

*Issued 15/3/1893.*

# PROCEEDINGS

## OF THE

# CHEMICAL SOCIETY.

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**No. 121.****Session 1892-93.**

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March 2nd, 1893. Dr. J. H. Gladstone, F.R.S., Vice-President, in the Chair.

Messrs. T. K. Rose, K. K. Kacker and C. M. Luxmoore were formally admitted Fellows of the Society.

It was announced that the following additions to the bye-laws proposed by the Council would be presented for consideration at the coming General Meeting:—

- 1.—In Bye-Law XI, after the words “The ordinary Scientific Meetings of the Society shall be held twice in every month, from November to June inclusive, except in the month of January, when the Society shall meet once only,” to add the words “and also at Easter, when, if the Council see fit, there shall also be only one meeting in the month.”
- 2.—In Bye-Law XIII, to add the following paragraph:—

“At all General Meetings of the Society, whether annual or extraordinary, no motion of a proposal to alter the bye-laws shall be considered of which due notice has not been given, at least 14 days previously, either at an ordinary Scientific Meeting, or through the agency of the “Proceedings,” or by means of a printed notice addressed to all the resident Fellows.”

Attention was directed to the following resolutions passed at a meeting held on March 1st, 1893, at the Royal Agricultural Society's rooms, H.R.H. the Prince of Wales, K.G., in the chair:—

“That, having regard to the great national importance of the series of experiments which have been carried on at Rothamsted during the last 50 years, it is desirable that some public recogni-

tion should be made of the invaluable services thus rendered to agriculture by Sir John Lawes, and also by Dr. Gilbert, who has been associated with the experiments during the whole period.

"That, with this object, subscriptions, to be limited to two guineas, be invited from all interested in agriculture, whether scientific or practical.

"That, in the opinion of this meeting, the testimonial might advantageously take the form of (1) a granite memorial, with a suitable inscription, to be erected at the head of the field where the experiments have taken place; (2) addresses to Sir John Lawes and Dr. Gilbert, accompanied (if funds permit) by a commemorative piece of plate."

Ordinary certificates were read for the first time in favour of Messrs John Charles Burnham, 179, Griffin Road, Plumpstead; James Cameron, Nobel's Explosive Co., Polmont Station, A.B.; Henry Williamson Dixon, 258, Hunslet Road, Leeds; Thomas Edwards, Brewery House, Rhymney; Hedley Gordon Jones, 15, Rectory Place, Woolwich.

Of the following papers those marked \* were read :—

**\*121. "The magnetic rotation and refractive power of ethylene oxide."  
By W. H. Perkin, Ph.D., F.R.S.**

The following values are recorded in the paper :—

$$d \ 4^{\circ}/4^{\circ} = 0.8909; \quad d \ 7^{\circ}/4^{\circ} = 0.88654; \quad d \ 7^{\circ}/7^{\circ} = 0.8867; \\ d \ 10^{\circ}/10^{\circ} = 0.8824.$$

Molecular magnetic rotation at  $8^{\circ} = 1.935$ .

Molecular refraction at  $7^{\circ}$ ,  $A = 17.680$ .

Dispersion,  $G - A = 0.5494$ .

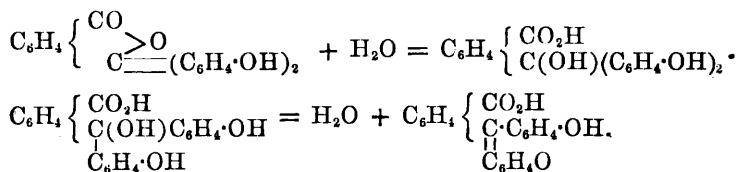
It is pointed out that the magnetic rotation is most remarkably low, and the refractive power also below the calculated value ( $A = 18$ ).

**\*122. "The origin of colour (including fluorescence). VII. The phthalins and fluoresceins." By Henry E. Armstrong.**

In the first of these communications on the origin of colour (these Proceedings, 1888, No. 4, p. 27), exception was taken to the formulæ assigned to phenolphthalein and its congeners. Although the exhibition of colour by these substances could not be accounted for by the formulæ ascribed to them, the data then available were insufficient to permit of more satisfactory formulæ being devised. The subse-

quent discovery of the rhodamines strengthened this conviction, and the intention to make these the subject of experimental study as soon as an opportunity occurred has long been kept in mind; fortunately this is no longer necessary, the technical value of these substances having led to their further investigation in various works laboratories, with the result that they have been shown, as was anticipated, to exhibit properties proving that they also are quinonoid compounds.

