Solubility and solubility product

- **Solubility**

... is the **maximum amount** of solute that can be dissolved in a solvent at a given temperature at a given volume at equilibrium.

- **Equilibrium**

... when the concentrations of products and reactants have become **equal** after the reaction has taken place

- **Concentration**

... is the **amount** of solute that can be dissolved in a solvent at a given volume

- **Solubility product constant(Ksp)**

... is the product of the **equilibrium** concentrations of the ions in a **saturated** solution of a salt. Each concentration is raised to the power of their stoichiometric coefficients in the balanced equation.

$$PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\,Cl^{-}_{(aq)}$$

$$Ksp = [Pb^{2+}]\,[Cl^{-}]^{2}$$

Ksp is considered unitless because it is derived from the ratio of activities or concentrations that cancel out, reflecting the equilibrium state of the system without specific units.

⇨ **Shortcut method of Ksp expression (without ion common)**

$AB_{(s)} \rightarrow Ksp = x^1 * x^1 = x^2$ **(ratio 1:1)**
$AB_{2\,(s)} \rightarrow Ksp = x^1 * (2x)^2 = 4x^3$ **(ratio 1:2)**
$AB_{3\,(s)} \rightarrow Ksp = x^1 * (3x)^3 = 27x^4$ **(ratio 1:3)**
$A_3B_{2\,(s)} \rightarrow Ksp = (3x)^3 * (2x)^2 = 108x^5$ **(ratio 3:2)**

Calculating molar solubility from Ksp

Example 6

Calculate the molar solubility of CaF_2(s) in its saturated solution, given that ksp $_{CaF2}$ = $3.2*10^{-11}$

$$\mathrm{CaF_2} \leftrightarrow \mathrm{Ca^{2+}} + \mathrm{2F^-}$$

$$K_{sp} = [Ca^{2+}]\,[F^-]^2$$

$$3.2 * 10^{-11} = [x][2x]^2 = 4x^3$$

$$x = \sqrt[3]{\frac{3.2 * 10^{-11}}{4}} = 0.0002\,\frac{mol}{L}$$

Calculating Ksp from molar solubility

Example 7

The solubility of Ag_2S in water is 8x10 $^{-15}$g/L, calculate the solubility product (Ksp), given that the M.wt of Ag_2S is 248 gm/mole

$$\frac{\mathrm{g}}{\mathrm{L}} = \mathrm{M}\,\frac{\cancel{\mathrm{mol}}}{\mathrm{L}} * \mathrm{M.wt}\,\frac{\mathrm{g}}{\cancel{\mathrm{mol}}}$$

$$\mathrm{M} = \frac{\mathrm{g/L}}{\mathrm{M.wt}} = \frac{8 * 10^{-15}\,\cancel{\mathrm{g}}/\mathrm{L}}{248\,\cancel{\mathrm{g}}/\mathrm{mol}} = 3.226 * 10^{-17}\ \mathrm{mol/L}$$

$$\mathrm{Ag_2S} \leftrightarrow \mathrm{2Ag^+} + \mathrm{S^{2-}}$$

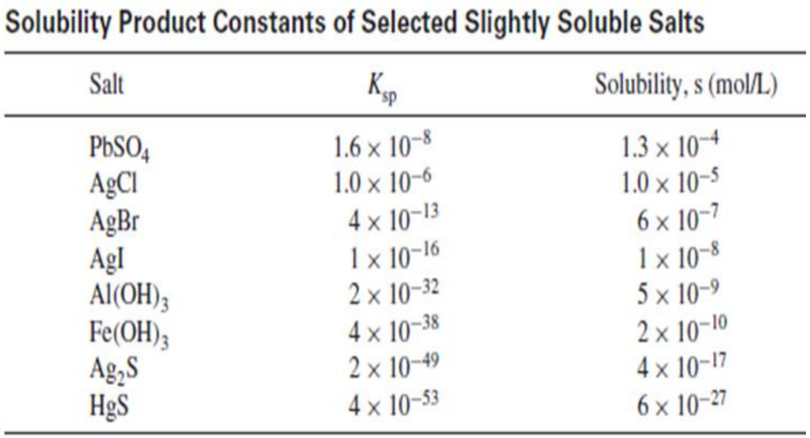
$$K_{sp} = [Ag^+]^2[S^{2-}]$$

$$K_{sp} = [2x]^2\,[x] = 4x^3$$

$$K_{sp} = 4(3.226 * 10^{-17})^3 = 1.34 * 10^{-49}$$

Solubility depends on the stoichiometry

The molar solubility is not necessarily directly proportional to the Ksp value since it depends on the stoichiometry of the salt.
The K_{sp} of AgI is 5 × 10^{15} larger than that of $Al(OH)_3$, but its molar solubility is only twice that of $Al(OH)_3$. That is, a 1:1 salt has a lower solubility than a non-symmetric salt for a given Ksp.



Solubility Product Constants of Selected Slightly Soluble Salts

Salt	K_{sp}	Solubility, s (mol/L)
$PbSO_4$	1.6×10^{-8}	1.3×10^{-4}
AgCl	1.0×10^{-6}	1.0×10^{-5}
AgBr	4×10^{-13}	6×10^{-7}
AgI	1×10^{-16}	1×10^{-8}
$Al(OH)_3$	2×10^{-32}	5×10^{-9}
$Fe(OH)_3$	4×10^{-38}	2×10^{-10}
Ag_2S	2×10^{-49}	4×10^{-17}
HgS	4×10^{-53}	6×10^{-27}

Example 8
Calculate the molar solubility of $PbSO_4$ and compare it with that of PbI_2.

$$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4{}^{2-}$$

$$[Pb^{2+}][SO_4{}^{2-}] = 1.6 \times 10^{-8}$$

$$(s)(s) = 1.6 \times 10^{-8}$$

$$s = 1.3 \times 10^{-4}\ M$$

Although the Ksp of PbI_2 (7.1 × 10^{-9}) is smaller than that of $PbSO_4$ (1.6 × 10^{-8}), the solubility of PbI^2 is greater, due to the non-symmetrical nature of the precipitate.

For electrolytes of the same valence type, the order of solubility will be the same as the order of the corresponding solubility products. But when we compare salts of different valence type, the order may be different. Compound AB will have a smaller molar solubility than compound AC_2 when both have identical Ksp values.
A smaller Ksp with a non-symmetrical precipitate does not necessarily mean a smaller solubility compared to a symmetrical one.

