.

## Molarity (*M*)

Molarity is the number of moles of solute in 1 L of solution.

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}}$$

the units of molarity are mol/L.

## Molality (*m*)

**Molality** is the number of moles of solute dissolved in 1 kg (1000 g) of solvent.

$$\text{molality} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

Molarity is generally easier to measure the volume of a solution, using precisely calibrated volumetric flasks, than to weigh the solvent. On the other hand, molality is independent of temperature; the volume of a solution typically increases with increasing temperature, so that a solution that is 1.0 *M* at 25°C may become 0.97 *M* at 45°C because of the increase in volume on warming.

## EXAMPLE

Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water. The molar mass of sulfuric acid is 98.09 g.

$$\text{moles of } H_2SO_4 = 24.4\ \cancel{\text{g } H_2SO_4} \times \frac{1 \text{ mol } H_2SO_4}{98.09\ \cancel{\text{g } H_2SO_4}}$$
$$= 0.249 \text{ mol } H_2SO_4$$

$$m = \frac{0.249 \text{ mol } H_2SO_4}{0.198 \text{ kg } H_2O}$$
$$= \boxed{1.26\ m}$$

## Practice Exercise

What is the molality of a solution containing 7.78 g of urea [$(NH_2)_2CO$] in 203 g of water?

## EXAMPLE

The density of a 2.45 *M* aqueous solution of methanol ($CH_3OH$) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

The total mass of 1 L of a 2.45 *M* solution of methanol is

$$1\ \cancel{\text{L soln}} \times \frac{1000\ \cancel{\text{mL soln}}}{1\ \cancel{\text{L soln}}} \times \frac{0.976\ \text{g}}{1\ \cancel{\text{mL soln}}} = 976\ \text{g}$$

Because this solution contains 2.45 moles of methanol, the amount of water (solvent) in the solution is

$$\begin{aligned}\text{mass of } H_2O &= \text{mass of soln} - \text{mass of solute}\\ &= 976\ \text{g} - \left(2.45\ \cancel{\text{mol } CH_3OH} \times \frac{32.04\ \text{g } CH_3OH}{1\ \cancel{\text{mol } CH_3OH}}\right)\end{aligned} = 898\ \text{g}$$

$$\begin{aligned}\text{molality} &= \frac{2.45\ \text{mol } CH_3OH}{0.898\ \text{kg } H_2O}\\ &= \boxed{2.73\ m}\end{aligned}$$

## Practice Exercise

Calculate the molality of a 5.86 *M* ethanol ($C_2H_5OH$) solution whose density is 0.927 g/mL.

## EXAMPLE

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid ($H_3PO_4$). The molar mass of phosphoric acid is 97.99 g.

Suppose that you start with a 100.0 g of the solution, then the mass of phosphoric acid is 35.4 percent, or 35.4 g, and mass of water must be 100.0% – 35.4% = 64.6% or 64.6 g.

$$\text{moles of } H_3PO_4 = 35.4\ \cancel{\text{g } H_3PO_4} \times \frac{1 \text{ mol } H_3PO_4}{97.99\ \cancel{\text{g } H_3PO_4}}$$
$$= 0.361 \text{ mol } H_3PO_4$$

The mass of water is 64.6 g, or 0.0646 kg.

$$\text{molality} = \frac{0.361 \text{ mol } H_3PO_4}{0.0646 \text{ kg } H_2O}$$
$$= \boxed{5.59\ m}$$

## Practice Exercise

Calculate the molality of a 44.6 percent (by mass) aqueous solution of sodium chloride.

## Example

A solution is made by dissolving 4.35 g glucose ($C_6H_{12}O_6$) in 25.0 mL of water at 25 $^oC$. Calculate the molality of glucose in the solution. Water has a density of 1.00 g/mL.

## Solution

Use the molar mass of glucose, 180.2 g/mL, to convert grams to moles:

$$\text{Mol } C_6H_{12}O_6 = (4.35 \text{ g } C_6H_{12}O_6)\left(\frac{1 \text{ mol } C_6H_{12}O_6}{180.2 \text{ g } C_6H_{12}O_6}\right) = 0.0241 \text{ mol } C_6H_{12}O_6$$

Because water has a density of 1.00 g/mL, the mass of the solvent is

$$(25.0 \text{ mL})(1.00 \text{ g/mL}) = 25.0 \text{ g} = 0.0250 \text{ kg}$$

Finally, the molality:

$$\text{Molality of } C_6H_{12}O_6 = \frac{0.0241 \text{ mol } C_6H_{12}O_6}{0.0250 \text{ kg } H_2O} = 0.964\ m$$

## Practice Exercise

What is the molality of a solution made by dissolving 36.5 g of naphthalene ($C_{10}H_8$) in 425 g of toluene ($C_7H_8$)?