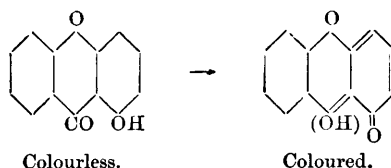
The *Chemiker Zeitung*, No. 104, December 28, 1892, contains an account of a communication made to the Heidelberg Chemical Society on December 16, by Professor Bernthsen, who points out that the rhodamines afford true ethereal salts when subjected to the conjoint action of alcohol and chlorhydric acid: in other words, that they afford carboxy-compounds and not lactone derivatives. After directing attention to other evidence in favour of the view that the colours of this class are members of the triphenylmethane group, he points out, in so many words, that the characteristic development of colour on adding alkali to phenolphthalein is, in all probability, due to the fact that the colourless lactone phenolphthalein is thereby hydrolysed and converted into a quinolic compound, which suffers dehydration, affording a coloured quinonoid compound:



In a more recent paper (*Berichte*, 1893, 172), Friedländer—who does not appear to be aware of Bernthsen's communication—has stated that phenolphthalein and hydroxylamine readily interact in an alkaline solution and form a hydroxime; this and other evidence he mentions leads him to express the opinion that in their coloured state phenolphthalein and the allied phthaleins which behave similarly in presence of alkali are all *quinonoid* compounds.

But, as so frequently happens at the present day, the patent literature contains statements which anticipate the views of Bernthsen and Friedländer, *e.g.*, a description being given of the formation of ethereal salts of rhodamines by the action of alcohol and chlorhydric acid in the French patent specification No. 224603, of the "Farbenfabriken vormals Friedr. Bayer und Co." (Elberfeld), dated September 28, 1892. It is pointed out in this specification that the rhodamines are to be regarded as carboxylic compounds, and the absence from the ethereal salts of the property which the rhodamines exhibit of forming salts and lakes is referred to as confirmatory of this view.

Friedländer is led to regard the fluoresceins as perhaps different from the phthaleins, as he was unable to obtain hydroximes from them, and speaks of their colour as conditioned by their xanthone-like structure. There appears to be no reason, however, why a distinction should be drawn between the intensely fluorescent rhodamines and the analogous oxygenated compounds—the fluoresceins. Even regarding them as xanthone derivatives, the appearance of colour in these latter is, it can scarcely be doubted, consequent on the occurrence of isodynamic change (*cf.* these Proceedings, 1892, 103).



The problem, therefore, remains practically the same; nevertheless, there can be little doubt that the phthalein-fluorescein group still offers interesting matter requiring further study.

Perhaps the point of chief interest claiming attention is the extraordinary ease with which the hydrolysis of the lactone is effected in the case of phenolphthalein, as evidenced by the fact that it is among the most sensitive of the known indicators of alkali: in contemplating the changes which may attend the dissolution of substances by water, such facts are undoubtedly of high importance. Perhaps the change is less a consequence of the instability of the lactone ring, and is mainly conditioned by the hydroxyl present in the para-position relatively to the carbon atom to which the phenolic radicles are attached—it is conceivable that a hydrated metallic derivative of the phenol is initially produced, and that the metal and water necessary to effect the hydrolytic change are thus brought into the intramolecular sphere of interaction. From this point of view, it would be interesting to determine the degrees of readiness with which phthalid and its various derivatives undergo hydrolysis. It is also worth noticing that, according to Bernthsen, the anhydrous rhodamine base forms a colourless solution in benzene and may be obtained in large, colourless crystals, while its solution in water is coloured and it forms an intensely coloured pentahydrate.

The recognition of the quinonoid character of such eminently fluorescent substances as the fluoresceins and rhodamines may be claimed as a most important argument on behalf of the view that fluorescence is a form of colour: indeed that—taken in conjunction with other facts—it goes far towards justifying the contention that

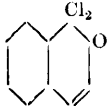
all quinonoid derivatives would be visibly fluorescent, were it not that, as in the case of certain quinine salts, as Hartley has pointed out, the rays which are the cause of the fluorescence sometimes become absorbed in the solution.

\*123. "The origin of colour. VIII. The limitation of colour to truly  
✓ quinonoid compounds. Change of colour as indicative of change of structure, as in the case of alizarin." By Henry E. Armstrong.

A quinonoid compound may be defined as a *hexaphene*, i.e., an unsaturated cycloid composed of six "elements" (*cf.* these Proceedings, 1892, 129), two "elements" of which are  $C\equiv R$  groups in either para- or ortho-positions.

