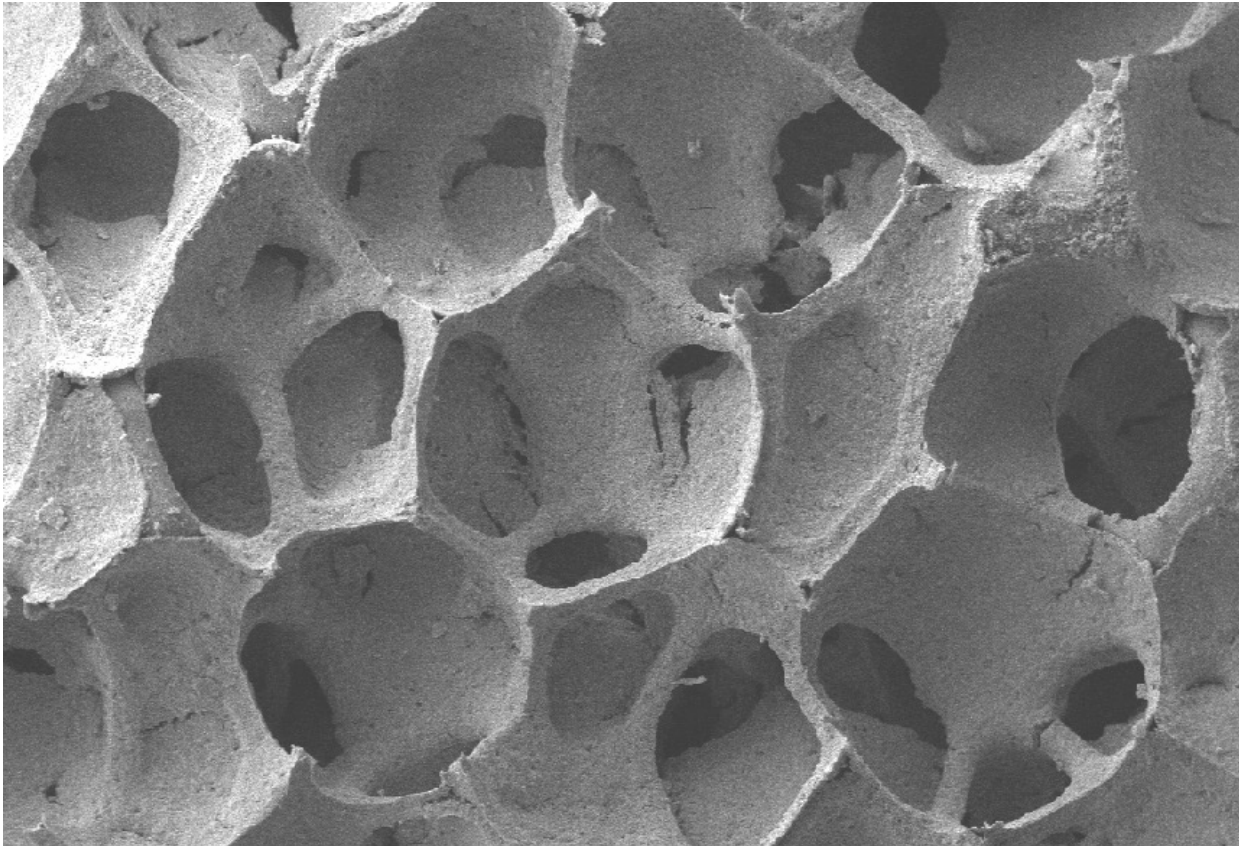
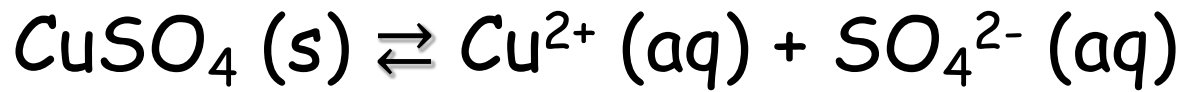


Salt solubility and heterogeneous equilibria

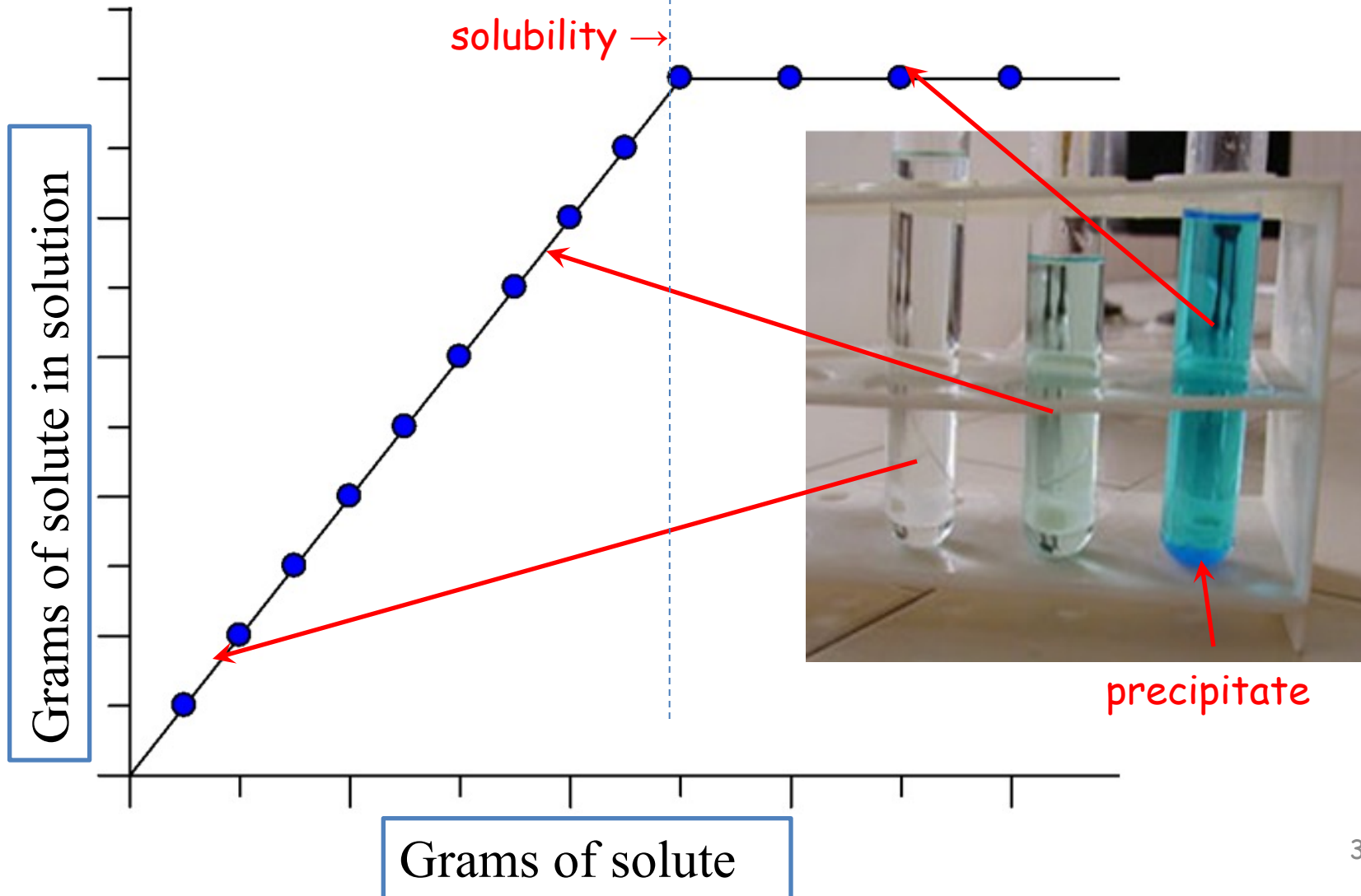


Hydroxyapatite : $\text{Ca}_5(\text{PO}_4)_3\text{OH}$

- The solubility of a substance in a solvent is determined by the balance of **intermolecular forces** between solvent and solutes and by the change in **entropy** that accompanies solvation.
- Factors like temperature and pressure can alter this balance, varying solubility.



