

## RESEARCH ITEMS.

The Determination of Some Combinatory Numbers concerning Groups, Graphs and Chemical Compounds.—Polya [*Acta. Math.*, B. 68, (3-4), pp. 145-253] has solved very interesting problems in this extensive article which are of great value for the organic chemist. Cayley had determined the number of topologically distinct graphs which has been generalised in a very extensive manner by Polya. The fundamental mathematical problem which he solves and on which he bases his results concerning the number of structure-isomers and stereo-isomers of some organic compounds is the following :

Let  $\phi^{(1)}, \phi^{(2)}, \dots$  etc., be a collection of packets, [He uses the word figure to emphasise its connection with the applications.] each of which contains a number of red, blue and yellow balls. All of them are supposed to be distinct from one another. Let  $\phi^{(\lambda)}$  contain  $\alpha_\lambda$  red balls,  $\beta_\lambda$  blue balls and  $\gamma_\lambda$  yellow balls. Let  $a_{klm}$  be the number of packets among these such that  $\alpha_\lambda = k, \beta_\lambda = l, \gamma_\lambda = m$ . Let  $\Lambda$  be a permutation group of  $s$  elements of order  $h$ . Let  $h_{j_1 j_2 \dots j_s}$  be the number of permutations of  $\Lambda$  of type  $[j_1, j_2, j_3, \dots, j_s]$ , i.e., the permutation when resolved into cycles in the ordinary way contains  $j_r$ ,  $r$ -dimensional cycles. Let us consider  $[\phi_1, \phi_2, \dots, \phi_s]$  an arrangement of  $s$  packets taken out of the given collection of packets, it being understood that a packet of the collection may occur any number of times in this arrangement. Let the total number of red, blue and yellow balls in this arrangement be  $k, l$ , and  $m$  respectively. Two such arrangements are considered to be equivalent *w.r.t.*  $\Lambda$  when there exists some permutation of  $\Lambda$  which carries one into the other. The problem to be solved is the determination of the total number  $A_{klm}$  of such arrangements (containing  $k$  red balls,  $l$  blue balls,  $m$  yellow balls) which are not equivalent *w.r.t.*  $\Lambda$ . For this purpose he considers the series

$$f(x, y, z) = \sum_{(klm)} a_{klm} x^k y^l z^m$$

and  $F(x, y, z) = \sum \Lambda_{klm} x^k y^l z^m$  and derives the following functional equation between them.

Let

$$\frac{1}{h} \sum_{(j)} h_{j_1 j_2 \dots j_s} f_1^{j_1} f_2^{j_2} \dots f_s^{j_s}$$

be called the *cycle-show-er* of the group [called the *haupt-characteristic* in the theory of representation of groups].

$$\text{Then } F(x, y, z) = \frac{1}{h} \sum_{(j)} h_{j_1 j_2 \dots j_s} [f(x, y, z)]^{j_1}$$

$$[f(x^2, y^2, z^2)]^{j_2} [f(x^3, y^3, z^3)]^{j_3} \dots \text{ etc.}$$

By means of this functional equation the coefficients can be determined in a recursive way.

The proof he gives is very interesting and comparatively simple. As a special case of this problem he gives an interesting particular example. Suppose there are 3 red balls, 2 blue balls and one yellow ball. We can place these at the six vertices of a regular octahedron in  $\frac{6!}{3!2!}$

different ways as is known from elementary permutation theory. Now suppose that we consider two such placings as not distinct if we could turn the octahedron in such a way that the former arrangement goes over into the latter. Then a particular case of this general problem is the determination of the total number of distinct arrangements with the modification. It comes out to be 3.

In a chapter of this article he treats of the problem of the distinct number of trees, i.e., one dimensional graphs which satisfy certain conditions. Thereby he precises various earlier definitions. The structural formula of a chemical compound can be considered as a topological *tree*. It may have to satisfy various conditions. If we consider the structural formula of paraffin, we easily see that if it contains  $n$  carbon atoms, it must contain  $2n + 2$  hydrogen atoms. The *tree* that corresponds is a *free-tree*, i.e., no single atom in it is specialised. If we consider an alcohol of the form  $C_n H_{2n+1} OH$  there corresponds a *tree with a specified root*, where the OH-radical in the structural formula must be considered as the root. He considers the OH-radical as the root. Then there will be three principal branches starting from the carbon atom to which the OH-radical is attached. According as the models we consider are the stereo-models, planar models or the topologically distinct models we have the permutation groups [of the principal branches] to be  $A_3$  the alternate group,  $Z_3$  the cyclic group, or  $S_3$  the symmetric group. The principal branches are considered as the packets of the mathematical problem. It is clear that we have only one variable  $x$  instead of  $x, y$  and  $z$  and both  $P(x)$  and  $f(x)$  are easily expressed in terms of  $r(x), s(x)$ , etc. By means of this analysis he obtains a series of interesting functional equations of these functions some of which are given below :—