Coloured substances generally appear to fall within this definition, as there do not appear to be any established cases of the existence of coloured substances—(a) containing a single  $C\equiv R$  group, or (b) in which two such groups are present in a cyclane or saturated ring, or (c) in which the cycloid contains any other number of elements than six. The succinosuccinic derivatives, &c., are but apparent exceptions to *b*, as those which are coloured may be regarded as isodynamic forms of the saturated compounds. Diacetyl and dibenzoyl (benzil) may be mentioned as exceptions to the general definition, but for this very reason it appears likely that they will eventually be obtained colourless; it is easy to account for the appearance of colour in diacetyl, as it undergoes condensation with extreme facility, yielding dimethylquinone (paraxyloquinone), an intensely yellow substance. Such a change is not likely to occur in the case of benzil, but this compound is so faintly yellow that the colour may well be due to impurity.

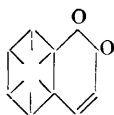
Some of the keto-chlorides described by Zincke appear to be ex-

ceptions to *a*, e.g., the compound , prepared by chlorinating

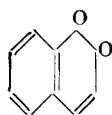
betanaphthol, the colour of which is a yellow of considerable intensity, and there is no reason to suppose that this is not characteristic of the pure compound. It is not improbable, however, that the group  $CCl_2$  in this and similar substances may be the true equivalent of a  $C\equiv R$  group. In an article on "The determination of the constitution of carbon compounds from thermochemical data," published in the *Phil. Mag.*, in February, 1887, summarising and briefly discussing the results described in the fourth volume of J. Thomsen's *Thermochemische Untersuchungen*, it was suggested that the greater development of heat which attends the formation of symmetrical

dichloro-derivatives may be due to the partial neutralisation of the (residual) affinity of the one chlorine atom by the other: in other words, that chlorine atoms are possessed of the power of directly entering into association while combined with another atom; in which case  $2\text{Cl}$  would be the equivalent of  $\text{R}''$ .

As the presence of two ortho- or para-carbonyl groups in a saturated ring apparently does not condition colour, it would seem that the two  $\text{C}\text{--}\text{O}\text{R}''$  groups are concerned *together with* the "ethenoid linkages" in the unsaturated ring in the production of colour; hence, the fact that compounds such as the naphthaquinones and the ketochloride before referred to are coloured is of importance, as evidence that *perhaps* a single ethenoid linkage in the ring is sufficient, and that it is not necessary that there should be two such, symmetrically situated with reference to the two  $\text{C}\text{--}\text{O}\text{R}''$  groups as in the benzoquinones; this, however, is on the assumption that the naphthaquinones are derivatives of *centric* and not of *ethenoid* benzene, hence the perhaps; the importance of this consideration will be more clearly realised after reference to the arguments made use of in the two following notes:—

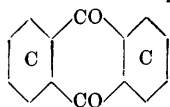


"Centric"  $\beta$ -naphthaquinone.



"Ethenoid"  $\beta$ -naphthaquinone.

Anthraquinone—which, it may be remarked, has scarcely any of the properties of a true quinone—may be referred to in this connection: if represented as a derivative of *centric* benzene, thus,

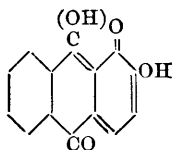


, the median group would appear to be saturated;

yet, as anthraquinone may be regarded as formed by the superposition of benzene and quinone, it would seem that the median group is still possessed of quinonoid characteristics; unless it be that the effect of the two  $\text{CO}$  groups is supplemented by that of the two symmetrically placed centric cycloids.

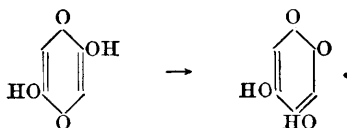
It would seem appropriate to here direct attention to the colour of alizarin in comparison with that of anthraquinone. The colour of paraquinones and their derivatives, in all cases in which the structure appears to be in no way open to question, is uniformly yellow; and red is characteristic of orthoquinones. How comes it then that alizarin is red? The conventional formula is not in accord with this

fact, but the colour may be accounted for by regarding alizarin as an isodynamic form of dihydroxyanthraquinone, *e.g.*,



On this assumption there is no difficulty in understanding why the monhydroxyanthraquinones are of no use as dye-stuffs; and why the introduction of two contiguous hydroxyls into anthraquinone is of such importance; furthermore, it is to be expected that a monethoxy-derivative prepared from alizarin if it contained an  $\alpha$ -ethoxy-group would resemble anthraquinone while one containing a  $\beta$ -ethoxy-group would more nearly resemble alizarin in colour: and, as a matter of fact, two such compounds have been described, one of which is yellow and the other red.

