SOLUTIONS: SOLUTE - SOLVENT SYSTEM

SCH4U_08 – 09

Solubility

The term *solubility* is commonly used in two senses – qualitatively and quantitatively.

Qualitatively, solubility is often used in a relative way when substances are classed as being ***soluble*, *low solubility* or *insoluble*.**

As for extremely low solubilities, the solute may be termed as having negligible solubility or as being insoluble.

The Table below lists solubilities generally associated with the qualitative terms.

Solubility	Qualitative	Examples
greater than 0.1 mol/L	*soluble*	$Na_2CO_{3\ (aq)}$
less than 0.1 mol/L	*low solubility*	$CaSO_{4\ (aq)}$
extremely low	*insoluble*	$CCl_{4(l)}$ - $H_2O_{(l)}$

The qualitative use of solubility is often too imprecise for many purposes.

The **quantitative** definition of solubility has a definite meaning.
In the quantitative sense, **solubility refers to the quantity of solute required to produce a saturated solution at a given temperature.**

Solubility is the concentration of solute in a saturated solution at a given temperature.

The **molar solubility** would be the number of moles of solute required to form one litre of a saturated solution at a specified temperature; i.e., <u>the maximum molar concentration of a solute.</u>

molar solubility = C (saturated solution) = n / v M = mol/L

Example: A saturated solution produced by dissolving hydrogen chloride gas in water is called concentrated hydrochloric acid. If 45.2 g of hydrogen chloride gas is required to prepare 100 mL of concentrated hydrochloric acid at 25 ^{O}C , what is the molar solubility of hydrogen chloride at 25 ^{O}C?

Calculation:

$$n\ (HCl) = m/M = 45.2\ g / 36.46\ g/mol = 1.24\ mol$$

$$C = n/v = 1.24\ mol / 0.100\ L = 12.4\ mol/L$$

The molar solubility of hydrogen chloride at 25^{O}C is 12.4 mol/L

FACTORS THAT AFFECT SOLUBILITY

The prediction of solubilities involves many variable such as relative size and relative charge of solute and solvent particles, interaction between solute and solvent particles, temperature, and pressure.

In spite of the complexity of factors that affect solubility, some general rules apply to many of the compounds first encountered in the study of chemistry.
These general rules are not laws and are therefore subject to exceptions.

A discussion of the four factors affecting solubility and some relevant general rules follows.

1. The Nature of Solute and Solvent

The rule like dissolves like where like refers to similarities in polarities of substances, has useful application for predicting solubilities. (Polarity is discussed in the Chemical Bonding Unit)

In general, **polar and ionic solutes** tend to be more soluble in **polar solvents** and **non polar solutes** tend to be more soluble in **non polar solvents**.
Thus, inorganic acids (which are polar) and bases and salts (which are ionic) tend to be much more soluble in water (which is highly polar).

Solvents such as carbon tetrachloride, hexane and benzene, which are non polar , are not soluble in polar water.

Sodium chloride, an ionic substance, is highly soluble in polar water, slightly soluble in weakly polar ethyl alcohol and insoluble in non polar carbon tetrachloride.

Gasoline, a non polar substance, is only slightly soluble in polar water but highly soluble in non polar carbon tetrachloride.

General Rules:
Polar and ionic solutes are soluble in polar solvents
Non polar solutes are soluble in non polar solvents

2. The Effect of Temperature

Since most solutes have a limited solubility in a given amount of solvent at a fixed temperature (i.e. are not miscible), the temperature of the solvent generally has a marked effect on the amount of solute that will dissolve.

For most **solids dissolved in liquids**, the dissolving process is **endothermic** and an increase in temperature results in an increase in solubility.

The effect of increased solubility of solids in liquids upon heating is illustrated in everyday experiences. For example, the solubility of soap and dirt in hot wash water is greater than in cold wash water.

For **most gases**, the dissolving **process is exothermic** and a decrease in temperature results in an

increase in solubility.
For example, when water in a kettle is heated but not boiled, dissolved air escapes as it becomes less soluble at higher temperatures.

For the dissolving of liquids in liquids, the effect of temperature is too variable and no useful generalization can be made.

In every case a new solubility under new temperature conditions is gradually established.

General Rules:

1. An increase in temperature generally increases the solubility of solids in liquids.
2. An increase in temperature generally decreases the solubility of gases in liquids.

3. The Effect of Pressure

Changes in pressure have very little effect on the solubility of solids and liquids.

However, changes in pressure have a marked effect on the solubility of gases.

The solubility of a gas in a liquid is directly proportioned to the pressure of that gas above the liquid.

For example, when a bottle of carbonated soft-drink is opened, the pressure is reduced and dissolved carbon dioxide bubbles out of the solution.

A new solubility under the new pressure conditions is gradually established.