Unsaturated Solution ← → Saturated Solution



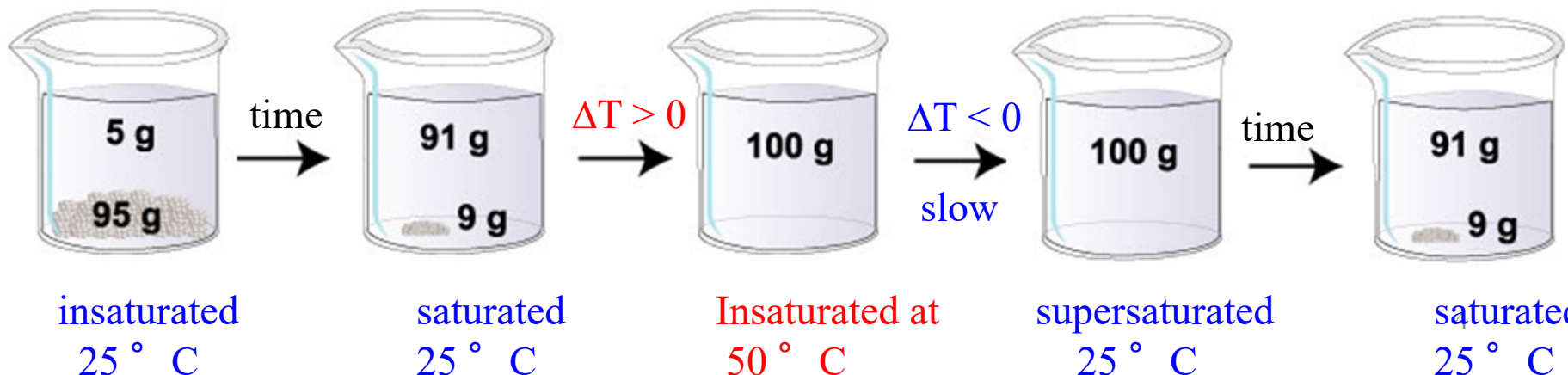
Solubility

It is defined as the maximum amount of solute that dissolves in a specified amount of solvent at a given temperature (and pressure for gases)

Saturated if, in a certain amount of solvent, it is not possible to dissolve further solute (each subsequent addition of solute forms a precipitate)

Unsaturated if the amount of solute dissolved is less than the amount needed to have a saturated solution

Supersaturated if the dissolved solute quantity is greater than the amount needed for a saturated one. Supersaturated solutions are unstable and tend to reach the state of saturated solutions by precipitation.



The solubility of a certain solute in a certain solvent depends not only on the characteristics of the two substances, but also on temperature and pressure.



Tahiti



Patagonia

Generally, an increase in temperature increases the solubility of solid substances, while that of the gaseous substances decreases.

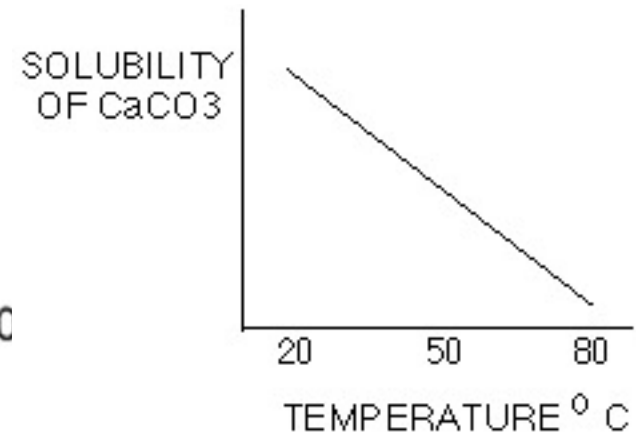
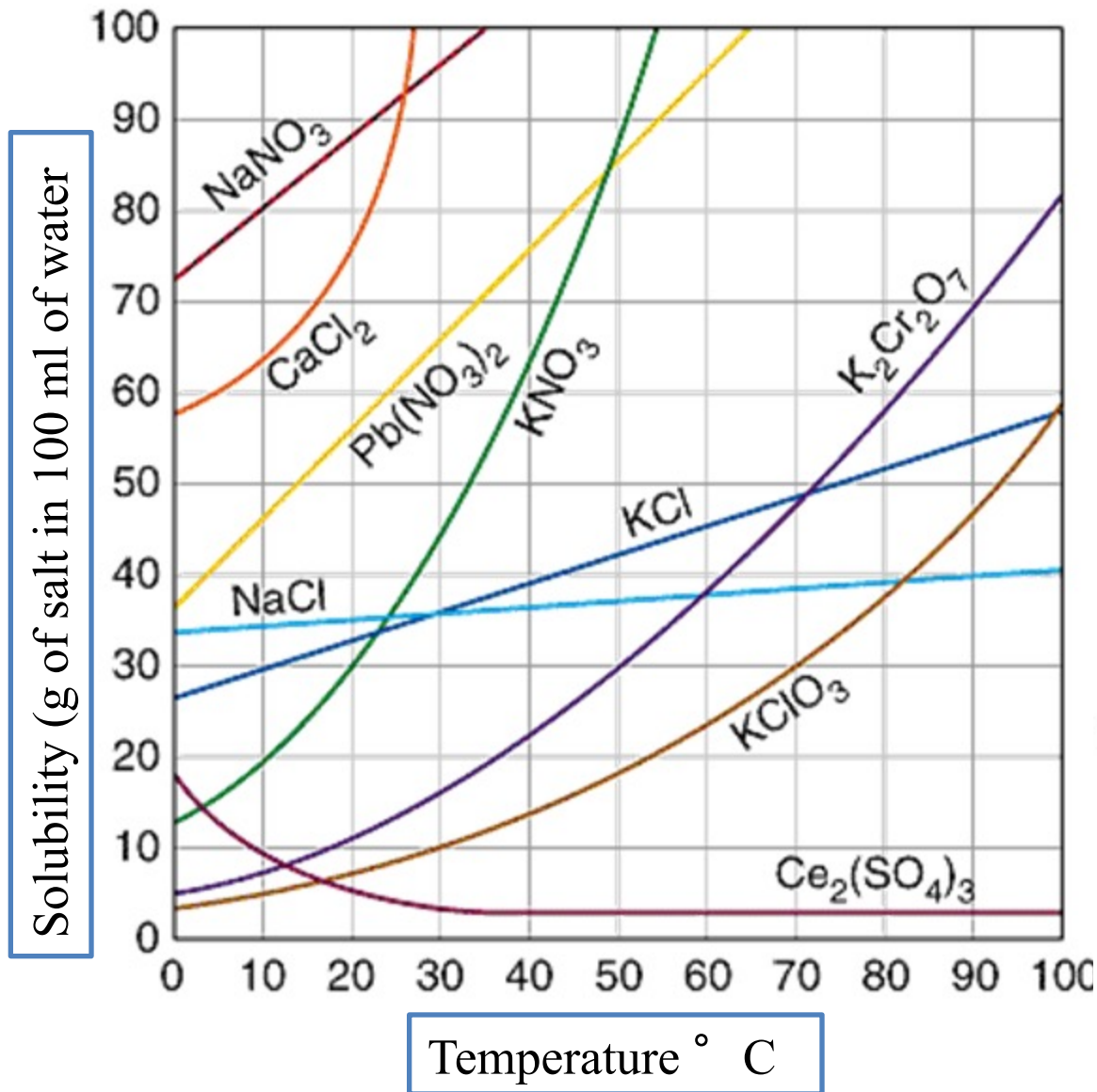
Eg tropical seas, warmer, are more "salty" than glacial ones.