Predicting precipitation [*Ionic product (Q) Vs solubility product (Ksp)]*

The *ionic product (Q)* of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (*Q*) for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations. An ion product can in principle have *any* positive value, depending on the concentrations of the ions involved. Only in the special case when its value is identical with K_s does it become the solubility product. A solution in which this is the case is said to be *saturated* .

Thus when $[Ag^+]^2\ [CrO_2{}^{-4}]=2.76\times10^{-12}$

at the temperature and pressure at which this value *Ksp* of applies, we say that the "solution is saturated in silver chromate".

The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur. The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

$$BaSO_{4\,(s)} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

$$Ksp = [Ba^{2+}]_{eq}\,[SO_4{}^{2-}]_{eq}$$

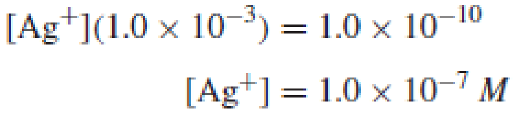
$$Q = [Ba^{2+}]_0\,[SO_4{}^{2-}]_0$$

- Ksp at equilibrium, Q at anytime

Q < Ksp	$\longrightarrow$	*Dissolution*	... the solution is *unsaturated* **(C < S)**
Q = Ksp	$\rightleftarrows$	*Equilibrium*	... the solution is *saturated* **(C = S)**
Q > Ksp	$\longleftarrow$	*Precipitation*	... the solution is *supersaturated* **(C > S)**

Example 9

What must be the concentration of added Ag^+ to just start precipitation of AgCl in a 1.0×10^{-3} M solution of NaCl?



$$[Ag^+](1.0 \times 10^{-3}) = 1.0 \times 10^{-10}$$

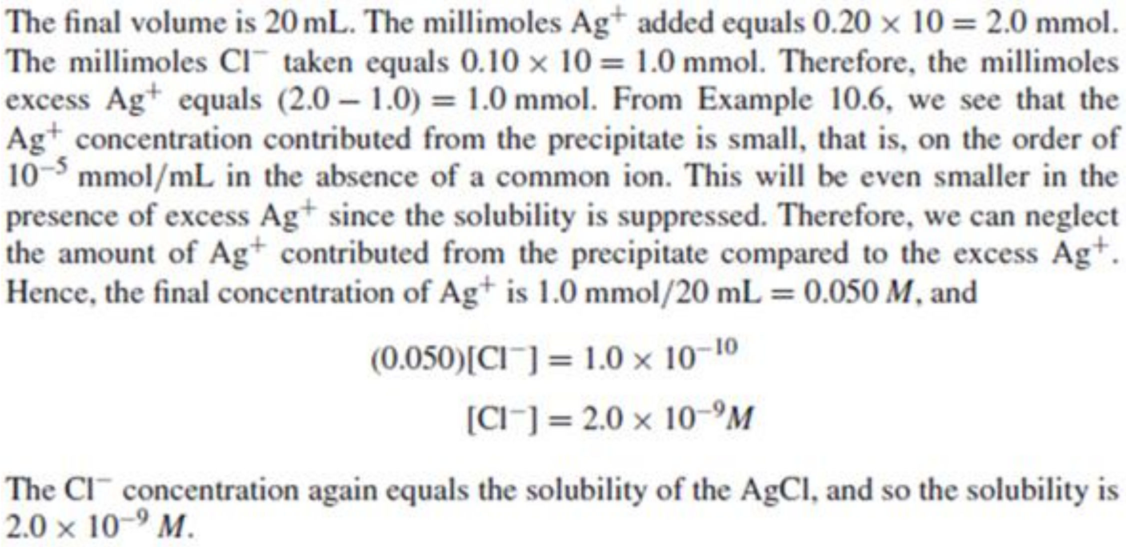
$$[Ag^+] = 1.0 \times 10^{-7}\ M$$

The concentration of Ag^+ must, therefore, just exceed 10^{-7} M to begin precipitation.

In reality supersaturation is needed before precipitation begins. In practice it is unlikely that precipitation will begin when Ag^+ just exceeds 10^{-7} M

Example 10

Ten milliliters of 0.20M $AgNO_3$ is added to 10 mL of 0.10M NaCl. Calculate the concentration of Cl^- remaining in solution at equilibrium, and the solubility of the AgCl.



The final volume is 20 mL. The millimoles Ag^+ added equals $0.20 \times 10 = 2.0$ mmol. The millimoles Cl^- taken equals $0.10 \times 10 = 1.0$ mmol. Therefore, the millimoles excess Ag^+ equals $(2.0 - 1.0) = 1.0$ mmol. From Example 10.6, we see that the Ag^+ concentration contributed from the precipitate is small, that is, on the order of 10^{-5} mmol/mL in the absence of a common ion. This will be even smaller in the presence of excess Ag^+ since the solubility is suppressed. Therefore, we can neglect the amount of Ag^+ contributed from the precipitate compared to the excess Ag^+. Hence, the final concentration of Ag^+ is 1.0 mmol/20 mL = 0.050 *M*, and

$$(0.050)[Cl^-] = 1.0 \times 10^{-10}$$

$$[Cl^-] = 2.0 \times 10^{-9} M$$

The Cl^- concentration again equals the solubility of the AgCl, and so the solubility is 2.0×10^{-9} *M*.

Because the Ksp product always holds, precipitation will not take place unless the product of $[Ag^+]$ and $[Cl^-]$ exceeds the ksp. If the product is just equal to Ksp, all the Ag^+ and Cl^- remains in solution.

- ➢ The solubility product must be exceeded for precipitation to occur.

Factors effecting solubility

1. Effect of temperature on solubility

Temperature has a significant impact on the solubility of substances in solvents, and its effects can vary depending on the nature of the solute and solvent involved. Here are the key effects of temperature on solubility:

1. **Increased Solubility of Solids**: For most solid solutes, solubility tends to increase with an increase in temperature. This is because higher temperatures provide more kinetic energy to the molecules, allowing them to overcome intermolecular forces and dissolve more readily. For example, sugar dissolves more easily in hot water than in cold water.

2. **Decreased Solubility of Gases**: In contrast to solids, the solubility of gases in liquids generally decreases with an increase in temperature. As temperature rises, gas molecules gain kinetic energy and are more likely to escape from the liquid phase into the gas phase. This is why carbonated beverages lose their fizz more quickly when warmed.