(1) Let  $\rho_n$  be the number of structurally distinct theoretically possible paraffins of the form  $C_n H_{2n+2}$  and  $R_n$  be the number of structure isomers of the form  $C_n H_{2n+1} OH$ . Let  $r(x) = \sum R_n x^n$ . Then we have the following functional equation for the determination of  $R_n$

$$r(x) = 1 + x \cdot \frac{r^3(x) + 3r(x)r(x^2) + 2r(x^3)}{6}$$

$\rho_n$  also can be calculated from  $r(x)$  by means of a slightly complicated formula.

(2) Let  $S_n$  be the number of stereo-isomers of alcohol of the molecular formula  $C_n H_{2n+1} OH$ ; and  $Q_n$  the number of structure-isomers of alcohol of the molecular formula  $C_n H_{2n+1} OH$  without any asymmetric carbon atom. If

$$s(x) = S_0 + S_1 x + S_2 x^2 + S_3 x^3 + \dots$$

and  $q(x) = Q_0 + Q_1 x + Q_2 x^2 + Q_3 x^3 + \dots$  then

$$s(x) = 1 + x \cdot \frac{s^3(x) + 2s(x^3)}{3}$$

$$q(x) = 1 + x q(x) q(x^2)$$

From  $S_n$  and  $Q_n$  the number of stereo-isomers of paraffin of the molecular formula  $C_n H_{2n+2} = \sigma_n$  and  $K_n =$  the number of structure-isomers of

Paraffin  $C_nH_{2n+2}$  without asymmetric carbon atoms can be easily calculated.

It is interesting to observe that  $q(x)$  is also equal to the continued fraction

$$1 - \frac{x}{1 - \frac{x^2}{1 - \frac{x^4}{\dots - \frac{x^{2n}}{1 - \dots}}}}$$

which is easily derived from its functional equation. He has also determined some upper bounds for these numbers and discussed the asymptotic behaviour of these as  $n \rightarrow \infty$ . For this purpose he has denoted the radius of convergence of these power series by  $k$ ,  $\rho$  and  $\sigma$  and has proved at first

$$1 > k > \rho > \sigma > \frac{4}{27}, \text{ etc.},$$

also that each of these functions has only one singular point on their respective circles of convergence, the point being a pole of the first order for  $q(x)$  and algebraical branch point for the others. By means of the following theorem, viz.,

$$\text{If } f(x) = a_0 + a_1x + \dots + a_nx^n + \dots$$

has  $x = 1$  as the only singular point on its circle of convergence  $|x| = 1$ , and in the neighbourhood of 1

$$f(x) = (1-x)^{-s} g(x) + (1-x)^{-t} h(x)$$

where  $g(x)$  and  $h(x)$  are regular at  $x = 1$ ,

$$s > t \geq 0 \text{ then } a_n \sim n^{s-1} \frac{g(1)}{\Gamma(s)}, [\text{where } g(1) \neq 0]$$

he has proved various asymptotic formulæ. Some are given below:—

$$R_n \approx \rho^{-n} n^{-\frac{3}{2}} \cdot \frac{b}{2\sqrt{\pi}} \text{ where } b \text{ is some constant,}$$

$$Q_n \approx k^{-n}, S_n \approx \sigma^{-n} n^{-\frac{3}{2}}, \text{ etc. He has also determined the same numbers for substituted paraffins, etc.}$$

K. V. I.

**Studies in the Synthesis of Flavonols : The Oxidation of Flavindogenides.**—Algar and Carey in the course of their experiments on the synthesis of flavonols (*Proc. Roy. Irish Acad.*, 1937, 44, B4, 37-43), have described the oxidation of a few 3-arylidene flavanones by potassium permanganate, when 3-hydroxy-3-benzoyl-flavanones were obtained. The oxidation products on gentle hydrolysis with alkali gave the corresponding flavanol and the acid RCOOH and on treatment with cold acetic anhydride and sulphuric acid, a monoacetate. The product obtained on boiling with acetic anhydride and sodium acetate had the same molecular formula as the starting hydroxy flavanone but its exact nature is still somewhat doubtful. The oxidation products showed no colouration with alcoholic ferric chloride but dissolved in concentrated sulphuric acid, a green or violet fluorescence developed on standing. The products obtained by applying the above reactions to 3-benzylidene-flavanone, 3-anisylidene flavanone, 3-piperonylidene flavanone and 3-benzylidene-3', 4'-methylenedioxy flavanone have been described.