In like manner, it may be suggested as probable that the chlor-anilates are not derivatives of paraquinone, and that their formation involves the occurrence of isodynamic change, thus:—



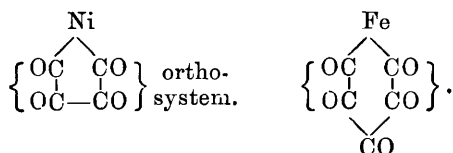
The arguments advanced in proof of their paraquinonoid nature do not appear to be in any way conclusive. Lastly, reference may be made to the *phenokinones* and *quinhydrones*: it is difficult to regard these as being other than members of that ill-understood and vaguely-defined class of substances termed molecular compounds. If so, the changes in the colour of quinones involved in their formation may arise from the weighting of the  $C \equiv R''$  groups by the attachment thereto of the phenol.

**\*124. "Note on optical properties as indicative of structure." By Henry E. Armstrong.**

In his "Notes on some recent determinations of molecular refraction and dispersion," recently communicated to the Physical Society (*Phil. Mag.*, 1893, 203), Dr. Gladstone directs attention to a number of curiously suggestive observations of special interest in connection with the all-fascinating enquiry into the correlations of properties and structure. The metallic carbonyls to which he

refers, in respect of physical properties as in many other respects, are compounds of extraordinary interest. The conclusion which both Mond and Gladstone favour that they are cycloids is undoubtedly that most in harmony with their general behaviour, affording as it does an explanation of the complete masking of the metal, comparable, for example, with that which sulphur suffers in thiophen.

The excessive refractive and dispersive power which the metallic carbonyls exhibit is probably, as Gladstone suggests, to be sought in the peculiar arrangement of the carbonyls; one object of this note is to call attention to the evidence which the optical data apparently afford of their *cooperative action*. The ketonic compounds hitherto studied from which the value  $\text{CO} = 8.4$  has been derived have been compounds containing single or isolated carbonyls, whereas—if represented as cycloids—the metallic carbonyls contain two “ortho-systems,” thus—



In this sense, they are in fact diorthoquinonoid and are comparable with coloured substances, but they are not truly quinonoid, the cycloid being saturated, and hence should not be coloured. (The nickel compound is colourless, but the iron compound is described as yellow; the instability of the latter, however, is such that this colour may be due to impurity.) There are only two orthoquinonoid systems, although there are five carbonyls in iron pentacarbonyl, so that one of the carbonyls should have the ordinary value and only four the value they apparently exhibit in nickel tetracarbonyl (11.9): consequently the molecular refraction should be

$$\begin{array}{rcl} 4\text{CO (orthoquinonoid)} & = & 4 \cdot 11.9 = 47.6 \\ \text{CO (ketonic)} & = & 8.4 \\ \text{Fe''} & = & 11.6 \\ \hline & & 67.6 \end{array}$$

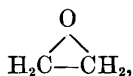
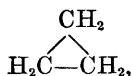
a value not far removed from that found, viz., 67.4.

If this argument be a sound one, it is to be anticipated that quinonoid compounds generally will be found to possess specially high refractive powers; and there is some evidence that this is the case: thus among the compounds examined by Gladstone (*C.S. Journ.*, 1870, 101–147; *Trans.*, 1884, 241) anthracene—a hydrocarbon which, as more than once pointed out, is probably quinonoid in struc



ture—is credited with a very high value, considerably above that calculated even if the value 6.1 be assigned to carbon. Gladstone has also stated that  $\beta$ -nitraniline has an abnormally high refractive power. I learn from Professor Mills that the compounds referred to as  $\alpha$ - and  $\beta$ -nitraniline which he gave to Gladstone were the meta- and para-derivatives; apparently, therefore, this result is in accord with the view previously advocated (these Proceedings, 1892, 101) that paranitraniline and similar coloured nitro-compounds are in reality quinonoid. Dr. Gladstone states, however, that both substances were examined in weak solutions, and, therefore, less than the usual confidence can be felt in the accuracy of the data.