3. **Endothermic vs. Exothermic Dissolution**: The effect of temperature on solubility can also depend on whether the dissolution process is endothermic (absorbs heat) or exothermic (releases heat):
- **Endothermic Dissolution**: If the dissolution process absorbs heat, increasing the temperature will increase solubility. An example is ammonium nitrate, which dissolves endothermically.
- **Exothermic Dissolution**: If the dissolution process releases heat, increasing the temperature may decrease solubility. An example is calcium sulfate, which dissolves exothermically.

4. **Equilibrium Considerations**: According to Le Chatelier's principle, if a system at equilibrium is subjected to a change in temperature, the equilibrium will shift to counteract that change. For endothermic dissolutions, increasing temperature shifts the equilibrium to favor more solute dissolving, while for exothermic dissolutions, it shifts to favor the formation of solid.

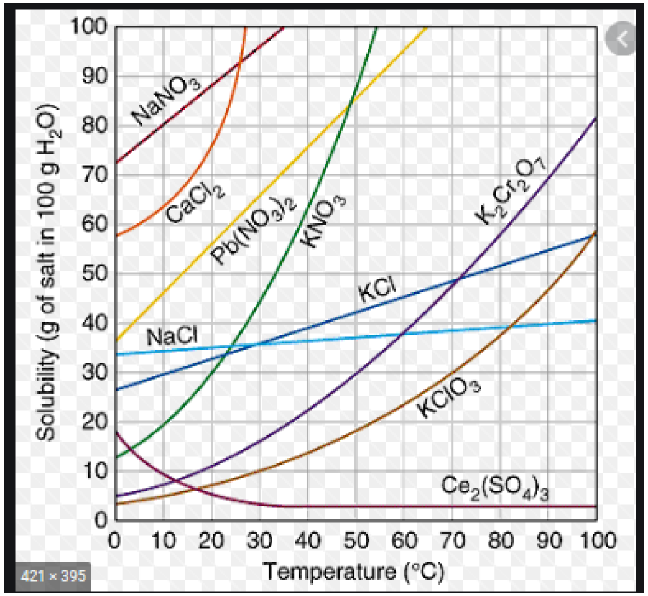
Example 11

Based on the diagram, answer the following questions:

⇨ Which substance is least soluble at 0°C? $KClO_3$

⇨Which substance is the most soluble at 0°C? $NaNO_3$

⇨What is the solubility of $K_2Cr_2O_7$ at 30°C? 15gm

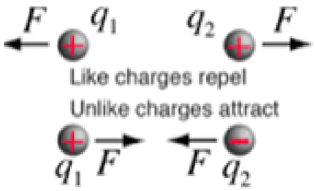


2. Effect of solute's nature on solubility

When ionic charge increases, the attraction between ions increases, and this leads to decrease the solubility.

Small ions are less soluble than large ions, as the bond between small ions is stronger that the bond between large ions with the same charge (see coulomb's law below).

The higher the charges on the ions, the stronger their electrostatic attraction for each other, and the harder it is for the solvent (i.e., water) to pull them apart. For example, if the calcium carbonate in marble were to dissolve too easily, think of how many buildings and statues would dissolve in the rain.

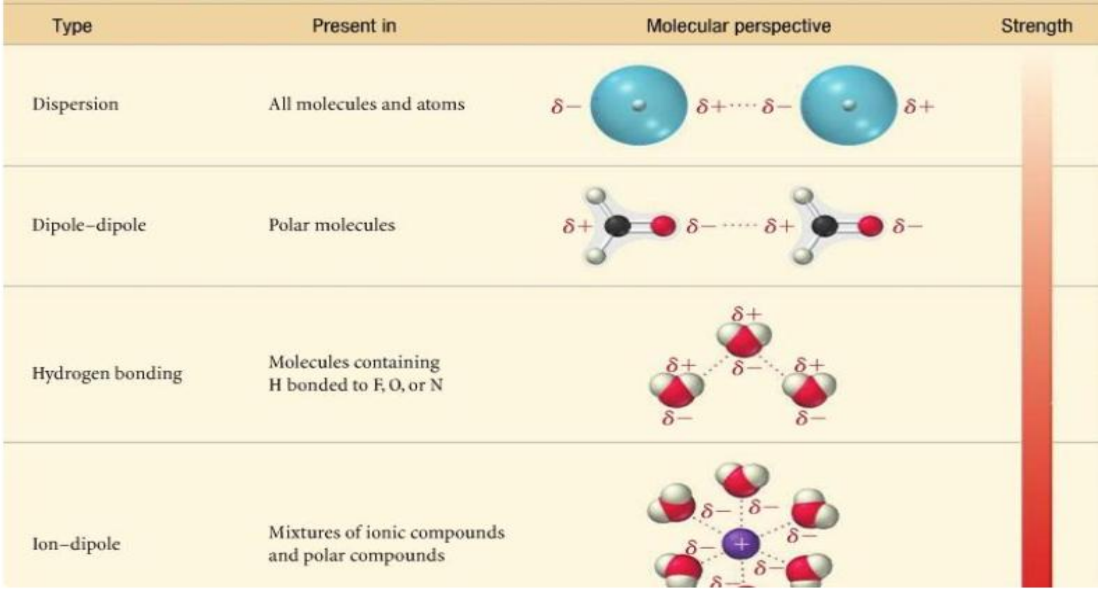


$$F = \frac{kq_1q_2}{r^2} = \frac{q_1q_2}{4\pi\varepsilon_0 r^2}$$

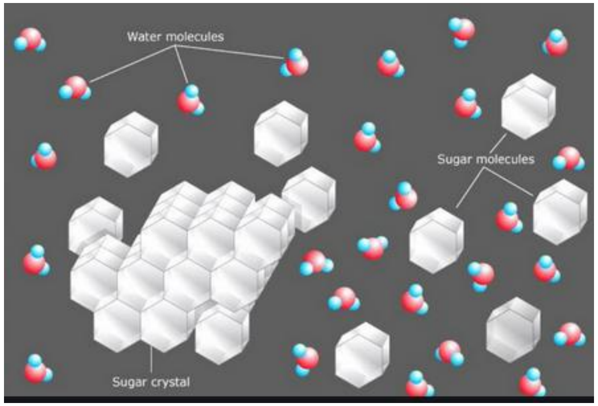
3. Effect of solvent’s nature on solubility