**Synthetic Cyperones and Their Comparison with  $\alpha$ - and  $\beta$ -Cyperones.**— $\alpha$ - and  $\beta$ -cyperones occurring in the oil of the tubers of

*Cyperus rotundus* have been synthesised by two different methods (P. S. Adamson, F. C. McQuillin, Robert Robinson and J. L. Simonsen, *J.C.S.*, 1937, 1576-1581) and the synthetic products have been found to be structurally identical with natural compounds, thus establishing the correctness of the constitution assigned to the cyperones. The application of the elegant cyclic ketone synthesis of du Feu, McQuillin and Robinson by condensation of *l*-diethylaminopentan-3-one and the sodio-derivative of *l*-dihydrocarvone and subsequent dehydration with sodium ethoxide gives  $\alpha$ -cyperone, and dehydration by cold 50 per cent. sulphuric acid gives  $\beta$ -cyperone. The synthetic  $\alpha$ -cyperone had lower optical activity than the natural ketone, the density, refractive index and boiling point being almost the same. The semicarbazone of the racemised synthetic  $\alpha$ -cyperone was crystallographically different from that of natural  $\alpha$ -cyperone, though polymorphism was not excluded. In the alternative method, the sodio-derivative of *l*-dihydrocarvone is condensed with ethyl- $\beta$ -chloropropionate and then with ethyl oxalate in alcoholic solution, ethyl-3-carbethoxy-1-methyl-4-isopropylcyclohexan-2-one-1- $\beta$ -propionate being obtained after removal of  $CO_2$ . The keto-acid obtained on hydrolysis was esterified and then condensed with zinc and ethyl- $\alpha$ -bromopropionate. On hydrolysis of the main product, a ketone closely resembling  $\beta$ -cyperone was obtained. The semicarbazones of the synthetic  $\beta$ -cyperone by the two methods had identical m.p. and the rotatory power was not very different. The cyperones get readily racemised.

**Production of the Latent Photographic Image by Hydrogen Peroxide.**—Besides radioactivity, phosphorescence and heat, traces of hydrogen peroxide are found to produce latent images on the photographic emulsions. The effect of increasing concentration of hydrogen peroxide has been found to be similar to that of increasing light intensity. The reaction is initially of the second order, the decrease of the apparent order of the net reaction with increasing density being probably due to a reverse reaction, causing developable grains to become undevelopable. An optimum concentration for the production of the maximum density of the latent photographic image by hydrogen peroxide in aqueous solution is indicated (Merton W. Jones and Julian M. Blair, *Journal of Chemical Physics*, 1937, 5, 835).

K. S. RAO.

**Glaciers and Glacial Lakes of the Wicklow Hills.**—In a paper on "A map of the glacier lakes and the local glaciers of the Wicklow Hills" Charlesworth (*Proc. Roy. Irish Acad.*, Section B, 44, No. 3) records further investigations of the glacial events in the Wicklow region during the later stages of the glacial period. After describing the local glaciers, the author gives a detailed account of the glacier lakes on the eastern and western sides, and illustrates his observations with a map. It is hoped in this way to help to visualise the further problems that may remain to be solved, in particular the consequences which may be expected to flow from the relationship of the products of the

local glaciers to the lacustrine sediments of the glacier lakes.

**The Meiotic Divisions in the Spermatogenesis of *Ichthyophis glutinosus*.**—The maturation divisions in the testis of *Ichthyophis* are described by B. R. Seshachar (*Zeitsch. f. Zell.*, 1937, 27, Part 2). The primary spermatocytes which are the products of division of the spermatogonia embark on the prophase of the first division after a brief period of rest. The leptotene filaments are formed soon after and the polar orientation of the filaments results in a leptotene bouquet. Parallel conjugation of the leptotene filaments gives rise to the thicker pachytene threads, the conjugation beginning at the proximal pole. When the fusion between the apposing filaments is more or less intimate the polarisation is lost and immediately after, splits appear along the threads at intervals, giving rise to the diplotene stage. The diplotene is followed by a pronounced and conspicuous diffuse stage where all individuality of the chromosomes is temporarily lost, the nucleus itself becoming a faintly staining reticulum, in its greatest developments. Soon, the chromosomes emerge from the diffuse mass and the bivalents which now appear more or less clear, twist about each other giving rise to the strepsinema. A condensation and contraction of the chromosomes give rise to the diakinesis where 21 deeply staining tetrads of different forms are seen arranged peripherally inside the nuclear membrane. The spindle is formed between the centrioles, the nuclear membrane is lost and the tetrads take their place on the spindle. 21 tetrads can be clearly seen in the metaphase plates of the division, the four components of each tetrad being seen clearly for the first time in anaphase. A conspicuous interkinesis separates the first and second divisions, when the nucleus resumes the appearance of a faintly staining network. The second division follows quickly separating each dyad into two monads. 21 dyads are seen in the metaphase plates of this division, while 21 monads can be counted in the anaphase plate. The resulting cells are the spermatids.