***Answer:*** 0.670 *m*

## Example

An aqueous solution of hydrochloric acid contains 36% HCl by mass. **(a)** Calculate the mole fraction of HCl in the solution. **(b)** Calculate the molality of HCl in the solution.

## Solution

**(a)** To calculate the mole fraction of HCl, we convert the masses of HCl and $H_2O$ to moles:

$$\text{Moles HCl} = (36 \text{ g HCl})\left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}}\right) = 0.99 \text{ mol HCl}$$

$$\text{Moles } H_2O = (64 \text{ g } H_2O)\left(\frac{1 \text{ mol } H_2O}{18 \text{ g } H_2O}\right) = 3.6 \text{ mol } H_2O$$

$$X_{HCl} = \frac{\text{moles HCl}}{\text{moles } H_2O + \text{moles HCl}} = \frac{0.99}{3.6 + 0.99} = \frac{0.99}{4.6} = 0.22$$

**(b)** To calculate the molality of HCl in the solution, We use the calculated number of moles of HCl in part (a), and the mass of solvent is 64 g = 0.064 kg:

$$\text{Molality of HCl} = \frac{0.99 \text{ mol HCl}}{0.064 \text{ kg } H_2O} = 15\ m$$

## Practice Exercise

A commercial bleach solution contains 3.62 mass % NaOCl in water. Calculate **(a)** the mole fraction and **(b)** the molality of NaOCl in the solution.

***Answer:*** **(a)** $9.00 \times 10^{-3}$, **(b)** 0.505 *m*.

## Example

A solution with a density of 0.876 g/mL contains 5.0 g of toluene ($C_7H_8$) and 225 g of benzene. Calculate the molarity of the solution.

## Solution

The volume of the solution is obtained from the mass of the solution (mass of solute + mass of solvent = 5.0 g + 225 g = 230 g) and its density.

$$\text{Moles } C_7H_8 = (5.0 \text{ g } C_7H_8)\left(\frac{1 \text{ mol } C_7H_8}{92 \text{ g } C_7H_8}\right) = 0.054 \text{ mol}$$

The density of the solution is used to convert the mass of the solution to its volume:

$$\text{Milliliters soln} = (230 \text{ g})\left(\frac{1 \text{ mL}}{0.876 \text{ g}}\right) = 263 \text{ mL}$$

Molarity is moles of solute per liter of solution:

$$\text{Molarity} = \left(\frac{\text{moles } C_7H_8}{\text{liter soln}}\right) = \left(\frac{0.054 \text{ mol } C_7H_8}{263 \text{ mL soln}}\right)\left(\frac{1000 \text{ mL soln}}{1 \text{ L soln}}\right) = 0.21\ M$$

**Comment:** Because the mass of the solvent (0.225 kg) and the volume of the solution (0.263 L) are similar in magnitude, the molarity and molality are also similar in magnitude:

$$(0.054 \text{ mol } C_7H_8)/(0.225 \text{ kg solvent}) = 0.24\ m$$

## Practice Exercise

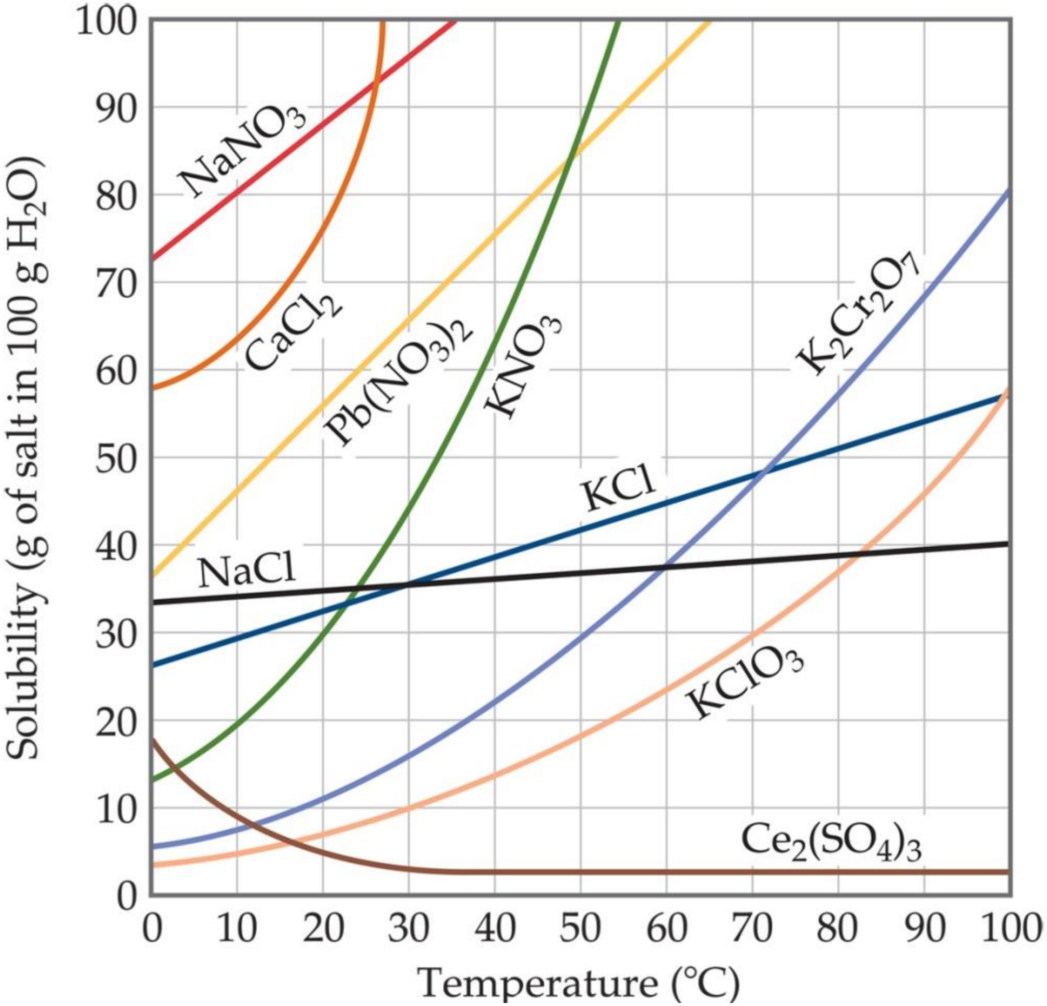
A solution containing equal masses of glycerol ($C_3H_8O_3$) and water has a density of 1.10 g/mL. Calculate **(a)** the molality of glycerol, **(b)** the mole fraction of glycerol, **(c)** the molarity of glycerol in the solution.