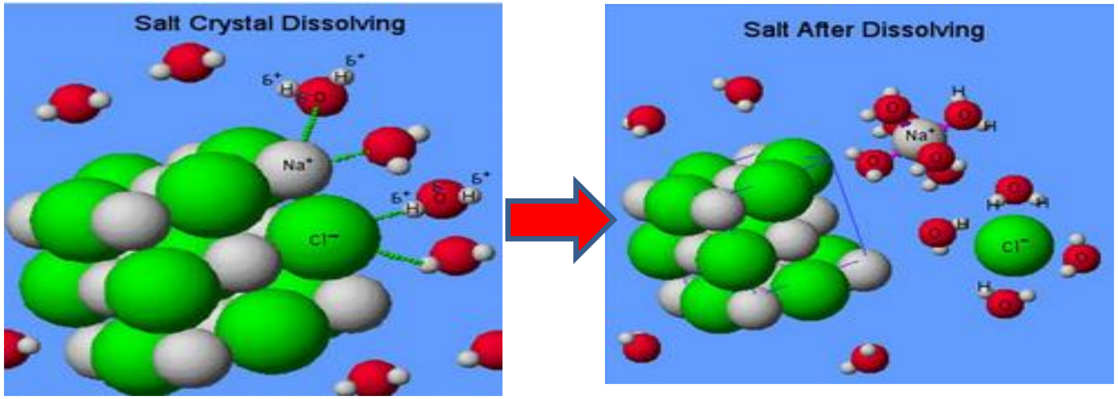
“Like dissolves like”

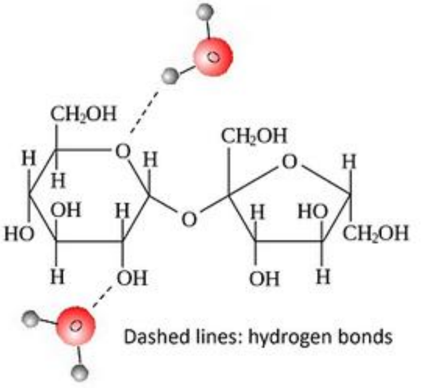
⇨Substances that exhibit similar types of intermolecular force dissolve in each other.
⇨Polar molecules and ionic compounds (like salt) will be more soluble in polar solvents (like water).
⇨Nonpolar molecules (like oil) will be more soluble in nonpolar solvents (like hexane).
If you introduce a solute into a solvent where it is not compatible, it may not dissolve effectively.



Type	Present in	Molecular perspective	Strength
Dispersion	All molecules and atoms	$\delta-$ $\delta+$ ···· $\delta-$ $\delta+$	
Dipole–dipole	Polar molecules	$\delta+$ $\delta-$ ····· $\delta+$ $\delta-$	
Hydrogen bonding	Molecules containing H bonded to F, O, or N	$\delta+$ $\delta-$ $\delta+$ $\delta-$ $\delta+$ $\delta-$	
Ion–dipole	Mixtures of ionic compounds and polar compounds	+ $\delta-$ $\delta-$ $\delta-$ $\delta-$ $\delta-$ $\delta-$	







Sucrose dissolved in water

4. Effect of common ion on solubility

The common ion effect refers to the decrease in solubility of an ionic compound when a common ion is added to the solution. This happens due to Le Chatelier's principle, which states that a system at equilibrium will shift to counteract changes. For example, consider the solubility of silver chloride (AgCl) in water. Without any common ions, AgCl has a certain solubility. If you add sodium chloride (NaCl), which provides a common ion (Cl^-), the equilibrium of AgCl dissociation shifts left, resulting in less AgCl dissolving in the solution. So, if the solubility of AgCl is 0.001 mol/L in pure water, adding NaCl could reduce its solubility to 0.0005 mol/L, effectively demonstrating the common ion effect.

Example 12

The Ksp for $BaSO_4$ is $1*10^{-10}$, calculate the solubility of barium sulphate $BaSO_4$ in a D.W and 0.002M $BaCl_2$.

In D.W

$$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$$

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$1 * 10^{-10} = [x][x] = x^2$$

$$x = [Ba^{2+}] = [SO_4^{2-}] = \sqrt[2]{1 * 10^{-10}} = 1 * 10^{-5}\,\frac{mol}{L}$$

In 0.002M $BaCl_2$

$$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$$

I	0.002	0
C	+x	+x
E	0.002+x	x

Use the concentration of the common ion as the initial concentration

you can only ignore **X** when it is being added or subtracted

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$1 * 10^{-10} = [0.002 + \cancel{x}][x]$$

$$1 * 10^{-10} = 0.002x$$

$$x = \frac{1 * 10^{-10}}{0.002} = 5 * 10^{-8}\,mol/L$$

Note that the solubility of $BaSO_4$ has been decreased by 200 times due to the affect of common ion Ba^{2+}

5. Effect of pH on solubility

pH can influence solubility by means of:

Acid-Base Reactions: For solutes that are weak acids or weak bases, pH can significantly impact solubility.

Weak Acids: The solubility of weak acids typically increases in a more basic (high pH) environment. This is because the weak acid (HA) dissociates into its conjugate base (A^-) and hydrogen ions (H^+). In a basic solution, the concentration of H^+ is lower, so the equilibrium shifts to produce more of the conjugate base, which enhances the solubility of the weak acid.

Weak Bases: Conversely, the solubility of weak bases generally increases in a more acidic (low pH) environment. Weak bases (B) accept protons to form their conjugate acids (BH^+). In an acidic solution, there are more H^+ ions available, which shifts the equilibrium to form more of the conjugate acid and increases the solubility of the weak base.

Salt Solubility: For salts formed from a strong acid and a strong base (like NaCl), pH usually doesn't have a significant effect on solubility because both the acid and base completely dissociate in water. However, for salts formed from a weak acid and a strong base (or vice versa), pH can impact solubility:

Salts of Weak Acids: Salts formed from weak acids and strong bases (like sodium acetate) can become more soluble in acidic solutions because the added H^+ ions shift the equilibrium to dissolve more of the salt to counteract the increase in H^+.

Salts of Weak Bases: Salts formed from weak bases and strong acids (like ammonium chloride) can become more soluble in basic solutions because the added OH^- ions react with the H^+ ions, reducing the concentration of H^+ and shifting the equilibrium to dissolve more of the salt.

Overall :

Increased pH (more basic): Generally increases the solubility of weak acids and decreases the solubility of weak bases.

Decreased pH (more acidic): Generally increases the solubility of weak bases and decreases the solubility of weak acids.