The dead sea, at 480 m below sea level



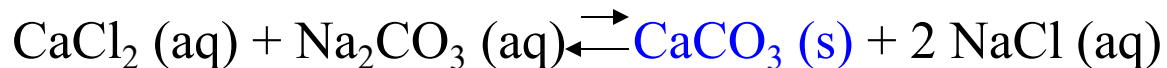
Dead sea: [salt] = 340 g/L (salts of Mg^{2+} , Na^+ , Ca^{2+} , K^+ , e Cl^- e Br^-).
On average in the sea: [NaCl] = 35 g/L

Solubility of some salts as a function of temperature at 1 Atm



Solubility of salts

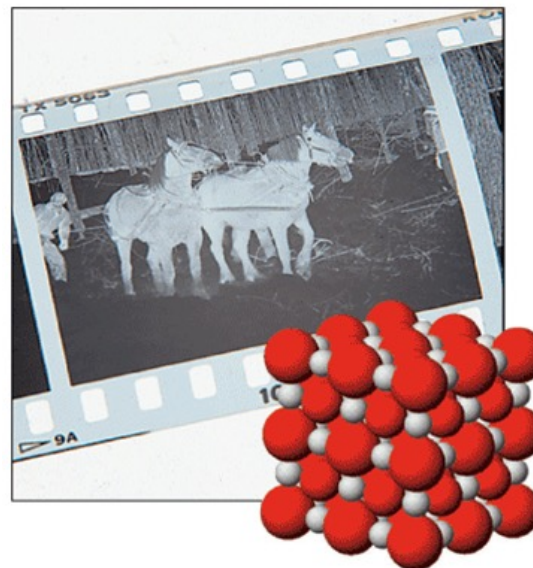
Precipitation reactions are exchange reactions in which one of the products is an insoluble compound in water.



The solubility of CaCO_3 is $\sim 58 \text{ mM}$ at 25°C and for AgBr it is $\sim 0.7 \text{ mM}$ at 25°C .



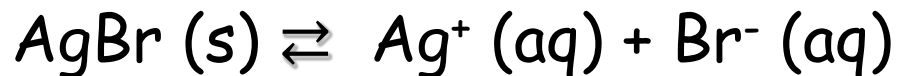
Stalactites CaCO_3



A b/W film is covered with AgBr , insoluble in water

The Solubility Product K_{sp}

If we add $AgBr$ to water, a small amount is dissolved and it establishes this equilibrium:



The concentrations of Ag^+ and Br^- in water are:

$$[Ag^+] = [Br^-] = 7.35 \times 10^{-7} \text{ M at } 25^\circ \text{ C.}$$

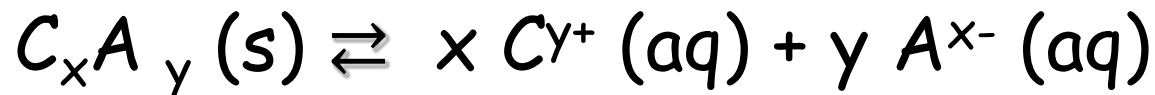
The amount of a scarcely soluble salt in water can be expressed in terms of a constant of equilibrium for the solubilization process:

$$K = \frac{[Ag^+] \cdot [Br^-]}{[AgBr]_{solid}} \rightarrow K \cdot [AgBr]_{solid} = [Ag^+] \cdot [Br^-] = K_{PS}$$

$$K_{PS} = [Ag^+] \cdot [Br^-] = 5.4 \cdot 10^{-13} \text{ M}^2$$

The value of the equilibrium constant reflects the solubility of a compound and it is defined as **solubility product**:

For a given salt, C_xA_y (C = cation and A = anion) the solubility product has this form:



$$K_{PS} = [C^{y+}]^x \cdot [A^{x-}]^y$$

dimensions $M^{(x+y)}$

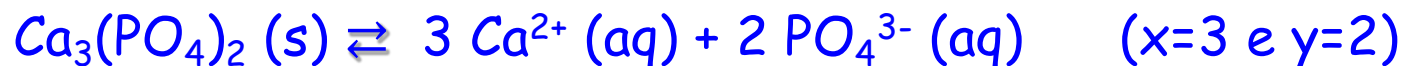
Esemples:



$$K_{PS} = [Ca^{2+}] [F^-]^2 = 5.3 \times 10^{-11} M^3$$



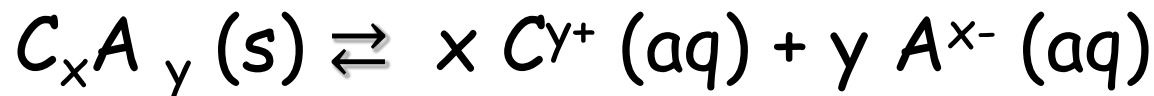
$$K_{PS} = [Ag^+]^2 [SO_4^{2-}] = 1.2 \times 10^{-5} M^3$$



$$K_{PS} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 2.0 \times 10^{-29} M^5$$

NB: K_{PS} is different from the solubility

If C_xA_y achieves the following equilibrium



If for S moles of C_xA_y we have xS moles of C^{y+} and yS moles of A^{x-} then:

$$[C^{y+}] = xS \text{ e } [A^{x-}] = yS$$

Substituting these 2 equations in the formula for the solubility product:

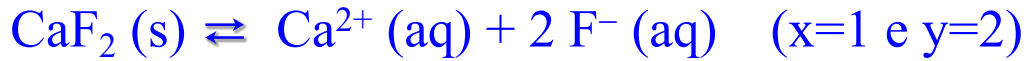
$$K_{PS} = (x \cdot S)^x \cdot (y \cdot S)^y = x^x \cdot y^y \cdot S^{x+y}$$

From which we deduce:

$$S = \left(\frac{K_{PS}}{x^x \cdot y^y} \right)^{\frac{1}{x+y}}$$

The relationship between solubility and the solubility product depends on the stoichiometry of the compound

Examples:



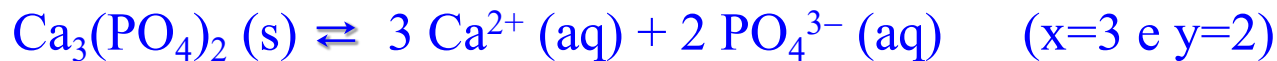
$$K_{\text{PS}} = [\text{Ca}^{2+}] \cdot [\text{F}^-]^2 = 5.3 \cdot 10^{-11} \text{ M}^3$$

$$S = \left(\frac{5.3 \cdot 10^{-11}}{1^1 \cdot 2^2} \right)^{\frac{1}{1+2}} = \left(\frac{5.3 \cdot 10^{-11}}{4} \right)^{\frac{1}{3}} = 2.4 \cdot 10^{-4} \text{ M}$$



$$K_{\text{PS}} = [\text{Ag}^+]^2 \cdot [\text{SO}_4^{2-}] = 1.2 \cdot 10^{-5} \text{ M}^3$$

$$S = \left(\frac{1.2 \cdot 10^{-5}}{2^2 \cdot 1^1} \right)^{\frac{1}{2+1}} = \left(\frac{1.2 \cdot 10^{-5}}{4} \right)^{\frac{1}{3}} = 1.4 \cdot 10^{-2} \text{ M}$$



$$K_{\text{PS}} = [\text{Ca}^{2+}]^3 \cdot [\text{PO}_4^{3-}]^2 = 2.0 \cdot 10^{-29} \text{ M}^5$$

$$S = \left(\frac{2.0 \cdot 10^{-29}}{3^3 \cdot 2^2} \right)^{\frac{1}{3+2}} = \left(\frac{2.0 \cdot 10^{-29}}{108} \right)^{\frac{1}{5}} = 7.1 \cdot 10^{-7} \text{ M}$$

