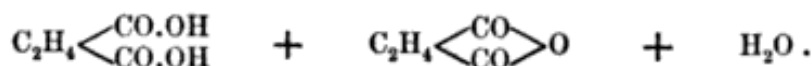
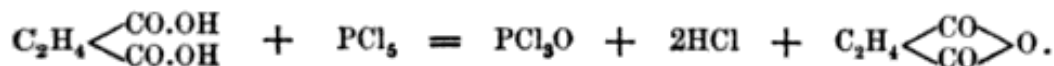


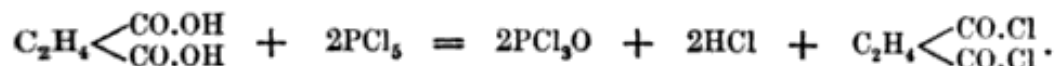
These bibasic acids, when heated, give off their water, and yield anhydrides which, when boiled with water, are reconverted into the acids :



The anhydrides are also produced by treating the acids with phosphorus pentachloride :



With excess of phosphorus pentachloride, acid chlorides or chloroanhydrides are produced ; thus :



**Oxalic Acid**,  $\text{C}_2\text{H}_2\text{O}_4 = \begin{matrix} \text{COOH} \\ | \\ \text{COOH} \end{matrix} = (\text{C}_2\text{O}_2)''(\text{OH})_2$ .—This important

acid exists ready formed in many plants as a potassium or calcium salt, and is produced by the oxidation of a great variety of organic compounds. In some cases the reaction consists in a definite substitution of oxygen for hydrogen ; thus oxalic acid is formed from ethene alcohol,  $\text{C}_2\text{H}_4\text{O}_2$ , by substitution of  $\text{O}_2$  for  $\text{H}_2$ , and from ethyl alcohol,  $\text{C}_2\text{H}_5\text{O}$ , by the same substitution and further addition of one atom of oxygen. But in most cases the reaction is more complex, consisting in a complete breaking up of the molecule. In this manner oxalic acid is produced in great abundance from more highly carbonized organic substances, such as sugar, starch, cellulose, etc., by the action of nitric acid, or by fusion with caustic alkalies.

Oxalic acid is also produced : *a.* As a sodium or potassium salt by direct combination of the alkali-metal with carbon dioxide :

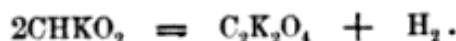


The sodium salt is obtained by passing carbon dioxide over a heated mixture of sodium and sand ; the potassium-salt by heating potassium-amalgam in the gas.\*

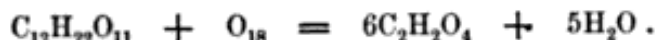
*b.* As an ammonium salt, together with other products, in the decomposition of cyanogen by water :



*γ.* As a potassium salt by heating potassium formate with excess of potash :



*Preparation.*—1. By the oxidation of sugar with nitric acid :

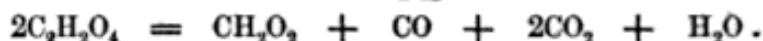


One part of sugar is gently heated in a retort with 5 parts of nitric acid of sp. gr. 1.42, diluted with twice its weight of water ; copious red fumes are then disengaged, and the oxidation of the sugar proceeds with violence and rapidity. When the action slackens, heat may be again applied to the vessel, and the liquid concentrated by distilling off the superfluous nitric acid, until it deposits crystals on cooling. These are drained, redissolved in a small quantity of hot water, and the solution is set aside to cool.

\* Kolbe and Drechsel, Chem. Soc. Journal [2], vi. 121.

2. By heating sawdust with caustic alkali. Many years ago, Gay-Lussac observed that wood and several other organic substances were converted into oxalic acid by fusion with caustic potash. Upon this observation, Messrs. Roberts, Dale & Co. have founded a method for the preparation of oxalic acid, which furnishes this acid at a much cheaper rate than any other process. A mixed solution of the hydrates of sodium and potassium, in the proportion of two molecules of the former to one of the latter, is evaporated to about 1.35 sp. gr., and then mixed with sawdust, so as to form a thick paste, which is placed in thin layers on iron plates. The mixture is now gradually heated, care being taken to keep it constantly stirred. The action of heat expels a quantity of water, and the mass intumesces strongly, with disengagement of much inflammable gas, consisting of hydrogen and carburetted hydrogen. The mixture is now kept for some hours at a temperature of  $204^{\circ}$  C. ( $400^{\circ}$  F.), care being taken to avoid charring, which would cause a loss of oxalic acid. The product thus obtained is a gray powder; it is now treated with water at about  $15.5^{\circ}$  C. ( $60^{\circ}$  F.), which leaves the sodium oxalate undissolved. The supernatant liquid is drawn off, evaporated to dryness, and heated in furnaces to recover the alkalies, which are caustified and used for a new operation. The sodium oxalate is washed and decomposed by boiling with slaked lime, and the resulting calcium oxalate is decomposed by means of sulphuric acid. The liquid decanted from the calcium sulphate is evaporated to crystallization in leaden vessels, and the crystals are purified by re-crystallization.

Oxalic acid separates from a hot solution in colorless, transparent crystals derived from an oblique rhombic prism, and consisting of  $C_2H_2O_4 \cdot 2H_2O$ . The two molecules of crystallization-water may be expelled by a very gentle heat, the crystals crumbling down to a soft white powder, consisting of anhydrous oxalic acid,  $C_2H_2O_4$ , which may be sublimed in great measure without decomposition. The crystallized acid, on the contrary, is decomposed by a high temperature into formic acid, carbon monoxide, and carbon dioxide, without leaving any solid residue:



The crystals of oxalic acid dissolve in 8 parts of water at  $15.5^{\circ}$ , and in their own weight, or less, of hot water: they are also soluble in spirit. The aqueous solution has an intensely sour taste and most powerful acid reaction, and is highly poisonous. The proper antidote is chalk or magnesia. Oxalic acid is decomposed by hot oil of vitriol into a mixture of carbon monoxide and carbon dioxide: it is slowly converted into carbonic acid by nitric acid, whence arises a considerable loss in the process of manufacture from sugar. The dioxides of lead and manganese effect the same change, becoming reduced to monoxides, which form salts with the unaltered acid.

**Oxalates.**—Oxalic acid, like other bibasic acids, forms with monatomic metals, neutral or normal salts containing  $C_2M_2O_4$ , and acid salts,  $C_2HMO_4$ . With potassium and ammonium it likewise forms hyper-acid salts, *e. g.*,  $C_2HKO_4 \cdot C_2H_2O_4$ , or  $C_4H_3KO_8$ . With most diatomic metals it forms only neutral salts,  $C_2M''O_4$ ; with barium and strontium, however, it forms acid salts analogous to the hyper-acid oxalates of the alkali-metals. It also forms numerous well-crystallized double salts. It is one of the strongest acids, decomposing dry sodium chloride when heated, with evolution of hydrochloric acid, and converting sodium chloride or nitrate in aqueous solution into acid oxalate.