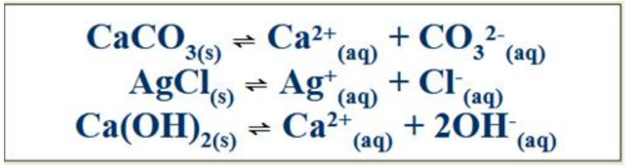
pH effect on solubility (illustration)

- Occurs when one of the ions in the salt is an acid or base $Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$
- Occurs when the salt is a conjugated base of a weak acid (BaC_2O_4, $CaCO_3$, ...)
- If the anion (A-) of the salt/precipitate is that of a weak acid, the salt/precipitate will dissolve more when in a strong acid (H+ ions will form HA with A^-)
- However, if the anion of the precipitate is that of a strong acid, adding a strong acid will have no effect on the precipitate dissolving more.

The stronger the acid, the weaker the conjugate base

A conjugate base of a strong acid (**weak base**) (e.g. Cl^-) ⇒ **no effect**
A conjugate base of a weak acid (**strong base**) (e.g. S^{2-}) ⇒ **S ↑**

e.g. How would the addition of HCl affect the solubility of $PbCl_2$? *No effect*
e.g. Predict the effect on solubility of adding a strong acid? *Increase ($CaCO_3$ & $Ca(OH)_2$), no effect on AgCl*



$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$
$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$
$$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

Example 13

The Ksp value of $Mg(OH)_2$ is 8.9×10^{-12}, what is the pH of a saturated solution of $Mg(OH)_2$?

$$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$$

		Mg^{2+}	$2OH^-$
I		0	0
C		+x	+2x
E		x	2x

$$K_{sp} = [Mg^{2+}]\,[OH^-]$$

$$8.9 * 10^{-12} = [x][2x]^2 = 4x^3$$

$$x = 1.305 * 10^{-4}\,\frac{mol}{L}$$

$$[OH] = 2x = 2 * 1.305 * 10^{-4} = 2.61 * 10^{-4}$$

$$pH = 14 - pOH = 14 - 3.583 = 10.4$$

Example 14

What pH is required to just precipitate iron (III) hydroxide from a 0.10M FeCl3 solution?

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$$

$$[Fe^{3+}][OH^-]^3 = 4 \times 10^{-38}$$

$$(0.1)[OH^-]^3 = 4 \times 10^{-38}$$

$$[OH^-] = \sqrt[3]{\frac{4 \times 10^{-38}}{0.1}} = 7 \times 10^{-13}\ \mathrm{M}$$

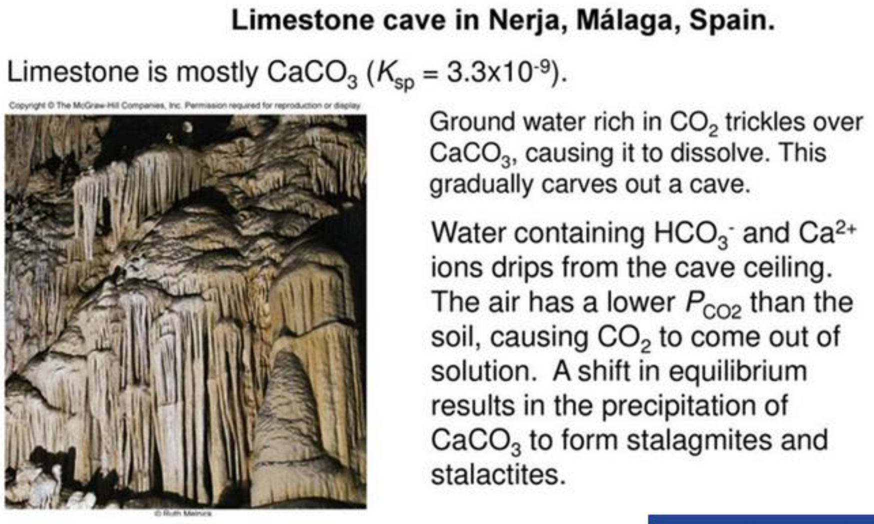
$$pOH = -\log\ 7 \times 10^{-13} = 12.2$$

$$pH = 14.0 - 12.2 = 1.8$$

$Fe(OH)_3$ actually precipitates in acid solution due to the small $K_{sp.}$

Note: that precipitation generally will not begin exactly at the calculated pH, as supersaturation is needed.

Applications of pH effect on solubility



Limestone cave in Nerja, Málaga, Spain.

Limestone is mostly $CaCO_3$ ($K_{sp} = 3.3 \times 10^{-9}$).

Ground water rich in CO_2 trickles over $CaCO_3$, causing it to dissolve. This gradually carves out a cave.

Water containing HCO_3^- and Ca^{2+} ions drips from the cave ceiling. The air has a lower P_{CO2} than the soil, causing CO_2 to come out of solution. A shift in equilibrium results in the precipitation of $CaCO_3$ to form stalagmites and stalactites.

© Ruth Melnick

If limestone ($CaCO_3$) deposit is near surface…sinkhole

Jamal and Associates, Orlando, F

Figure 62. Spectacular, sudden collapse of the land surface commonly accompanies the formation of a sinkhole, such as this one that formed at Winter Park, just north of Orlando, Fla., in 1981.

6. Effect of complex-ion formation on solubility

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base.

When a solute forms a complex ion with a ligand, the solubility of the original solute can increase. This is often because the complex ion is more stable in solution than the individual ions.

Consider a metal salt like silver chloride (AgCl), which is only sparingly soluble in water. When chloride ions (Cl^-) are present, they can form complex ions with silver ions (Ag^+) in the presence of a complexing agent (such as ammonia, NH_3).

The complex ion formed $[Ag(NH_3)_2]^+$ can increase the solubility of AgCl in the solution because the formation of the complex ion effectively reduces the concentration of free Ag^+ ions, shifting the dissolution equilibrium of AgCl to dissolve more of the solid.

Practically NH_3 dissolves only AgCl which has relatively large K_{sp} value because the value of K_f for $Ag(NH_3)^{2+}$ is small.

The larger the K_{sp} value of the salt and the value of K_f of the metal complex the more the effect of the complexing agent on dissolving the salt and vice versa.