***Answer:*** **(a)** 10.9 $m$, **(b)** $X_{C3H8O3} = 0.163$, **(c)** 5.97 $M$

# 12.4
# The effect of temperature on solubility

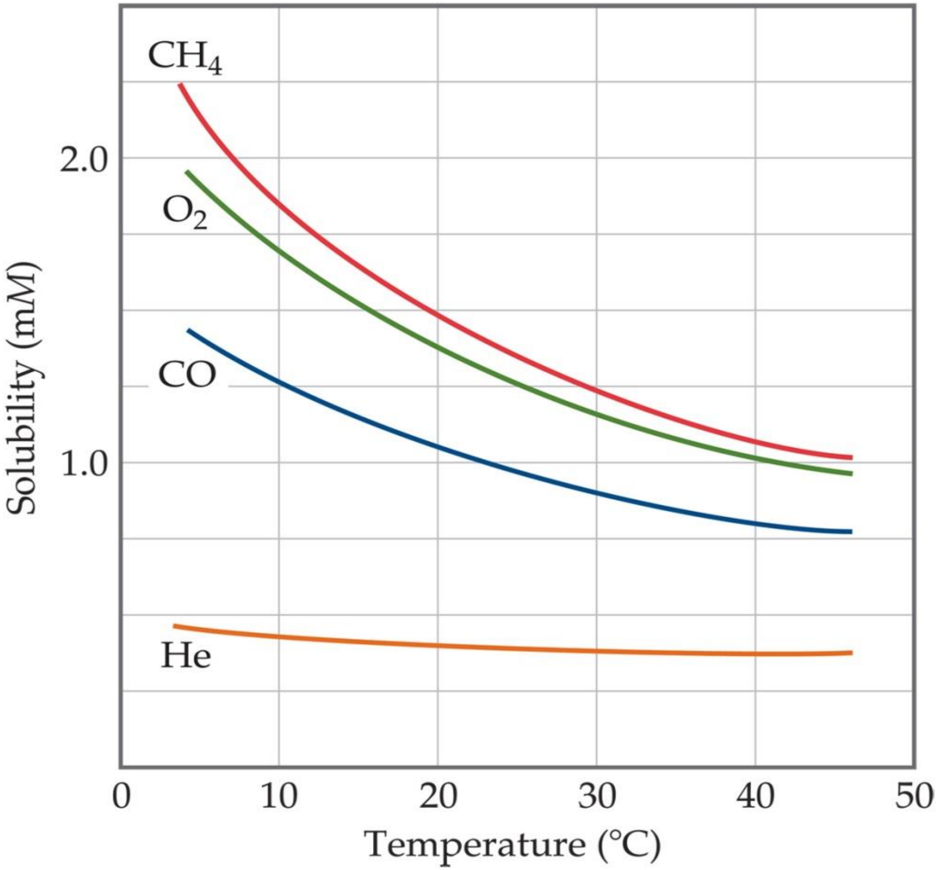
# Solid Solubility and Temperature

In most but certainly not all cases, the solubility of a solid substance increases with temperature.



# Gas Solubility and Temperature

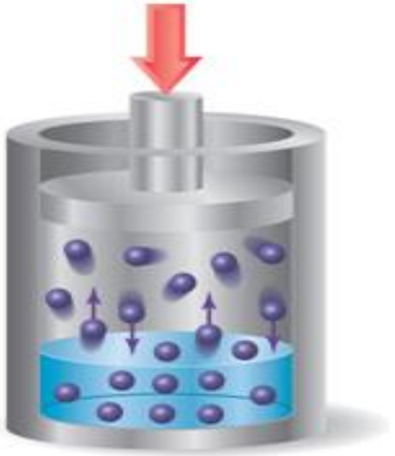
The solubility of gases in water usually decreases with increasing temperature



# 12.5
# The effect of pressure on the solubility of gases

# Henry's Law

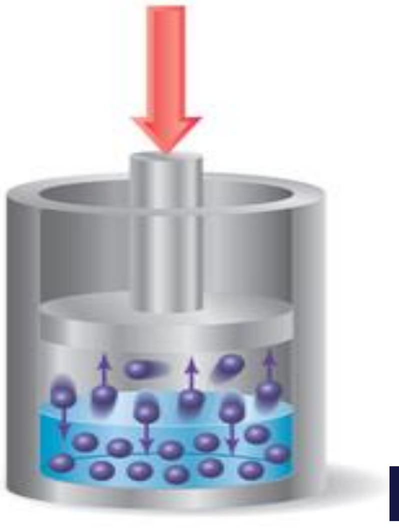
For all practical purposes, external pressure has no influence on the solubilities of liquids and solids, but it does greatly affect the solubility of gases.



The quantitative relationship between gas solubility and pressure is given by ***Henry's law,*** which states that *the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:*

$$c \propto P$$

$$\boldsymbol{c = kP}$$



***c:*** is the molar concentration (mol/L) of the dissolved gas;
***P:*** is the pressure (in atm) of the gas over the solution at equilibrium; and,
***k:*** is a constant (for a given gas) that depends only on temperature. The constant *k* has the units mol/L·atm.

## EXAMPLE

The solubility of nitrogen gas at 25°C and 1 atm is $6.8 \times 10^{-4}$ mol/L. What is the concentration (in molarity) of nitrogen dissolved in water under atmospheric conditions? The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

The first step is to calculate the quantity *k*

$$\begin{aligned} c &= kP \\ 6.8 \times 10^{-4}\ \text{mol/L} &= k\ (1\ \text{atm}) \\ k &= 6.8 \times 10^{-4}\ \text{mol/L} \cdot \text{atm} \end{aligned}$$

Therefore, the solubility of nitrogen gas in water is

$$\begin{aligned} c &= (6.8 \times 10^{-4}\ \text{mol/L} \cdot \text{atm})(0.78\ \text{atm}) \\ &= 5.3 \times 10^{-4}\ \text{mol/L} \\ &= \boxed{5.3 \times 10^{-4}\ M} \end{aligned}$$

## Practice Exercise

Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 atm. The Henry's law constant for oxygen is $1.3 \times 10^{-3}$ mol/L·atm.


Thank You!