General Rules:

1. Changes in pressure have no appreciable effect upon the solubility of solids and liquids.
2. The solubility of gases in liquids is directly proportional to the pressure of gas (partial pressure) above the surface of the liquid. ((<u>HENRY'S LAW</u>))

FACTORS WHICH AFFECT SOLUBILITY

(A) The Nature of solute and solvent

Some solutes are insoluble in certain solvents. Generally, "<u>Like dissolves Like</u>". This means that a POLAR SOLVENT such as WATER or acid will dissolve an IONIC SOLUTE such as <u>salt</u>.

<u>Gasoline, benzene or carbon tetrachloride</u> (dry cleaning solvent) are <u>NON-POLAR SOLVENTS</u> and they will best dissolve non-polar solutes such as fats, oils, paints.

Water does not dissolve fats and oils very well. (Use of a <u>soap</u> or detergent helps, because the soap molecule has a polar end which dissolves in the water and a non-polar end which dissolves in the fat. An <u>emulsion</u> is formed. In our digestive tract, BILE acts as an emulsifier of fats.)

<u>POLAR SOLVENTS</u> have molecules that are dipoles and have positive and negative 'ends'. Water is the best example: $^{\delta+}H — ^{\delta-}O — H^{\delta+}$

Polar solvents are best for dissolving ELECTROLYTES (Acids, Bases and Salts).

<u>NON-POLAR SOLVENTS</u> such as acetone, ether, benzene, turpentine or CCl_4 (dry-cleaning) have

non-polar molecules and will best dissolve solutes that also have non-polar molecules like waxes, fats, oils, grease, paint pigments, etc.

(B) Temperature

Generally, (there are few exceptions), an increase in temperature increases the solubility of a substance, since both solvent and solute molecules have more kinetic energy.

(NOTE: The opposite is true in the case of gases in liquids. ****An increase in temperature decreases the solubility of a gas in a liquid. e.g. If you heat 7-UP, the CO_2 gas escapes. Cold soda water has more dissolved CO_2 solute.)

(C) Pressure

Pressure has no effect on the solubility of solids or liquids in liquids.

It has, however a major effect on the solubility of a gas in a liquid. The higher the pressure above the solution the more gas can be dissolved. HENRY'S LAW.

Carbonated drinks are bottled under pressure. A human body under high gas pressure such as a diver will have an increase in dissolved air in its blood. Escaping bubbles of nitrogen gas cause the BENDS as pressure drops too fast. [To resolve this: -- slow decompression.]

(D) Size of Solute Particles

This applies only in the case of SOLIDS. e.g. icing sugar will dissolve rapidly while lump sugar will take longer.
NOTE: Only the RATE of dissolving is affected.

SOLUBILITY IS NOT AFFECTED. i.e. You can dissolve ground-up solids faster, but you can not dissolve MORE. (Solubility is max. mol/L.)

(E) Agitation (Stirring)

Stirring will increase the RATE (speed) of dissolving of solids or liquids in a liquid.
Example: Stirring coffee speeds up the dissolving of the sugar and milk. It does not NOT change solubility.
No matter how much you agitate a solution you cannot dissolve more solid or liquid solute above solubility.

However, agitation of a solution of gas in liquid (Pepsi) does reduce solubility as the gas molecules escape.

TYPES OF SOLUTIONS CLASSIFIED BY CONCENTRATION

1. CONCENTRATED SOLUTION means that quite an amount of solute has been dissolved. Generally, any greater than 3.0 mol/L are considered to be concentrated, but this is an arbitrary number.

2. DILUTE SOLUTION means that not much solute is dissolved. Generally, less than 0.3 mol/L is dilute, but again an arbitrary figure.
(A dilute solution of potassium cyanide would be very concentrated for a human body – deadly poison.)

3. SATURATED SOLUTION (Temperature related)
A saturated solution is at the limit of solubility for that particular solute at that particular temperature. e.g. Since the solubility of NaCl at 25 °C is 6.0 mol/L, a saturated solution of salt will have dissolved 6.0 moles of NaCl.
<u>You can dissolve no more salt</u> unless you increase temperature and change solubility.

4. UNSATURATED SOLUTION (“Room for More”)
An unsaturated solution has a <u>concentration below solubility</u>. More solute can still be dissolved at that temperature. In a saturated solution excess solute will remain as sold at the bottom of the beaker.

SOLUTIONS, SATURATED SOLUTIONS AND CHEMICAL EQUILIBRIUM

In most chemical reaction considered up to now, if there was apparent evidence for a reaction, a complete reaction was assumed. That chemical reactions proceed completely from reactants to products was sufficient to satisfy a limited perspective of reactions.

To this point, Collision Theory, as an explanation for reactions, was restricted to the consideration of collisions among reactant particles only. An extension of the theory to other particle collisions suggests other possibilities.

Chemists believe that particles, in their random motion, undergo more than just reactant-reactant particle collisions.
Unless products are removed immediately upon their formation, product-product particle collisions are inevitable.
Hence, products can reform reactants. Essentially all chemical reactions are potentially reversible: i.e., once product particles are formed, these particles in turn can reform reactant particles.