Example 15

Calculate the molar solubility of AgCl (Ksp = 1.8 x10^{-10}) in pure water and in 3M NH_3?

$$AgCl_s \leftrightarrow Ag^+ + Cl^-$$

I	0	0
C	+x	+x
E	x	x

$$K_{sp} = [Ag^+]\,[Cl^-]$$

$$1.8 * 10^{-10} = [x][x] = x^2$$

$$x = \sqrt[2]{1.8 * 10^{-10}} = \boxed{1.3 * 10^{-5}\,\frac{mol}{L}}$$

$$\cancel{Ag}^+ + 2NH_3 \leftrightarrow Ag(NH_3)_2^+ \qquad K_f = 1.6x10^7$$

$$AgCl_s \leftrightarrow \cancel{Ag}^+ + Cl^- \qquad K_{sp} = 1.8x10^{-10}$$

$$AgCl_s + 2NH_{3\,(aq)} \leftrightarrow Ag(NH_3)^+_{2\,(aq)} + Cl^-_{(aq)} \qquad K = K_{sp} * K_f = 2.9x10^{-3}$$

I	3.0	0	0
C	-2x	+x	+x
E	3.0-2x	x	x

$$k = \frac{[Ag(NH_3)_2^+]^1[Cl^-]^1}{[NH_3]^2}$$

$$2.9x10^{-3} = \frac{[x]^1[x]^1}{[3.0 - 2x]^2}$$

$$\boxed{x = 0.14\ M}$$

Note that the solubility of AgCl has been increased due to the affect of complex-ion formation

The NH_3 ligand remove Ag^+ and shifts the equilibrium to the right, increasing the solubility of AgCl

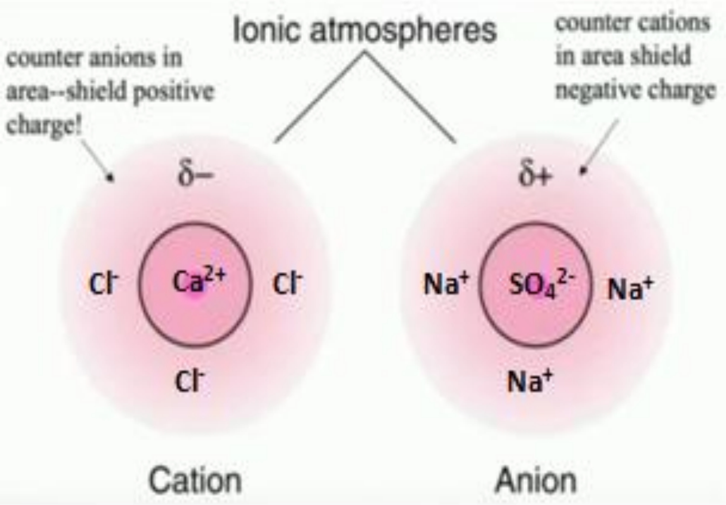
7. Effect of ionic strength on solubility

Ionic strength refers to the concentration of ions in a solution and significantly affects the solubility of ionic compounds. As ionic strength increases, solubility often increases due to reduced electrostatic interactions between ions. This phenomenon occurs because higher ionic strength leads to more shielding of charged ions, effectively reducing the force of attraction between oppositely charged ions in a solid.
For example, consider calcium sulfate ($CaSO_4$). In a solution with low ionic strength, the solubility might be around 0.2 g/L. However, if a salt like sodium chloride (NaCl) is added to the solution, increasing the ionic strength, the solubility of calcium sulfate could rise to 0.5 g/L or more.

Ionic strength (μ)
- Addition of salt to solution increases ionic strength
- Added salt is inert ➔ does not interact or react with other ions

In general, *increasing* ionic strength *increases* salt solubility

The *greater* the ionic strength of a solution, the *higher* the charge in the ionic atmospheres



More ions added, more ions can be present in ionic atmospheres

Ionic strength: measure of the total concentration of ions in solution
Sum extends over *all* ions in solution

$$\mu = \frac{1}{2}\left(c_1 z_1^2 + c_2 z_2^2 + \ldots\right) = \frac{1}{2}\sum_i c_i z_i^2$$

Where: C_i is the concentration of the ith species and z_i is its charge

Example 16
A solution contains 0.100 M sodium nitrate ($NaNO_3$) and 0.200 M $MgCl_2$. Find the ionic strength of the solution? *(Answer: 0.7 M)*

Factors affecting solubility (summary)

- **Temperature (S↑)**

... Solubility increases with temperature

- **Nature of Solute**

... When ionic charge increases, the attraction between ions increases, solubility decreases

... Small ions is less soluble than large ions, as the bond between small ions is stronger that the bond between large ions with the same charge.

- **Nature of Solvent**

... Like dissolves like

- **Common ion (S↓)**

... the presence of common ions reduce solubility

- **pH the solution (S↑ OR S↓)**

... Occurs when one of the ions in the salt is an acid or base $Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$

... Occurs when the salt is a conjugated base of a weak acid (BaC_2O_4, $CaCO_3$, ...)

⇨ Ex. ionic compound with basic anion

solubility will increase as the pH of the solution decreases (H+ reacts with the basic anion)

$$CaCO_3\,(s) \rightleftarrows Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$$

$$CO_3^{2-}\,(aq) + H^+\,(aq) \rightarrow HCO_3^-\,(aq)$$

Anion decreases → Shift to the right

- **Formation of complex ion (S↑)**

The solubility of an ionic compound may increase dramatically if a solution containing a Lewis base is added

As the complex ion forms, [cation] in solution decreases

$$AgCl\,(s) \rightleftarrows Ag^+\,(aq) + Cl^-\,(aq)$$

$$Ag^+\,(aq) + 2\,NH_3\,(aq) \rightleftarrows [Ag(NH_3)_2]^+\,(aq)$$

- **Electrolyte strength (S↑)** ... The presence of other electrolytes increase solubility
- **Particle size** ... Smaller particles are more dissolved

When a solute dissolves, the action takes place only at the surface of each particle. When the total surface area of the solute particles is increased, the solute dissolves more rapidly.

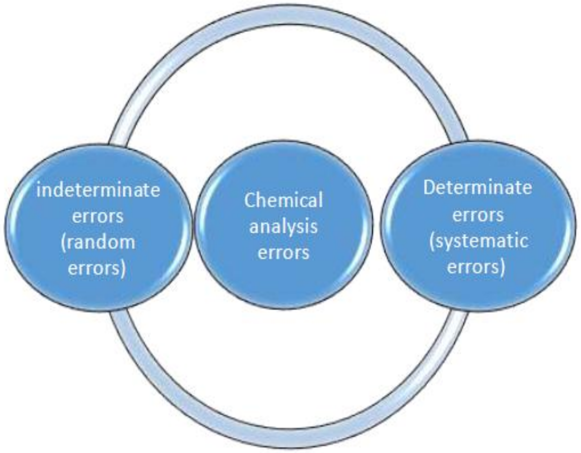
Analytical Statistics

Errors in chemical analysis

It is impossible to perform a chemical analysis that is totally free of errors or uncertainties, but only to minimize errors to acceptable values. Errors can be caused by faulty equipment or bad laboratory practice; proper equipment maintenance, appropriate training, calibrations, standardizations, and analyses of known samples can sometimes be used to lessen all. Errors must be controlled and assessed so that valid analytical measurements can be made and reported.

