7. *Doubly-Linked Carbon Atoms.—*When carbon atoms are doubly linked, as in derivatives of ethylene, H2C:CH2, the two tetrahedra representing the four groups around each carbon may be supposed to have two summits combined, as was supposed with one in simple linking. Fig. 5 represents this supposition, from which follows that the six atoms in question are situated in a plane and may be represented by a plane figure:—

The chief consequence is that as soon as the two atoms or groups attached to each carbon are different, two stereo-isomers may be looked for:—

Such has been found to be the case, fumaric and maleic acids,

forming the oldest and one of the most simple examples ; the simplest is α-chlorpropylenc (H3C)HC :CClH.

The nature of this stereo-isomerism is quite different from that in antipodes. There is no enantiomorphism in the supposed con­figurations, and so no rotatory power, &c., in the corresponding compounds, which, on the other hand, show differences far deeper than antipodes do, having different melting points, solubility, heat of formation, chemical properties, &c., behaving in these as ordinary isomers. These isomers, having some relation to those in cyclic compounds, may be also denoted as *cis-*(maleic) and *trans-*(fumaric) forms, a close analogy existing indeed in those ring systems of which the simplest type is:—

this has been realized in the 1, 3-tetramethylene dicarboxylic acids, which exist in a trans- and cis-form :—

When two double carbon linkings are present, as in H2C:C:CH2, the four hydrogen atoms form the summits of a tetrahedron accord­ing to the development in fig. 4 ; and consequently the introduction of different groups may bring enantiomorphism and optical antipodes. This has been realized in the compound 1-methyl-*cyclo*-hexylidene-4- acetic acid (formula I.), first prepared by W. H. Perkin and W. J. Pope in 1908, and resolved into its components by fractional crystal­lization of its brucine salt by Perkin, Pope and Wallach. The substance resolved by W. Marckwald and R. Meth in 1906, which was regarded as this acid, was really the isomeric 1-methyl-Δ3- cydσ-hexene-4-acetic acid (formula 11.), which contains asymmetric carbon atoms (see *Journ. Chem. Soc.,* 1909, 95, p. 1791; cf. ibid., 1910, 97, p. 486).

8. *Numerical Value of Optical Rotation.*—To express the value of optical rotation either specific or molecular rotation may be chosen, the first being the deviation caused by a layer of 1 decimetre in length when the substance in question is supposed to be present with specific gravity 1, the latter is this value multiplied by one-hundredth of the molecular weight. Specific rotation is indicated by [α]tD, where the suffix indicates the wave-length of the light in question, D being that of the sodium line, and *t* the temperature; [M]tD is the corre­sponding value of molecular rotation. Both values vary with the solvent used, and probably are most adapted to solve problems touching relations of rotatory power and configuration, -when they apply to extreme dilution in the same liquid.

One of the most general rules, relating to rotatory power, is that for electrolytes, *i.e.* salts in aqueous solution, viz. the limiting rota­tion in dilute solution only depends on the active radicle. Oudemans found that for such active bases as quinine in its salts with hydro­

chloric, nitric, chloric, acetic, formic, sulphuric, oxalic, phosphoric, perchloric acids the specific rotation (calculated for the base) only varies from -272° to —288°; H. H. Landolt found the same thing for active acids, the mono lithium, sodium, potassium and ammonium tartrates varying only between 27∙5° and 28∙5° (calculated for the acid). A corresponding rule may be expected where both base and acid have rotatory power; the molecular rotation will be the sum of those for base and acid in salts with inactive radicles. Each of these rules, finds sufficient explanation in Arrhenius’s view of electrolytic dissociation, which admits that diluted electrolytes are split up in their ions, and so the salts of quinine (Q) owe their

rotatory power to the ion QH, those of acid tartrates to the ion C4H5O6, and quinine-tartratc to both.

With.non-electrolytes relations are less evident. One general obser­vation is that non-saturation, especially cyclic structure, augments rotatory power. The saturated compounds, hydrocarbons, alcohols, ethers, amines and acids rarely show specific rotations higher than 10°, and some of them, as mannite, CH2OH(CHOH)4CH2OH, for instance, show such small values that only a more thorough investigation, due to the theoretical probability of rotatory powers in asymmetric natural products, has detected the optical activity.

Unsaturated compounds generally show larger rotative powers; amyl alcohol with —5° produces an aldehyde with 15°; succinic (diamyl) ether with 9° produces fumaric ether with 15°, &c. Cyclic configuration especially leads to the highest values known: the lactic acid with 3° leads to a lactone with —86°,

mannosaccharic acid, HO2C(CHOH)4CO2H, to a dilactone (with two rings, formed by the loss of two molecules of water) with 202°, whereas the original acid only shows a small rotation.

A second conception, which connects rotation with configuration in non-electrolytes, is due to Alexander Crum Brown and P. A. Guye. It starts from the simple assumption that, as rotatory power is due to the difference of the four groups around the asymmetric carbon, so its amount may correspond to the amount in this. So, generally speaking, take some property, denoted by K1, ... K4 respectively, a function:—

(K1-K2) (K1-K3) (K1-K4) (K2-K3) (K2-K4) (K3-K4) would express what is. wanted. It becomes zero when two groups are equal ; it changes its sign, retaining its value, when K1 is inter­changed with K2, &c. The. chief difficulty in application is to point out that property which is here dominating. It has been supposed to be weight, and then the above expression divided by (Kι+K2+K3+K4)6 might be proportional to specific rotation. This explains, for instance, that in the homologous series of glyceric

ethers

, augmenting the heaviest group, ·CO2R, first

augments the specific rotation, which then passes through a minimum (the theoretical limit being zero) :—

Ether of methyl, ethyl, propyl, butyl, hexyl, octyl, [α]D = -4∙8°, -9∙2°, -12∙9°, -13∙2°,-11∙3°,-10∙2°.

But the serious objection is met that groups of equal weight and different structure often allow considerable rotatory power as in 'methyl acetylamygdalate, with —146°, though in the formula C6H5HC(OC2H3O) (CO2CH3) the third and fourth groups are of equal weight. It is in this way especially that other properties might be tested, such as volume or density, and perhaps qualities related to light, such as refractive power and the dielectric constant. At­tempts to. connect the rotatory power of a compound with more asymmetric carbons to the action of each of these separately, *i.e.* by the so-called optical superposition have not been very successful. In the four stereo-isomeric acids CO2H(CHOH)3CH2OH of the following configurations

We might suppose the upper asymmetric carbon to produce a rotation + A or — A, the other ± B and ± C. The rotations then were A — B — C, A + B + C, — A. — B + C and — A + B — C or zero in total. This supposition is in so far related to that of Crum Brown and Guye that it admits that the smallest conceivable change, *i.e.* stereo-isomeric change, in one group does not influence the rotation caused by the asymmetric carbon attached to it. It has not been tested in this case, but substances as propyl- and isopropyl-glycerate only differ in specific rotation from — 12∙9° to