If product-product particle collisions do not result in significant particle rearrangements, then the extent of products reforming reactants is small, or even negligible.

In this case the reaction can be considered complete, or irreversible.

However, if product-product particle collisions result in significant rearrangements of particles, then reactions in the forward and reverse directions occur simultaneously, and the reaction is *reversible*.

The reversibility of chemical reactions and other processes, including many processes in nature, gives rise to the phenomenon of *dynamic equilibrium*.

Some of the characteristics of a dynamic equilibrium can be observed in a solute-solvent system, in particular, a saturated solution.

Saturated Solutions

Some substances dissolve in each other in all proportions.
Examples are water and antifreeze, or gasoline and kerosene.
Such substances are said to be *miscible*.

Most other substances are *partially soluble*, that is, one dissolves in the other to a concentration that reaches a definite limiting value at which point the solution is said to be *saturated*.

For example, when a solute is stirred in water at 20°C, the solute dissolves rapidly at first, then more and more slowly.
Eventually, dissolving appears to stop and the concentration of solute dissolved in the water no longer increases but remains constant.

No matter how long or how vigorously the mixture of solute and water is stirred (provided the temperature is kept constant) the concentration remains constant.

This solution is now *saturated* with solute.
Chemists believe that the dissolving action does not cease when the saturating point is reached.
There is evidence to suggest that molecules of the solute continue to leave the solid and pass into the solution, while other molecules of solute, previously dissolved, return to the solid state from the solution.

To explain the constant macroscopic properties the rate of these two opposing processes must be exactly equal at saturation.

The number of particles of solute leaving the solid and entering the solution in unit time is equal to the number of solute particles leaving the solution and crystallizing out on the solid in the same unit of time.

The solution process at saturation is an example of a *dynamic equilibrium*.

A *saturated solution* may be defined as a solution in which the dissolved solute is in equilibrium with excess undissolved solute at a specific temperature.

$$\textbf{undissolved solute} \quad \underset{\textbf{crystallizing}}{\overset{\textbf{dissolving}}{\rightleftharpoons}} \quad \textbf{dissolved solute}$$

$I_{2(s)}$ - $I_{2(aq)}$ System – A Further Analysis

Suppose solid iodine is dissolved in an alcohol-water mixture and the addition and dissolving of solid iodine is continued until excess, undissolved solute is present.

At this point the solution is saturated.

It can be empirically verified by successive filtrations and mass determinations, that the quantity of undissolved iodine remains unchanged over time.

Since the volume of alcohol-water remains constant, this is a *closed system.*

At saturation no apparent changes are occurring, the colour intensity, the volume of solution and quantity of dissolved and undissolved iodine all remain constant.

However, at the molecular level, processes are believed to be continuing.
Molecules are leaving the surface of the undissolved iodine and are tending to increase the concentration of iodine in solution.

At the same time, dissolved iodine molecules are striking and crystallizing upon the undissolved iodine causing the concentration of iodine molecules in solution to decrease.

Even though some molecules are dissolving and others are crystallizing (reversible processes), no net change is apparent because the two processes are taking place at the same rate.

In other words, the $I_{2(s)}$ - $I_{2(aq)}$ system is at a state of equilibrium in which

Rate of dissolving = Rate of crystallization

$$I_{2\,(s)} \rightleftharpoons I_{2\,(aq)}$$

(The double arrows indicate a state of equilibrium.)

The dynamic nature of the $I_{2(s)}$ - $I_{2(aq)}$ equilibrium can be confirmed through experiments involving radioactive iodine isotopes.

Suppose a saturated solution of iodine is prepared and then filtered to remove all excess undissolved iodine.

Further, suppose that a predetermined mass of radioactive solid iodine is added to the saturated solution.

Subsequent filtration and testing for mass changes and for radioactivity with a Geiger counter will indicate two things.

1. The mass of undissolved iodine has remained unchanged.

2. Some radioactive iodine has gone into solution. (The solution is now radioactive.)

Both observations confirm that although the quantity of dissolved and undissolved iodine has remained constant, some dissolving and consequently some crystallization must have occurred.

In general, the $I_{2(s)}$ - $I_{2(aq)}$ system at equilibrium illustrates the typical characteristics of any system equilibrium, namely:

1. The apparent constancy in regard to quantities of reactants and products at equilibrium.

2. The dynamic nature in regard to two or more reversible processes taking place at the same rate

Chemical Equilibrium

Solubility is one example of chemical equilibrium.

The phenomenon of chemical equilibrium is encountered in many chemical systems and examples of equilibrium in nature are numerous.

All equilibria, regardless of origin, have the following main characteristics in common:

1. The equilibrium state requires a *closed system*; i.e., a system which does not gain or lose matter.

2. The equilibrium state is a dynamic state where two or more reversible (opposing) processes are taking place at the same time and at the same rate so that no net change is apparent.