Type of errors in a chemical analysis

Basically, chemical analysis are affected by two types of errors which include determinate errors (also known as systematic errors), and indeterminate errors (also known as random errors).



➢ Determinate errors

Determinate errors (also known as systematic errors) have a definite value from identified sources. There are three types of systematic errors that include instrumental error, method error, and personal error.

1. Instrumental errors are caused by non-ideal instrument behavior, by faulty calibrations, or by use under inappropriate conditions. Pipettes, burettes, and volumetric flasks may hold or deliver volumes slightly different from those indicated by their graduations. Calibration eliminates most systematic errors of this type. Errors of these types usually are detectable and correctable.

2. Method errors are initiated by the non-ideal chemical or physical behavior of the reagents and reactions on which an analysis is based; often introduce systematic method errors. Such sources of non-ideality include the slowness of some reactions, the incompleteness of others, the instability of some species, the lack of specificity of most reagents, and the possible occurrence of side reactions that interfere with the measurement process. Errors inherent in a method are often difficult to detect and hence, these errors are usually the most difficult to identify and correct.

3.Personal Errors result from the experimenter's carelessness, inattention, or personal limitations. Many measurements require personal judgments. Examples include estimating the position of a pointer, the color of a solution at the end point in a titration, or the level of a liquid with respect to a graduation in a pipette or burette. Digital and computer displays on pH meters, laboratory balances, and other electronic instruments eliminate number bias because no judgment is involved in taking a reading.

Determinate errors that lead to a higher value or result than a true or accepted one are said to show a positive bias; those leading to a lower value or result are said to show a negative bias.

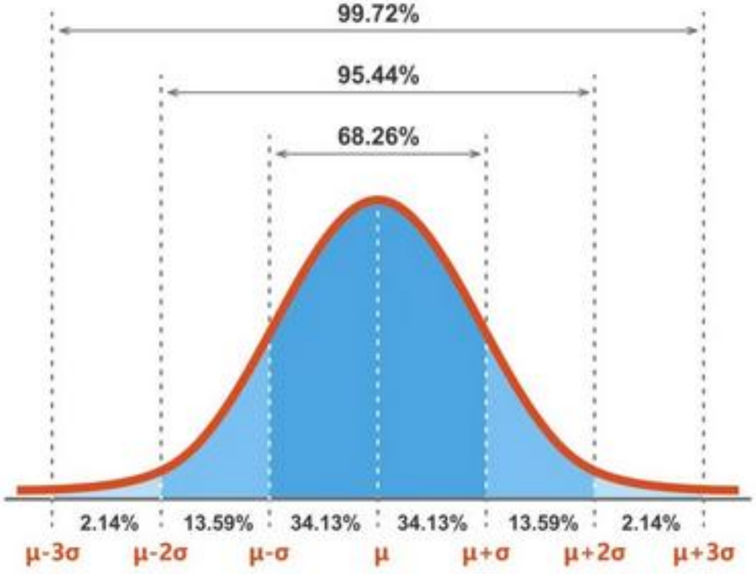
- **Indeterminate errors**

Indeterminate errors (known as random errors) are caused by the many uncontrollable variables that accompany every measurement. It is impossible to eliminate them, but they can be minimised by careful experimental design and control. Environmental factors such as temperature, pressure and humidity, and electrical properties such as current, voltage and resistance are all susceptible to small continuous and random variations described as noise. These contribute to the overall indeterminate error in any physical or physicochemical measurement, but no specific source can be identified.

The distribution of errors was first studied by Carl F. Gauss. When a large number of replicate readings, at least 50 numbers are taken of a continuous variable, the results attained will usually be distributed about the mean in a roughly symmetrical manner. The mathematical model that best satisfies such a distribution of random error is called the normal Gaussian distribution.

Gaussian distribution curve is a bell-shaped that is symmetrical about the mean as shown in the figure. This curve satisfies the equation:

