Learn About ...

PHOSPHORIC ACID

H_3PO_4

About 10 million tons of phosphoric acid, H_3PO_4, are produced in this country each year. Most of the acid (about 80%) is used in the production of agricultural fertilizers, with the remainder being used for detergent additives (about 10%), cleaners, insecticide production, and cattle feed additives. The commercial method of preparation is the addition of sulfuric acid to phosphate rock.

$$3\ H_2SO_4(\ell) + Ca_3(PO_4)_2(s) + 6\ H_2O(\ell) \longrightarrow 2\ H_3PO_4(s) + 3\ CaSO_4{\cdot}2\ H_2O(s)$$

Pure anhydrous phosphoric acid is a white solid which melts at 42.35°C to form a viscous liquid. In aqueous solution, phosphoric acid behaves as a triprotic acid, having three ionizable hydrogen atoms. The hydrogen ions are lost sequentially.

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \qquad K_{a1} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad K_{a3} = 1.7 \times 10^{-12}$$

Phosphoric acid is not a particularly strong acid as indicated by its first dissociation constant. It is a stronger acid than acetic acid, but weaker than sulfuric acid and hydrochloric acid. Each successive dissociation step occurs with decreasing ease. Thus, the ion $H_2PO_4^-$ is a very weak acid, and HPO_4^{2-} is an extremely weak acid.

Salts of phosphoric acid can be formed by replacing one, two or three of the hydrogen ions. For example, NaH_2PO_4, sodium dihydrogen phosphate, can be formed by reacting one mole of phosphoric acid with one mole of sodium hydroxide.

$$H_3PO_4(aq) + NaOH(aq) \longrightarrow NaH_2PO_4(aq) + H_2O(\ell)$$

[*net ionic form*: $H_3PO_4(aq) + OH^-(aq) \longrightarrow H_2PO_4^-(aq) + H_2O(\ell)$]

Similarly, Na_2HPO_4 (disodium hydrogen phosphate) and Na_3PO4, (trisodium phosphate) could be formed by the reaction of one mole of H_3PO_4 with two and three moles of NaOH, respectively. *(Be sure you are able to write net ionic equations for these processes.)*

Salts containing the anion $H_2PO_4^-$ are weakly acidic. The tendency of this ion to dissociate is greater than its tendency to hydrolyse, that is, its K_{a2}, is larger than its K_b.

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = 6.2 \times 10^{-8}$$

$$H_2PO_4^-(aq) + H_2O(\ell) \rightleftharpoons H_3PO_4(aq) + OH^-(aq) \qquad K_b = K_w/K_{a1} = 1.3 \times 10^{-12}$$

Because $H_2PO_4^-$ is weakly acidic and of low toxicity, it is used as the acid in some baking powders. These baking powders contain NaH_2PO_4 and $NaHCO_3$ (sodium bicarbonate). The leavening action of baking powders results from the production of carbon dioxide gas by an acid-base reaction between these two ingredients.

$$H_2PO_4^-(aq) + HCO_3^-(aq) \longrightarrow HPO_4^{2-}(aq) + H_2O(\ell) + CO_2(g)$$

In the reaction between them, $H_2PO_4^-$ acts as the Brønsted-Lowry acid, HCO_3^- as the base. A comparison of the ionization constants for these two ions reveals that $H_2PO_4^-$ is a stronger acid than HCO_3^-.

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = 6.2 \times 10^{-8}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 4.8 \times 10^{-11}$$

Salts containing the anion HPO_4^- are weakly basic. The tendency of this ion to hydrolyse is greater than its tendency to dissociate.

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad K_{a3} = 1.7 \times 10^{-12}$$

$$HPO_4^{2-}(aq) + H_2O(\ell) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq) \qquad K_b = K_w/K_{a2} = 1.6 \times 10^{-7}$$

Solutions containing the phosphate ion, PO_4^{3-}, are quite basic. This ion has no acidic hydrogen, and its base ionization constant (hydrolysis constant) is relatively large.

$$PO_4^{3-}(aq) + H_2O(aq) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq) \qquad K_b = 5.9 \times 10^{-3}$$

As a result, solutions of soluble phosphates tend to have the same slippery, soapy feel as solutions of strong bases, such as NaOH or KOH.

Phosphoric acid is used primarily in the manufacture of fertilizers, detergents, and pharmaceuticals. In the steel industry, it is used to clean and rust-proof the product. It is also used as a flavoring agent in carbonated beverages (read the ingredients list on a can of Coca-Cola), beer, jams, jellies and cheeses. In foods, phosphoric acid provides a tart, acidic flavor. A recent study reported in the journal *Epidemiology* (Vol 18, pp 501–506, July 2007), found that drinking two or more cola beverages per day doubled the risk of chronic kidney disease. Cola beverages have been associated with kidney changes that promote kidney stones, which may be a result of the phosphoric acid in colas.

In the manufacture of detergents, phosphoric acid is used to produce water softeners. Water softeners remove Ca^{2+} and Mg^{2+} ions from hard water. If not removed, these hard-water ions react with soap and form insoluble deposits that cling to laundry and the washing machine. Phosphates produced from phosphoric acid are used extensively as water softeners (builders) in detergents. The most widely used phosphorus compound in solid detergent mixtures is sodium tripolyphosphate, $Na_5P_3O_{10}$. As a water softener, sodium tripolyphosphate binds to Ca^{2+} and Mg^{2+}, forming soluble chemical species, called complexes or chelates. These complexes prevent the Ca^{2+} and Mg^{2+} from reacting with soap and forming deposits.

Most phosphoric acid is used in the production of fertilizers. Phosphorus is one of the elements essential for plant growth. Organic phosphates are the compounds which provide the energy for most of the chemical reactions that occur in living cells. Therefore, enriching soils with phosphate fertilizers enhances plant growth.

Increasing the phosphate concentration in surface waters also enhances the growth of aquatic plant life. Run-off from fertilized farm lands can stimulate plant growth in lakes and streams. Waste water that contains phosphates from detergents can have the same effect. Lakes that are rich in plant nutrients suffer from accelerated eutrophication. When the lush aquatic plant growth in a nutrient-rich lake dies, the decomposition of the dead plant material consumes dissolved oxygen. This consumption reduces the level of dissolved oxygen to a point where it is insufficient to support animal life. To reduce the threat of lake eutrophication, many localities have banned the use of phosphates in detergents. In some cases, the phosphates have been replaced by carbonates. In others, new detergents have been developed that do not react with the Ca^{2+} and Mg^{2+} ions of hard water.