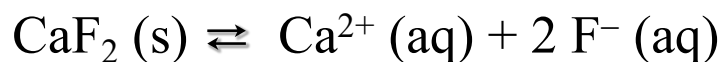
Some compounds with low solubility and their K_{PS}

formula	name	K_{PS} (25 ° C)	solubility S (M)
CaCO_3	Calcium carbonate	$3.4 \cdot 10^{-9} \text{ M}^2$	$5.8 \cdot 10^{-5}$
MnCO_3	Manganese II carbonate(II)	$2.3 \cdot 10^{-11} \text{ M}^2$	$4.8 \cdot 10^{-6}$
FeCO_3	Iron II carbonate(II)	$3.1 \cdot 10^{-11} \text{ M}^2$	$5.6 \cdot 10^{-6}$
CaF_2	Calcium fluoride	$5.3 \cdot 10^{-11} \text{ M}^3$	$2.4 \cdot 10^{-4}$
AgCl	Silver chloride	$1.8 \cdot 10^{-10} \text{ M}^2$	$1.3 \cdot 10^{-5}$
AgBr	Silver bromide	$5.4 \cdot 10^{-13} \text{ M}^2$	$7.3 \cdot 10^{-7}$
CaSO_4	Calcium sulphate	$4.9 \cdot 10^{-5} \text{ M}^2$	$7.0 \cdot 10^{-3}$
BaSO_4	Barium sulphate	$1.1 \cdot 10^{-10} \text{ M}^2$	$1.0 \cdot 10^{-5}$
SrSO_4	Strontium sulphate	$3.4 \cdot 10^{-7} \text{ M}^2$	$5.8 \cdot 10^{-4}$
Ca(OH)_2	Calcium hydroxide	$5.5 \cdot 10^{-5} \text{ M}^3$	$2.4 \cdot 10^{-2}$
Mg(OH)_2	Magnesium hydroxide	$5.6 \cdot 10^{-12} \text{ M}^3$	$1.1 \cdot 10^{-4}$
CaC_2O_4	Calcium oxalate	$1.3 \cdot 10^{-9} \text{ M}^2$	$3.6 \cdot 10^{-5}$
$\text{Ca}_3(\text{PO}_4)_2$	Calcium phosphate	$2.0 \cdot 10^{-29} \text{ M}^5$	$7.1 \cdot 10^{-7}$

Relationship between solubility and K_{PS}



Cubic crystals of fluorite



If at 25 ° C we measure $[\text{Ca}^{2+}] = 2.4 \times 10^{-4} \text{ M}$, which is K_{PS} ?

$$[\text{F}^{-}] = 2 [\text{Ca}^{2+}] = 2 \cdot 2.4 \cdot 10^{-4} = 4.8 \cdot 10^{-4} \text{ M}$$

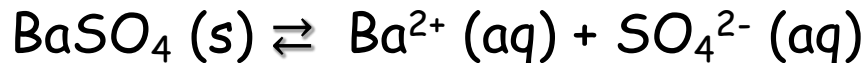
therefore:

$$K_{PS} = [\text{Ca}^{2+}] \cdot [\text{F}^{-}]^2 = 2.4 \cdot 10^{-4} \cdot 4.8 \cdot 10^{-4} = 5.3 \cdot 10^{-11} \text{ M}^3 \text{ a } 25 \text{ } ^\circ \text{ C.}$$

The solubility is $S = [\text{Ca}^{2+}] = [\text{F}^{-}] / 2 = 2.4 \times 10^{-4} \text{ M}$

Barium sulphate is opaque to x-rays and it is used in to examine the digestive tract

barium sulphate is insoluble in water and therefore in organic liquids can not be absorbed by the body and can not exert toxic or lethal action.



$$K_{ps} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}] = 1.1 \times 10^{-10} \text{ M}^2$$

$$\text{solubility} = [\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 1.0 \times 10^{-5} \text{ M}$$

Barium is characterized, as all positive contrast agents, by a high atomic number ($Z = 56$)



Relationship between solubility and K_{PS}

K_{PS} values for low soluble salts can be used to calculate the solubility of a salt or to determine if a precipitate will form when solutions of its cation and its anion are mixed.

Example 1: for Barium sulphate at 25 ° C is $K_{PS} = 1.1 \cdot 10^{-10} \text{ M}^2$. Calculate its solubility: a) in moles /L e b) g/L ($M_{BaSO_4} = 233 \text{ g/mol}$)



Equation	$BaSO_4 (s) \rightleftharpoons$	$Ba^{2+} (aq)$	+	$SO_4^{2-} (aq)$
Initial amount(M)		0		0
Amount dissolved(M)		+x		+x
At equilibrium (M)		x		x

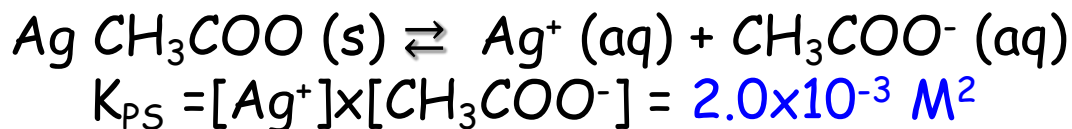
$$K_{PS} = [Ba^{2+}] \cdot [SO_4^{2-}] = x^2 \quad x = \sqrt{K_{PS}} = \sqrt{1.1 \cdot 10^{-10}} = 1.0 \cdot 10^{-5} \text{ M}$$

a) Solubility in mol/L è $1.0 \cdot 10^{-5} \text{ M}$

b) Solubility in g/L è $1.0 \cdot 10^{-5} \cdot 233 = 0.0024 \text{ g/L}$

Solubility and the "common ion effect"

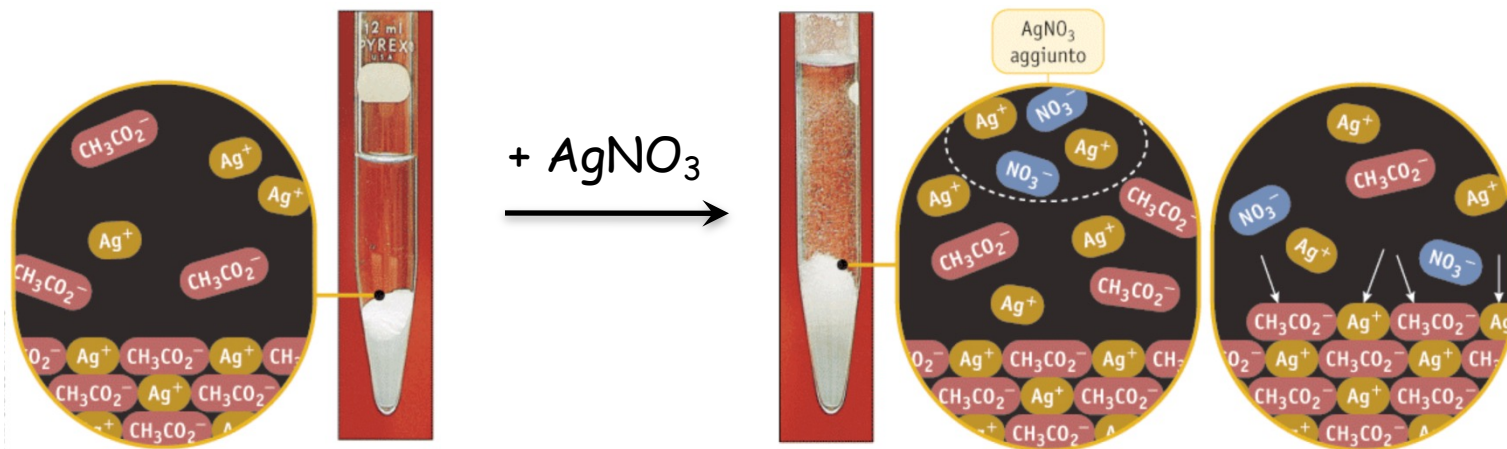
What happens if to a saturated solution of an insoluble salt one adds its cation or anion?



In the saturated solution we have $[\text{Ag}^+] = [\text{CH}_3\text{COO}^-] = (K_{PS})^{\frac{1}{2}} = 0.045 \text{ M}$.

If we add 0.1 M AgNO_3 to this solution

$$Q = [\text{Ag}^+] [\text{CH}_3\text{COO}^-] = 0.145 \times 0.045 = 6.5 \times 10^{-3} \text{ M}^2 > K_{PS}$$



According to Le Châtelier principle, some Silver acetate will precipitate .