$$\boxed{1/(\sigma\sqrt{2\pi})\ e^{-(x-\mu)^2/2\sigma^2}}$$

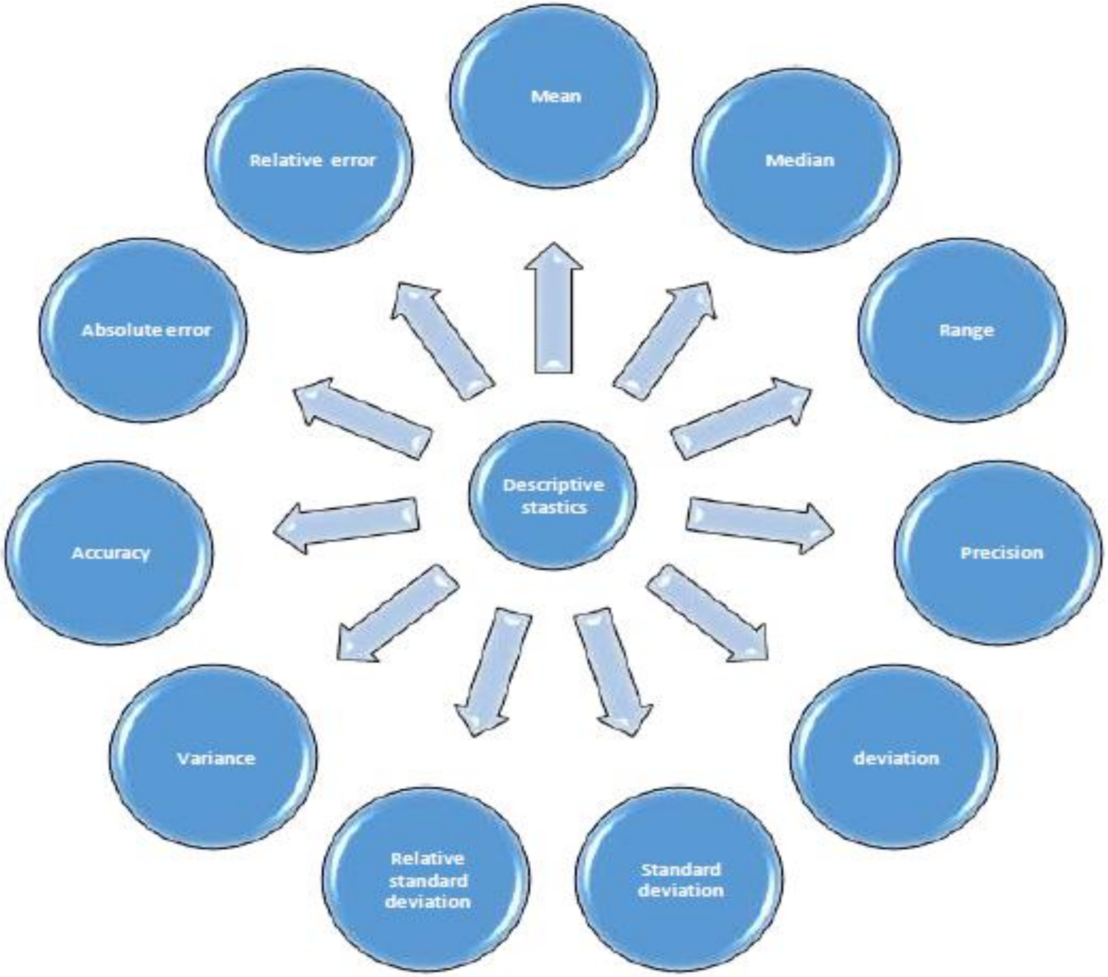


Normal or Gaussian distribution curve

Where, σ = standard deviation μ = mean of total population.

Descriptive statistics

There are certain terms in statistics which must be defined; as they form the basis defining the measure of dispersion of data that causes errors in analytical results:



Descriptive stastics

Mean

Median

Range

Precision

deviation

Standard deviation

Relative standard deviation

Variance

Accuracy

Absolute error

Relative error

The mean or average is obtained by dividing the sum of replicate measurements by the number of measurements in the set.

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}$$

The symbol Σxi means to add all of the values xi for the replicates; xi represents the individual values of x making up the set of N replicate measurements.

Example 17

If a titration is repeated four times and titre values are 10.1, 9.9, 10.0 and 10.2 mL, calculate the mean?

Mean = 10.1+ 9.9+ 10 + 10.2/4 = 40.2/4 = 10.05 mL

The median is the middle value in a set of data that has been arranged in numerical order. For an odd number of values, the middle value is the median, for an even no value, the average of the two middle values is the median.

For the odd values 18, 19, 20, 21, and 22, the median is equal to (20).

For the even values 18, 19, 20, 21, 22, and 23, the median is equal to 20+21/2 =20.5**.**

The range is the difference between the greatest and least values of data.

Precision is the agreement between multiple measurements made in the same way. It implies nothing about their relation to the true value. Describes the reproducibility of measurements. The precision of a set of replicate data may be expressed as standard deviation, relative standard deviation, and variance.

Deviation is how much each measurement differs from the mean. This is an important number and is called the deviation.

Standard deviation (S) is the square root of the sum of the individual deviations squared, divided by the number of readings based on the normal error (Gaussian) curve. It is an important term in the analysis of random numbers.

$$s = \sqrt{\frac{\sum_{i=1}^{i=N} (x_i - \bar{x})^2}{N-1}}$$

Relative standard deviation (RSD) (also known as coefficient of variation (CV)) is the standard deviation expressed as a percentage of the measured value.

Relative standard deviation (RSD) % = (S/ mean) × 100

The variance is the square of standard deviation, which is designated as S^2. The variance is fundamentally more important in statistics than is S itself. Variance, S^2 = (Standard deviation)^2

$$S^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}$$

Example 18

An iron core gives the following results during the Fe estimation as the value 7.08, 7.21, 7.12, 7.09, 7.16, 7.14, 7.07, 7.14, 7.18, 7.11. Calculate the mean, the standard deviation, relative standard deviation, and variance for the values.

The mean, $\bar{x}$= (7.08 + 7.21 + 7.12 + 7.09 + 7.16 + 7.14 + 7.07 + 7.14 + 7.18 + 7.11)/10
= 71.3/10
=7.13
Standard deviation = S = √(7.08-7.13)^2 + (7.21-7.13)^2 + ………….(7.18-7.13)2 + (7.11-7.13)^2 /9
S = √181.98 x 10^{-4} /9
S = 4.49 x 10^{-2}
S = 0.0449
Relative standard deviation (RSD) = (S/mean) × 100
RSD = 0.0449/7.13 × 100
RSD = 0.62 %
Variance (S2) = 181.98× 10^{-4}/9
S2= 2 × 10^{-2}
S2=0.002

Accuracy is the closeness of a measurement or the mean of multiple measurements, to its true or accepted value. The term accuracy is commonly stated in terms of absolute error and relative error.

Absolute errors refers to the difference between a measured value and the true or known value:

$$E = Xi - Xt$$

Where E is the absolute error, X_i is the measured or experimental value and X_t is the true value. If the measurement result is low, the sign is negative; if the measurement result is high, the sign is positive.

The relative error of a measurement is the absolute error divided by the true value. Relative error may be expressed in percent, parts per thousand, or parts per million, depending on the magnitude of the result:

$$Er = \frac{E}{Xt} \times 100$$

$$Er = \frac{Xi - Xt}{Xt} \times 100$$

Where E_r is expressed as percentage relative error, E is the absolute error, X_i is the measured or experimental value and X_t is the true value.

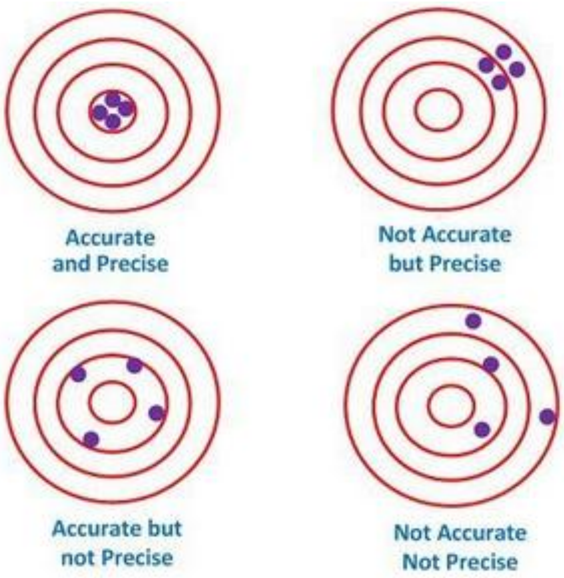
Example 19

The measured weight of a pineapple is approximate as 682.325 g, but the original weight is 684.075 g. Determine the absolute and relative error in the weighing?

Absolute error = 682.325 – 684.075 = -1.75 g

Relative error = -1.75/684.075 × 100 = -0.25

The relationship between precision and accuracy are demonstrated in the figures:



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