**Chromosomes of Pyrgomorphinae.**—An examination of the chromosomes of eight genera of Pyrgomorphinae has been made by T. Ramachandra Rao (*Journ. Morph.*, September 1937, 16, No. 2). In the spermatogonia of all the genera studied, there are 19 rod-shaped telomitic chromosomes which differ considerably regarding their actual sizes in the different genera. However, an analysis of the measurement of second spermatocyte chromosomes shows that as regards proportional sizes and insertion there is some degree of uniformity within the subfamily. In *Aularches*, *Atractomorpha*, *Chrotogonus*, *Colemania* and *Pyrgomorpha*, the members of the smallest pair of autosomes appear as roundish or oval bodies and are comparable in shape, relative size and behaviour with the 'small' dot-like chromosomes of the general Acrididæ, while in *Orthacris* and *Zarytes* they are not so and merge into the general series. The sex chromosome is the largest one in the complexes, or the second largest as in *Pecilocerus*. The usual forms of tetrads occur in the

spermatocytes. It is found that the number of ring tetrads in any genus depends upon the length of the chromosomes; in genera with longer chromosomes there are more of them than in genera with shorter ones. While no final explanation has been offered regarding the chromosome relationship between this subfamily and the other Acrididæ, some points arising out of the present study have been briefly discussed, and it is shown that a simple process of elimination of two pairs is not sufficient to explain the smaller chromosome number in Pyrgomorphinae.

**The Occurrence of V-shaped Centrioles in the Spermatocytes of some Neuropteran Insects.**—Among the insects several species of Lepidoptera, Hymenoptera and Orthoptera have been reported upon with regard to the structure and behaviour of their centrioles. And the work previously done has been summarized by Johnson (*Zeit. Wiss. Zool.*, 1931, 140, 116-62); and recently by Risley (*Zeit. Wiss. Zool.*, 1936, 148, 133-58). But the group, Neuroptera, had remained unknown in this direction.

In a recent paper with the above-mentioned title (*Annot. Zool. Japan*, September 30, 1937, 16, No. 3), J. J. Asana and S. Makino record their observations on a comparative study of the Centrioles in the species representing the Neuropteran genera, *Palpares*, *Macronemurus*, *Myrmeleon*, *Myrmecaelurus* and *Neuroleon*.

The two V-shaped centrioles, with their widely diverging, thin rod-like arms, come to lie at the opposite poles as the metaphase spindle of the primary spermatocyte is formed. The concavity of the V-shaped centrioles is sometimes directed towards the equatorial plate of the spindle and sometimes away from it. In the telophase of the primary spermatocyte division, the two arms of each of the two V-shaped centrioles break apart, and as two slender, rod-like bodies they enter into interkinesis.

These centrioles of the Neuropteran species materially differ in shape and length of their arms from those of Lepidoptera. They also differ, though not so widely, from those of Orthoptera. But curiously enough Neuroptera show greater resemblance in the shape of their centrioles to Chelonia, recently investigated by Risley (1936) in his paper above cited.

**A Trichomonas from the Blood of a Hamster.**—Trichomonads from Mammalian blood are rare and W. L. Yakimoff and A. I. Sprinholz-Schmidt (*Journ. Roy. Micros. Soc.*, September 1937, 57, Part 3), report the occurrence of a Trichomonas from the blood of *Cricetulus furunculus*. A broad spindle-shaped body, a central axostyle protruding posteriorly as a spine, an anterior elongated nucleus, and three anterior and one posterior flagella characterise the animal. A few metachromatic granules were also found in the cytoplasm. Though the examination of the blood was done after the death of the host, there is every reason to believe that they are normally parasites in the blood of the host and their presence in blood is not due to secondary invasion from the alimentary canal.