How much silver acetate will precipitate if we considered 1 L of solution ($M_{\text{AgCH}_3\text{COO}} = 277.26 \text{ g/mol}$)?

Equation	$\text{AgCH}_3\text{COO (s)} \rightleftharpoons$	$\text{Ag}^+ \text{ (aq)} +$	$\text{CH}_3\text{COO}^- \text{ (aq)}$
Initial amount (M)		0.045	0.045
Added amount (M)		0.045+0.1	0
Reacting amount (M)		-x	-x
At equilibrium (M)		0.145-x	0.045-x

$$K_{\text{PS}} = [\text{Ag}^+] \cdot [\text{CH}_3\text{COO}^-] = 2.0 \times 10^{-3} \text{ M}^2$$

$$2.0 \times 10^{-3} = (0.145 - x)(0.045 - x) \quad x = 0.0276 \text{ M}$$

0.0276 mol/L will precipitate, that is $0.0276 \times 277.26 = 7.6 \text{ g}$

K_{PS} , reaction quotient and precipitation

Q allows one to predict if:

- i) a precipitate will be formed, if the ionic concentrations are known
- ii) what are the ionic concentrations necessary to induce the precipitation of a salt that has a low solubility



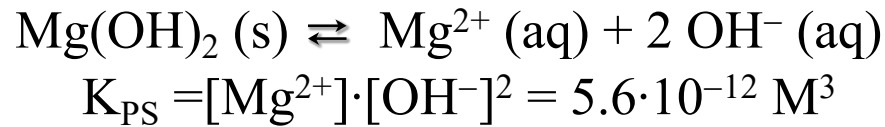
If in a solution we have Ag^+ e Cl^- at given concentrations $Q = [\text{Ag}^+] [\text{Cl}^-]$

if $Q = K_{PS}$, the solution is saturated and the system is at equilibrium

if $Q < K_{PS}$, the solution is not saturated

if $Q > K_{PS}$, the solution is beyond saturation and the system is not at equilibrium, we will observe precipitation.

Example 3: The solubility product for magnesium hydroxide at 25 ° C is $K_{PS} = 5.6 \cdot 10^{-12} \text{ M}^3$. Initially $[\text{Mg}^{2+}] = 1.5 \cdot 10^{-6} \text{ M}$. a) if we add enough NaOH to achieve $[\text{OH}^-] = 1.0 \cdot 10^{-4} \text{ M}$, will Mg(OH)_2 precipitate? b) if it does not precipitate, will it do so if OH^- is increased up to $1.0 \cdot 10^{-2} \text{ M}$?



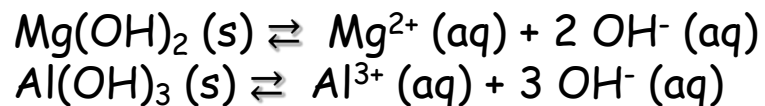
a) $Q = [\text{Mg}^{2+}] \cdot [\text{OH}^-]^2 = (1.5 \cdot 10^{-6}) \cdot (1.0 \cdot 10^{-4})^2 = 1.5 \cdot 10^{-14} < K_{PS}$
The solution is not saturated, and there will not be precipitation

b) $Q = [\text{Mg}^{2+}] \cdot [\text{OH}^-]^2 = (1.5 \cdot 10^{-6}) \cdot (1.0 \cdot 10^{-2})^2 = 1.5 \cdot 10^{-10} > K_{PS}$
 Mg(OH)_2 will precipitate until the Mg^{2+} e OH^- decrease to reach the values for which $[\text{Mg}^{2+}] \cdot [\text{OH}^-]^2 = K_{PS}$

Alkali with low solubility

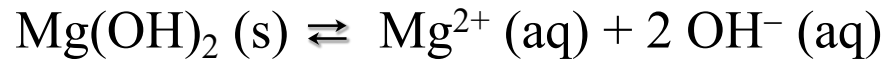
Acid and base solutions are tolerated by our body (eg in food) only if their acidity or basicity is modest. Concentrated solutions of acids or bases are caustic and, by skin contact or if ingested, they produce severe tissue damage. It is therefore not possible to administer concentrated solutions of these compounds for therapeutic purposes.

Some commonly used compounds used in the symptomatic treatment of **gastric hyperacidity** are **strong bases with low solubility**, which have great potential basicity (because they can release large amounts of the hydroxide ion if they dissolve), but yield a weakly basic pH. An example used for this purpose is milk of magnesia.



A suspension of Mg(OH)_2 e Al(OH)_3

Magnesium hydroxide has a low solubility



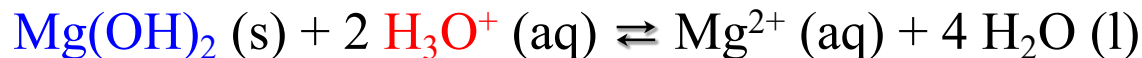
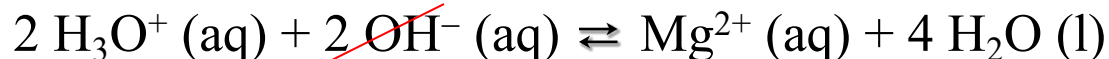
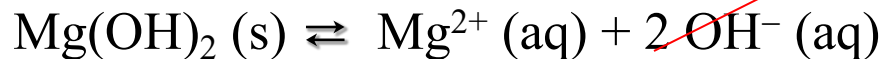
$$K_{\text{PS}} = [\text{Mg}^{2+}] \cdot [\text{OH}^-]^2 = 5.6 \cdot 10^{-12} \text{ M}^3$$

The pH of the saturated solution is ($[\text{Mg}^{2+}] = S$ e $[\text{OH}^-] = 2 \cdot S$)

$$[\text{OH}^-] = 2 \cdot S = 2 \cdot \sqrt[3]{\frac{K_{\text{PS}}}{4}} = 2 \cdot \sqrt[3]{\frac{5.6 \cdot 10^{-12}}{4}} = 2.2 \cdot 10^{-4} \text{ M}$$

$$\text{pOH} = -\log_{10} 2.2 \cdot 10^{-4} = 3.65 \rightarrow \text{pH} = 10.35$$

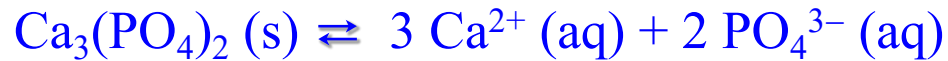
Excess of acid in the gastric environment is neutralized:



Net reaction

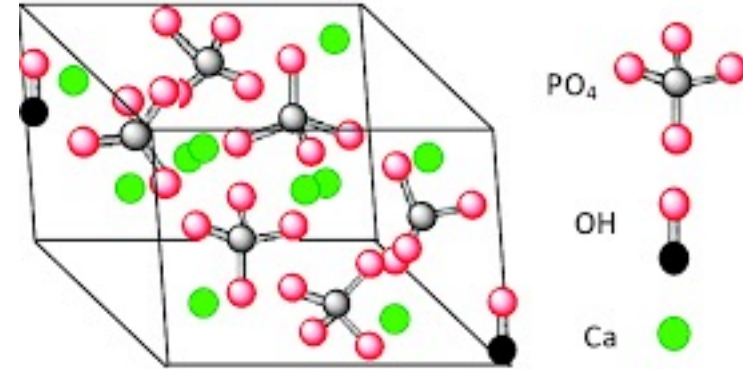
Low solubility salts from weak acids

1) The bone inorganic matrix is made of calcium phosphate (actually hydroxyapatite)

