

SOLUTIONS: SOLUTE - SOLVENT SYSTEM

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.

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.

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

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., the maximum molar concentration of a solute.

$$\text{molar solubility} = C (\text{saturated solution}) = n / v \quad M = \text{mol/L}$$

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 °C, what is the molar solubility of hydrogen chloride at 25 °C?

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

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

The molar solubility of hydrogen chloride at 25°C is 12.4 mol/L

SOLUTIONS

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. ((HENRY'S LAW))

FACTORS WHICH AFFECT SOLUBILITY

(A) The Nature of solute and solvent

Some solutes are insoluble in certain solvents. Generally, "Like dissolves Like". This means that a POLAR SOLVENT such as WATER or acid will dissolve an IONIC SOLUTE such as salt. Gasoline, benzene or carbon tetrachloride (dry cleaning solvent) are NON-POLAR SOLVENTS 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 soap 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 emulsion is formed. In our digestive tract, BILE acts as an emulsifier of fats.)

POLAR SOLVENTS have molecules that are dipoles and have positive and negative 'ends'. Water is the best example. Polar solvents are best for dissolving ELECTROLYTES (Acids, Bases and Salts).

NON-POLAR SOLVENTS 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 CO₂ gas escapes. Cold soda water has more dissolved CO₂ 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 press drops too fast. Solution -- 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. e.g. 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

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.

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.)

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. You can dissolve no more salt unless you increase temperature and change solubility.

UNSATURATED SOLUTION (“Room for More”)

An unsaturated solution has a concentration below solubility. More solute can still be dissolved at that temperature. In a saturated solution excess solute will remain as solid at the bottom of the beaker.