Livinge and Dewar's determination of the molecular refraction of nitrous oxide in the liquid state is also referred to by Gladstone, who points out that the value observed (11.418) favours the view that the nitrogen in nitrous oxide has the low value which this element exhibits in nitriles, viz., 4.1. The determination of the structure of nitrous oxide is of special importance, as it is one of a group of compounds, including trimethylene, ethylene oxide and diazoimide, all of which it is the fashion at the moment to formulate as cycloids:—



But, apparently, there is no valid evidence to justify the practice, and it is in no way necessary to adopt such a course. Unfortunately we are without knowledge of the optical properties of trimethylene, but we have J. Thomsen's remarkable observation that its heat of combustion exceeds that of the isomeric propylene by 6690 units. I have on several occasions discussed the properties of this hydrocarbon and have pointed out how its unique behaviour with bromine and bromhydric acid may be explained by electrolytic considerations (cf. Morley and Muir's *Watts' Dictionary of Chemistry*, 3, Art. "Isomerism.") Granting the accuracy of Thomsen's figures, there appears to be no way of avoiding the conclusion that it is an open chain hydrocarbon, and, therefore, that free affinities may exist at the end of a chain; its dissimilar behaviour towards bromine and bromhydric acid precludes the application of von Baeyer's explanation of the instability of a ring of three atoms, as such a ring should prove unstable to bromine as well as to bromhydric acid, the former being in all other cases the more active agent in attacking hydrocarbons.

Ethylene oxide, in like manner, has an abnormally low heat of formation; in fact, on this account, J. Thomsen has gone so far as to represent it by the formula  $\text{CH}_2\cdot\text{O}\cdot\text{CH}_2$ , an expression offending against all recognised canons. If, however, trimethylene be written

$\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$ , ethylene oxide may be written  $\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$ . Perkin's results, referred to in a previous note (*ante*, p. 52), show that it is abnormal in its optical behaviour; they are most significant as affording evidence—assuming an open chain formula—that the optical effect of free affinities is below the normal, and it may be anticipated that trimethylene will afford low values. It is worth noting that carbonic oxide, in which we believe that certain of the affinities of the carbon atom, if not free, are “self engaged,” has a molecular refraction (7.5) considerably below the value of CO in ketonic compounds: it would seem that the ordinarily accepted refraction equivalents are not to be regarded as measures of the effect of the “affinities” proper, but of the affinities *engaged between atoms*.

Passing now to the nitriles and nitrous oxide, we have the most indefinite ideas as to the former: they are conventionally represented as compounds of triad nitrogen, but this practice is but the outcome of formal obedience to certain artificial and dogmatic rules of valency, and has no real justification. As we must admit the existence of latent affinities in carbonic oxide—which may be written  $\text{<CO>}$ —we may also admit the possibility of their existence in nitrogen, and may represent the nitriles as compounds of the form  $\text{<}\overset{\text{X}}{\underset{|}{\text{C}}}\text{—N>}$ . Nitrous oxide, on this assumption, would be  $\text{<N—O—N>}$ . Diazoimide might, in like manner, be regarded as  $\text{<N—NH—N>}$ , a formula which is implied in Mendeleef's assumption that it is a dinitrile. No diazoimide derivatives have hitherto been examined: Dr. Perkin had the kindness to determine the refractive power of the phenyl derivative, of which a quantity was placed at my disposal by Professor Tilden: the results are as follows:—

$d_{10^\circ/10^\circ}$  1.0980;  $d_{15^\circ/15^\circ}$  1.09318;  $d_{25^\circ/25^\circ}$  1.08527.

	<i>t.</i>	<i>n.</i>	$\frac{n-1}{d}$ .	$\frac{n-1}{d}$ P.
A.....	11.7	1.54719	0.49943	60.431
C.....	„	1.55407	0.50571	61.191
D.....	„	1.56063	0.51170	61.916
F.....	„	1.57793	0.52749	63.826

Deducting from the value of aniline, 52.09, the value of two hydrogen atoms, 2.6, and adding twice the highest value of nitrogen, 2.51, the theoretical value is  $A = 59.89$ , which is lower by 0.54 than that found; so that diazophenimide has proportionally a somewhat higher molecular refraction than even aniline.

These results do not indicate that diazophenimide is a dinitrile; neither is it possible to deduce from them any special argument in

favour of the formula  $\text{Ph}\cdot\text{N} \begin{smallmatrix} \text{N} \\ | \\ < \text{N} \end{smallmatrix}$ : the problem, in fact, remains unsolved.

Consideration of the facts makes it appear probable that a solution of the difficulty *may* be found, and not only so, but that it may be possible ere long to carry on the enquiry into the interrelationship of structure and physical properties on more fruitful lines than has of late been possible.

In the case of paraffinoid compounds generally, both carbon and hydrogen seem to have a fixed optical value, and it may be supposed also that this is true of hydrogen in all cases; seemingly also, *ethenoid carbon*—carbon as it is in ethylene, whatever may be the mode in which the atoms are united—has a constant value. The variations which are noticed in paraffinoid and ethenoid derivatives must on these assumptions be ascribed to variations in the radicles displacing hydrogen; and it should be easy therefore, by studying a considerable number of properly chosen compounds, to determine which radicles are, and which are not, subject to variation and the circumstances which condition variation.