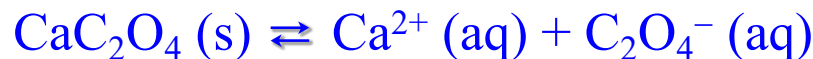


$$K_{\text{PS}} = [\text{Ca}^{2+}]^3 \cdot [\text{PO}_4^{3-}]^2 = 2.0 \times 10^{-29} \text{ M}^5$$

$$\text{solubility} = 7.1 \times 10^{-7} \text{ M}$$

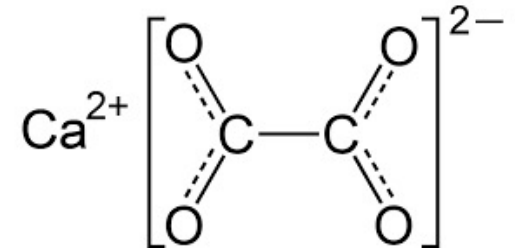


2) In 90% of cases kidney stones are made of calcium oxalate



$$K_{\text{PS}} = [\text{Ca}^{2+}] \cdot [\text{C}_2\text{O}_4^{2-}] = 1.3 \times 10^{-9} \text{ M}^2$$

$$\text{solubility} = 3.6 \times 10^{-5} \text{ M}$$



Renal colic and the solubility product

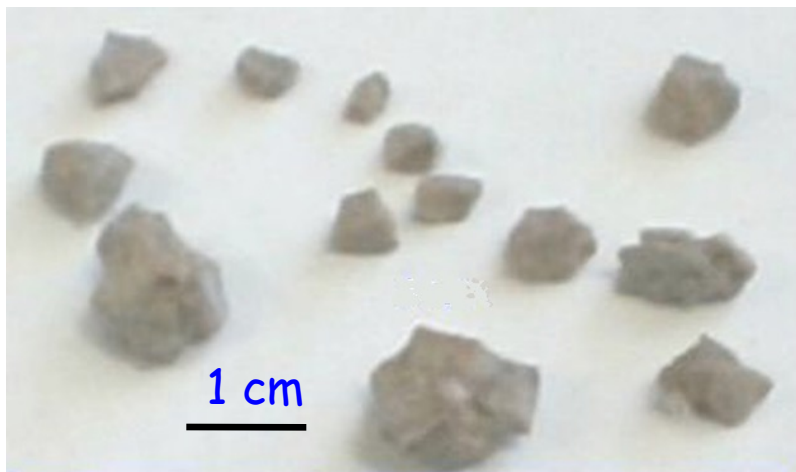
Renal colic affects about 1.2 million people each year, and is about 1% of the causes of hospitalization. Kidney stones, which cause them, are a problem that can arise at any level of the urinary tract, mainly form in the kidney, with a frequency that reaches 12% for men, about double that for women, and a peak of incidence around 35 years.

Renal colic generally results from the mobilization of a kidney stone and usually manifests itself with violent pain in the right or left lumbar region, which radiates to the respective flank and then to the genitals; nausea and vomiting are also often present.

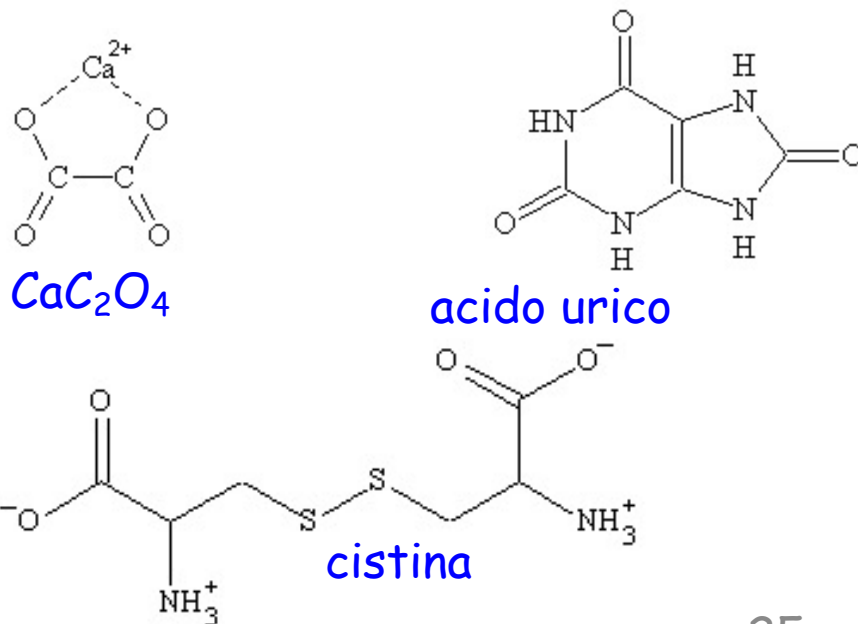


Kidney stones can be visible to X-rays (contain calcium) or invisible to X-rays (if calcium is not present)

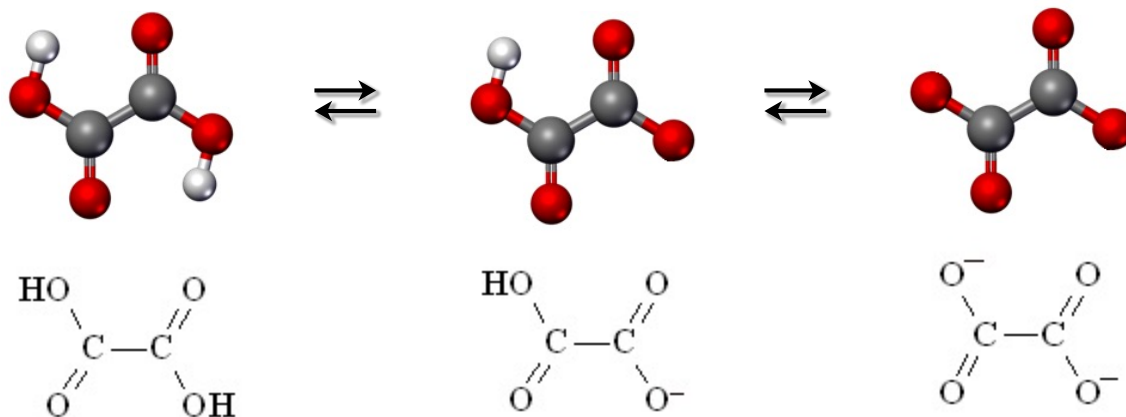
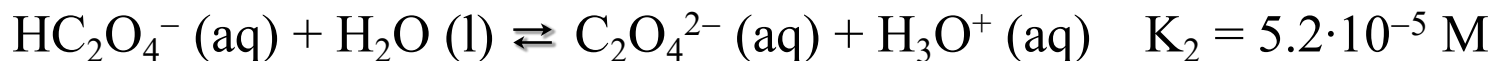
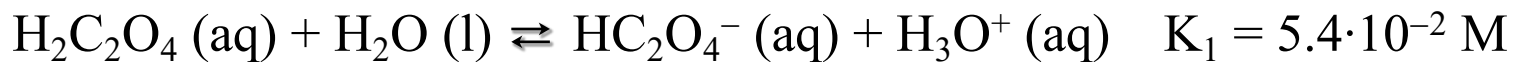
- 60-90%: **calcium oxalate** or calcium phosphate
- 10-15%: kidney stones made of **struvite** ($\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$)
- 5-10%: **uric acid**
- 1%: made by **cistine** (oxidized dimer of cysteine).



Kidney stones made of calcium oxalate (CaC_2O_4)

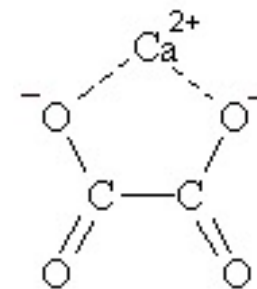
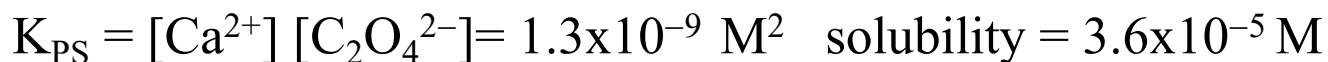
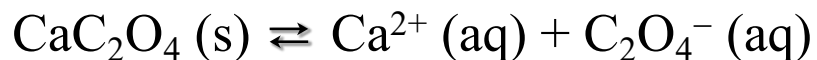


Oxalic acid is a weak diprotic acid

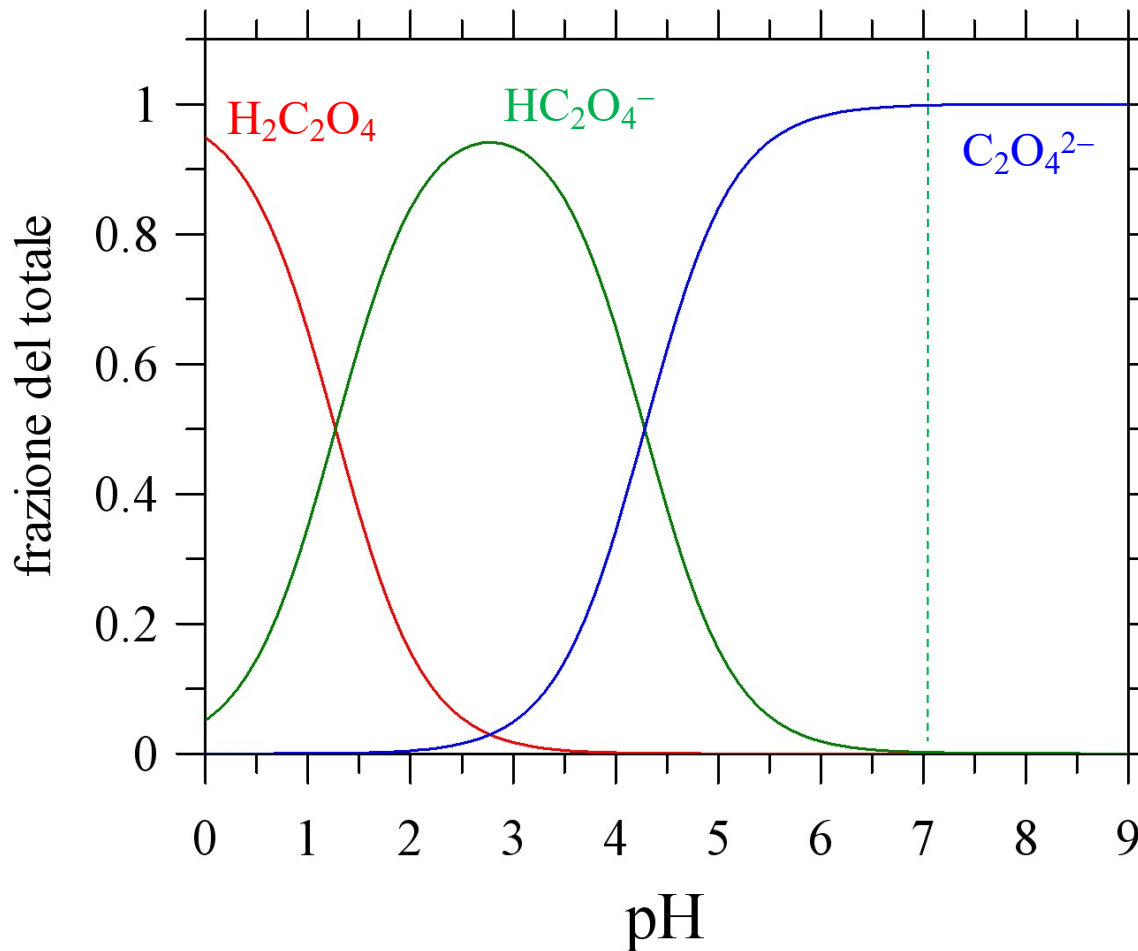
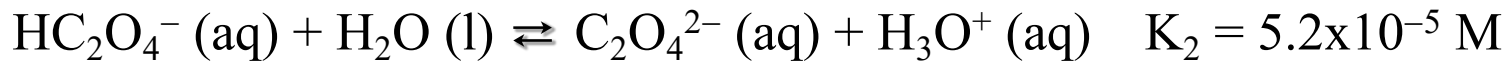
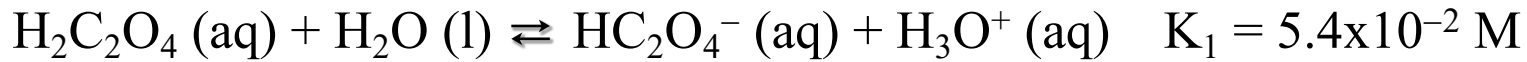


In water its solubility is 143 g/L at 25 ° C (1.59 M).

If Ca²⁺ is added however, the resulting salt (Calcium oxalate) is rather insoluble:



What conditions favour calcium oxalate formation??



pH of urine: 4.6–8.0

A pH > 7 is 99% present as oxalate $\text{C}_2\text{O}_4^{2-}$

Data from “Interpretation of Diagnostic Tests” by J. Wallach, Little Brown & Company Eds, 1979

$[\text{Ca}^{2+}]$ in urine = 2–8 mM

$$K_{\text{PS}} = [\text{Ca}^{2+}] [\text{C}_2\text{O}_4^{2-}] = 1.3 \times 10^{-9} \text{ M}^2$$

$$[\text{C}_2\text{O}_4^{2-}] = K_{\text{PS}} / [\text{Ca}^{2+}] = 1.3 \times 10^{-9} / 0.008 = 1.6 \times 10^{-7} \text{ M}$$

Therefore at pH > 7, a $[\text{Ca}^{2+}] > 1 \text{ mM}$ and oxalate > 10^{-7} M , a precipitate will appear, that could lead to kidney stone formation.

In Hyperoxaluria

urinary oxalate > 40 mg/die = $1.3 \times 10^{-9} \text{ moli/die}$

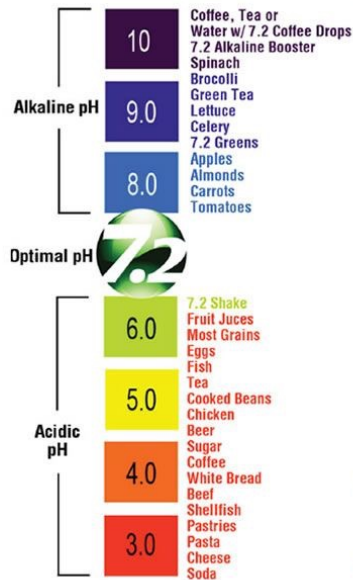
volume of urine = 600–2500 mL/die

$[\text{oxalate}] = 2\text{--}7 \times 10^{-4} \text{ moli}$

$$Q = [\text{Ca}^{2+}] [\text{C}_2\text{O}_4^{2-}] = 2.0 \times 10^{-3} \times 2.0 \times 10^{-4} = 4.0 \times 10^{-7} \gg K_{\text{PS}}$$

Hyperoxaluria can be primary or caused by excessive ingestion of foods containing oxalate (eg, rhubarb, spinach, cocoa, peanuts, pepper, tea) or by excessive reabsorption of oxalates due to various intestinal diseases (eg. bacterial overgrowth syndrome, chronic pancreatitis or biliary disease)

Acid Forming Foods



Alkaline Food Choices



DIET AND KIDNEY STONES

HAVE

- Green tea
- Water with lemon, lime or orange slices or juice
- Low-fat yogurt, kefir or milk
- Broccoli
- Bok choy
- Kale
- Coffee
- Bananas
- Papaya
- Cantalopes
- Raw red and yellow pepper