In the case of benzenoid compounds, there is no evidence of constancy. Even in the case of the hydrocarbons, the value of the  $\text{C}_6$  group rises from  $\text{C} = 6$  (very nearly) in benzene to  $\text{C} = 6.15$  in mesitylene, the only apparent alteration made consisting in introducing methyl in place of hydrogen. As all the evidence derived from the study of paraffinoids seemingly shows that  $\text{CH}_3$  has an invariable value, it is only logical to suppose that the variation arises in the cycloid; in other words, that whereas the ethenoid  $\text{C}_2$  system apparently has an invariable optical effect, the benzenoid  $\text{C}_6$  system has a variable optical effect. There is nothing surprising in this conclusion—it is in absolute accordance with the experience derived from the study of the chemical behaviour of the benzenoid compounds. The variation, in many cases, is very considerable: that of aniline, for example, which has a molecular refractive power  $A = 52.09$ . Assuming  $\text{NH}_2$  to be  $5.1 + 2.1.3 = 7.7$ , and deducting the value of  $5\text{H} = 6.5$ , the value of  $\text{C}_6$  in aniline is  $52.09 - 7.7 - 6.5 = 37.89$ , and  $\text{C} = 6.31$ . There is no reason why the value should not be still higher in diazophenimide: to determine the value of the  $\text{N}_3$ , either  $\text{N}_3\text{H}$  or one of its paraffinyl derivatives should be examined. The chemical properties of diazophenimide are such—its nitro-derivatives are hydrolysed with such facility—as entirely to justify the assumption that the  $\text{N}_3$  has a very special influence on the properties of the cycloid.

The strongest confirmation of the view here put forward is afforded

by diphenyl, in which each carbon apparently has the value 6.39: the two radicles of which this hydrocarbon is composed being alike, and being both benzene residues and directly conjoined—putting the hydrogen aside—there can be no question that the variation is due to the variation in the optical effect of the  $C_6$  group.

If it can thus be shown either that the ethenoid group has an invariable effect whatever number of such groups may be present in the compound or that its effect is invariable except in certain cases in which a co-operative effect is traceable, and the benzenoid group be proved to have a variable optical effect, the most absolute demonstration will have been secured of the existence in benzenoid compounds of a peculiar structure such as is foreshadowed in the centric formula first proposed by me in February, 1887.

The following may be referred to as illustrative of the problems requiring consideration. Among haloid compounds, methylene iodide is altogether peculiar, its refraction equivalent (58.22) being much above the calculated value (52.1); this may be a case of co-operative action. The high dispersive power of carbon bisulphide is perhaps to be accounted for in some such manner. In iodoform, an eminently remarkable substance on account of its *colour* and other exceptional properties, the third iodine atom appears to exert an influence comparable with that of an ethenoid group in quinone and to determine the appearance of colour. In this case the effect is seemingly produced within the sphere of affinity around the carbon atom, much as in the case of quinonoid compounds it is produced within the cycloid sphere of affinity. Bromopicrin, if the value found by Gladstone be correct, appears to be an example involving a negative influence, a cause which, perhaps, also prevails in the case of acetylenic compounds, the abnormally low refractive power of which is highly remarkable. The aldehydes offer many peculiarities. It is to be remembered that Thomsen has represented aldehyde as  $CH_3 \cdot C(OH)$ ; the oxygen in such a compound would have a lower value than in ketones, but the one atom of carbon, being in the carbonic oxide or dyad state, would probably have a lower value than 5: so that, by assigning the full value to both carbon atoms and the ketonic value to oxygen, the equivalent would be over-estimated. But no indication that such is the case is actually afforded by aldehyde.

The refraction equivalent of benzaldehyde is about two, and that of salicylic aldehyde about three, units above the calculated value; this may be due to an increase in the cycloid value, but it is conceivable that the cycloid and the ketonic groups in some way co-operate; and it is even possible to represent salicylic aldehyde as a quinonoid compound. It is noteworthy that both these aldehydes are very active substances, and prone to yield condensation products. Cinnamic

aldehyde is one of the most refractive and dispersive of known substances, and its refraction equivalent (75.3) is much above the calculated value, 65.4. It may be represented as  $C_6H_5 \cdot CH \oslash CH \cdot C \oslash OH$ , or even as  $C_6H_5 \cdot CH \oslash C \oslash CH \cdot OH$ , and it would seem probable that the high refractive power is conditioned by a co-operative influence of the contiguous cycloid and ethenoid groups. From this point of view, it is important to examine allene,  $CH_2 \oslash C \oslash CH_2$ . Stilbene,  $C_6H_5 \cdot CH \oslash CH \cdot C_6H_5$ , is another equally striking instance, its refraction equivalent (113.39) being also very much higher than the calculated value (101).