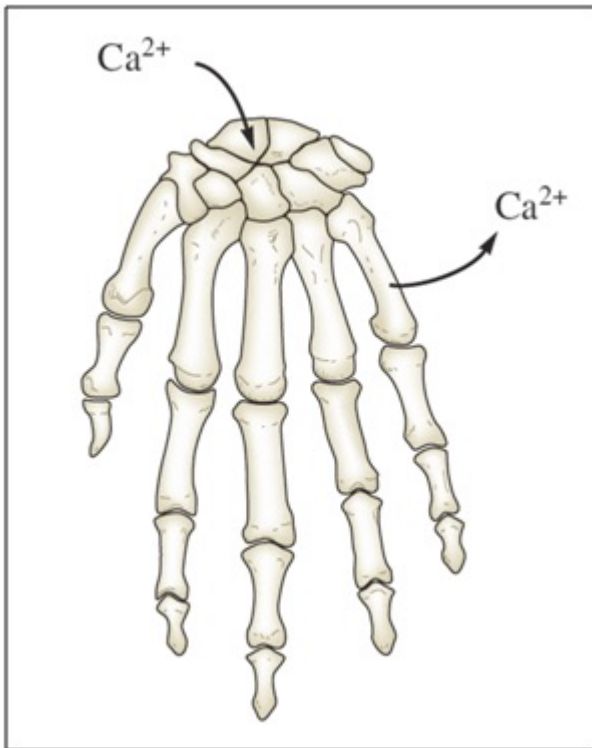
AVOID

- More than 500 mg of calcium, 2000 IU of vitamin D, and 500 mg of vitamin C supplement a day
- Salty and sugary foods
- Cold cuts and other processed meats
- Grapefruit juice
- Swiss chard
- Spinach
- Rhubarb
- Potatoes and yams
- Beets
- Raspberries
- Tofu, miso and other soya foods
- Nuts and seeds
- Beans
- Wheat bran
- Buckwheat
- Dark chocolate and cocoa powder
- Black tea

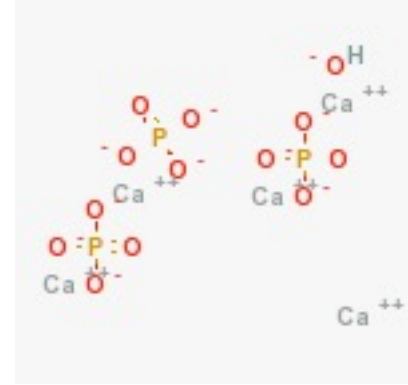
HIGH-OXALATE FOODS

Calcium

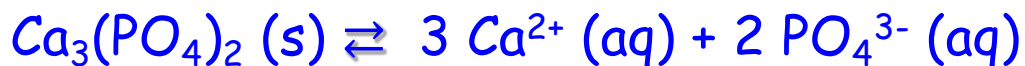
Calcium in body fluids is constantly **exchanged** at millions of construction sites. The reconstruction repairs microfractures and imperfections, allows the growth of the organism and helps in the repair of fractures.



Calcium

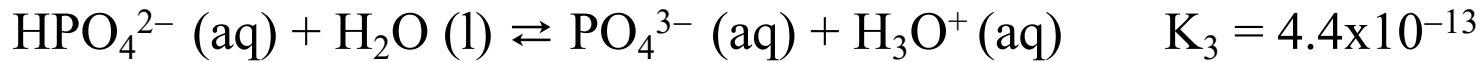
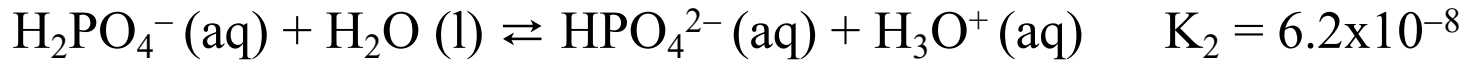
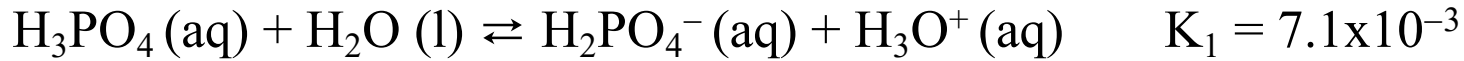


- 1 kg / 70 kg body weight
 - 98% in bones as hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. The OH^- ion can be substituted by F^- , Cl^- , CO_3^{2-}
 - 1% interstitial fluid
 - 1% in plasma
- Ca^{2+} , free and ionized in plasma is 45% del totale (1.1-1.3 mM)
- Ca^{2+} complexed w/ phosphate (5%), citrate (5%), HCO_3^- and albumine (45%)
 - Ca^{2+} and PO_4^{3-} in plasma are close to the solubility
 - In complex with albumin, free $[\text{Ca}^{2+}]$ decreases and the precipitation of calcium phosphate is avoided

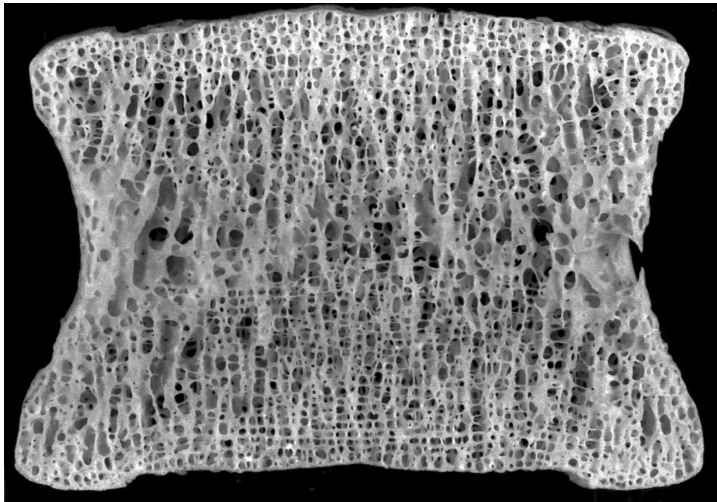
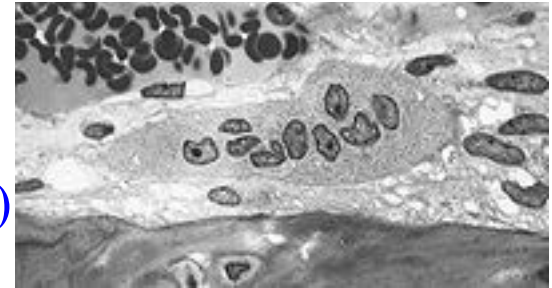
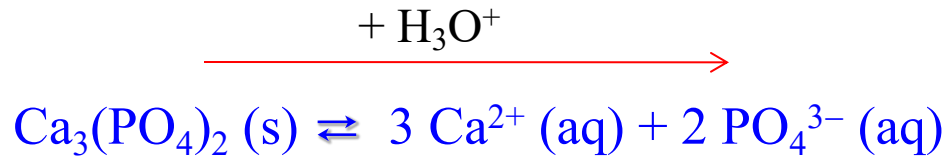


$$K_{\text{pS}} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = 2.0 \times 10^{-29} \text{ M}^5 \quad \text{solubility} = 7.1 \times 10^{-7} \text{ M}$$

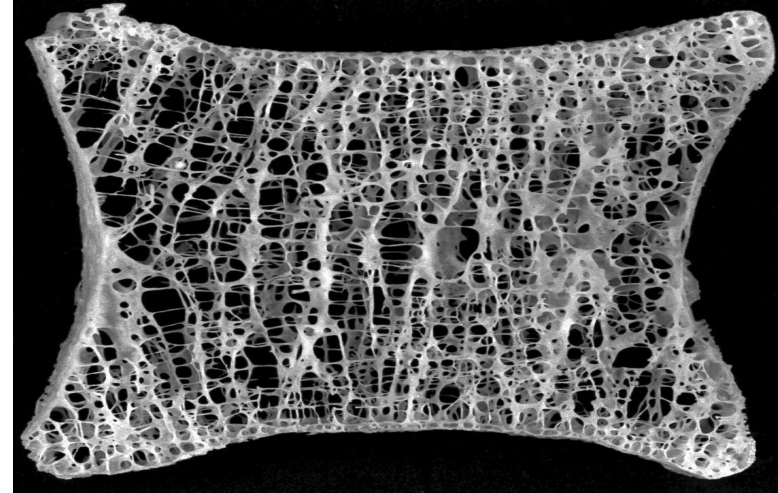
Phosphoric acid



Osteoclasts produce acidic equivalents and enzymes that dissolve the bone matrix.



Normal bone



osteoporosis