The arguments here made use of in correlating optical properties and structure are undoubtedly applicable to the discussion of other physical properties, and, as some of these are apparently the measure of intra- and others of extra-molecular effects, it is all important that a careful comparison should be made with the object of elucidating reciprocal relationships.

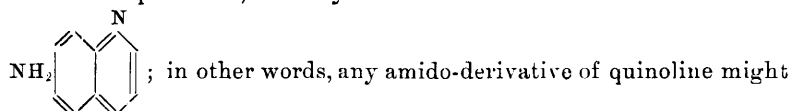
In conclusion, attention may be directed to the *anomalous colour dispersion* displayed by rosaniline and other colouring matters. In these compounds the two  $C \oslash R$  groups are of totally distinct types, and apparently the effect has not been noticed in the case of compounds in which the quinonoid groups are alike or similar. Biot has shown that the phenomena of anomalous *rotatory* dispersion exhibited by tartaric acid solutions are simulated by a mixture of two optically active mutually indifferent substances having different rotatory dispersive powers; it seems not improbable that the two dissimilar quinonoid groups which condition colour in rosaniline and substances which behave like it condition anomalous colour dispersion in consequence of their dissimilarity.

125. "The origin of colour. IX. Note on the appearance of colour in quinoline derivatives and of fluorescence in quinine." By Henry E. Armstrong.

The arguments put forward in the previous note have far-reaching consequences. The increase in refractive power observed on comparing the homologues of benzene with benzene might be ascribed to a passage from the centric to the ethenoid form—assuming the former to have a slightly lower optical value than the latter; and such a view would be in accordance with the observed change in chemical behaviour, but it would not account for the change in the case of aniline and other compounds, as the optical value of carbon in these rises above that which is seemingly characteristic of the ethenoid form.

That the change takes place in some cases, there can be little doubt, especially when von Baeyer's researches are taken into account. The object of the present note is to point out that its occurrence

would account for the appearance of fluorescence and colour in quinoline derivatives which has been discussed in a previous note (these Proceedings, 1892, 143). Assuming quinoline to be a centric cycloid and that the introduction of  $\text{NH}_2$  has a very marked effect, as in the case of aniline, it is possible that the compound may thereby be caused to acquire an ethenoid structure; but such an ethenoid compound would be quinonoid, as may be seen on reference to the formula



be quinonoid, and therefore coloured, probably either orange or red.

In like manner, an ethenoid form of naphthalene would be quinonoid; it is, therefore, possible that the fluorescence exhibited by many naphthol and naphthylamine derivatives is characteristic of the pure substances, and does not always originate in impurities.

If the argument here used be justified, the non-appearance of colour and fluorescence in naphthalene derivatives will afford evidence of a centric structure similar in character to that which the peculiar optical behaviour of benzenoid compounds affords of a special structure different from the ethenoid form in benzene.

#### DISCUSSION.

The CHAIRMAN (Dr. Gladstone) said that he would like to consider the suggestive remarks of Professor Armstrong on molecular refraction more carefully before committing himself to a definite opinion; the idea of a "co-operative influence," such as had been put forward, was, he thought, worthy of all attention. It had long struck him as an unexplained phenomenon, that while in the aromatic substances in general 6.1 is indicated as the atomic refraction of each of the double-linked carbons, the value was very appreciably lower in benzene itself and in toluene; and that when the compound becomes very complex, the value becomes larger than 6.1. Thus aniline is certainly more refractive than would be anticipated from the usual run of benzene compounds and compound ammonias. Carbon in such compounds as naphthalene or phenanthrene has a much higher refractive power, to which he had, some years ago, provisionally assigned the value of 8.8. It had been remarked that the ethylene bonds in open-chain compounds ought to retard light differently from the double bonds in the aromatic series. This was not to be easily recognised in the refraction of A, but it was, undoubtedly, the case in the dispersion. Such considerations must have much weight in the discussion of the structure of carbon compounds exhibiting special properties.

Dr. PERKIN said, in reference to Dr. Armstrong's remarks on the very high values obtained for the refractive power of the carbonyl compounds of nickel and iron, it must be remembered that these compounds were examined in the pure condition, whereas all other determinations of the refractive power of nickel and iron were made with dissolved salts and do not necessarily give true values for these metals. In the case of zinc compounds, he had found that the value of this metal in zinc ethyl was 15.9, whereas solutions of zinc salts gave only 9.8. Therefore it was not safe to infer that in the carbonyl compounds nickel and iron had the values they apparently possessed in salts. Through the kindness of Mr. Mond, he had had the opportunity of measuring the magnetic rotation of the nickel and iron carbonyl compounds, and had found that they gave very high rotations; but at present no other compounds of these metals had been examined.

As to the values given for the refraction of carbon and hydrogen being perfectly constant, even in saturated compounds this appears to be doubtful. Taking the case of ethylene oxide, they must be somewhat lower than usually given, and, in some of the amines, they appear to be higher; this is seen on comparing primary and tertiary amines, the refraction, but more especially the dispersion, increasing as we pass from the former to the latter. In the aromatic series this is very evident. Aniline itself has an abnormally high value, but, as methyl is introduced into this compound, the refraction increases with each methyl introduced much more than the change of composition requires, the increase for the first methyl being 8.36, and the change of dispersion no less than 1.37, and that for the second methyl 8.51, and of dispersion 1.22; whereas the calculated difference in each case is 7.6 only, and for the dispersion 0.34. Corresponding results are observed in reference to the magnetic rotation of all these compounds, though in a much more striking manner.

Dr. Armstrong had also made reference to the refractive power of two nitranilines; that these should be high is only consistent with their being derivatives of aniline. As to whether the difference of position of the  $\text{NO}_2$  group would influence the refractive power of these substances in any marked degree, the data we have would be against such an assumption. Dr. Gladstone had measured several series of ortho-, meta- and para-compounds at his request, and had found them to give nearly identical results.

Mr. MOND drew attention to the very different values deducible for nickel, the atomic refraction calculated from Kundt's observations with the metal being 6.12, while that calculated from the oxide is 9.82 (*cf.* Mond and Nasini, *Zeit. phys. Chem.*, **8**, 150).

# Ethereal Salts of Glyceric Acid.

## Inactive.

Ethereal salt.	Density, 15°/15°.	Difference.	Boiling point.
Methyl .....	1.2814	0.0905	119—120° (14 mm.).
Ethyl .....	1.1903	0.0156	120—121° (14 mm.).
Propyl (normal) .....	1.1453	—	126—127° (14 mm.).
Isobutyl .....	1.1024	—	128—130° (13 mm.).

## Active.

Ethereal salt.	Density, 15°/15°.	Difference.	Observed rotation in 198.4 mm. tube, $\alpha$ .	Specific rotation, $[\alpha]_D$ .	Molecular rotation, $M \cdot \frac{[\alpha]_D}{100}$ .	Deducted specific rotation of glyceric acid ( $C_3H_5O_4$ ), $[\alpha]_D$ .	Boiling point.
Methyl .....	1.2798	0.0877	-12.2°	-4.8°	-5.76°	-5.43°	120° (13 mm.)
Ethyl .....	1.1921	0.0473	-21.7	-9.18	-12.30	-11.60	—
Propyl (normal) .....	1.1448	0.0293	-29.4	-12.94	-19.15	-18.07	—
Isopropyl .....	1.1303	0.0252	-26.5	-11.82	-17.49	-16.50	114—116° (13 mm.).
Butyl (normal) .....	1.1155	—	-24.4	-11.02	-17.85	-16.84	131—139° (14 m.m.).
Isobutyl .....	1.1051	—	-31.2	-14.23	-23.05	-21.75	—
Butyl (secondary) .....	1.1052	—	-23.2	-10.58	-17.14	-16.17	123—126° (13.5 mm.).



**\*126. "The ethereal salts of glyceric acid, active and inactive." By Percy Frankland, Ph.D., B.Sc., F.R.S., and John MacGregor, M.A.**

The following table contains the names of the glycerates, inactive and laevorotatory, which the authors have prepared, together with their densities, observed specific and molecular rotations, as well as the specific rotation of glyceric acid as deduced from the rotations of the several salts.

The method of preparation adopted for the methylic, ethylic, normal propylic and normal butylic glycerates consisted in heating glyceric acid (either inactive or active) with an excess of the particular alcohol in a sealed tube at about  $180^{\circ}$  C., and then fractioning the resulting products by distillation under greatly reduced pressure. In the case of the secondary alcohols, this method yielded an unsatisfactory result, and consequently the isopropylic and secondary butylic salts were prepared by saturating a mixture of glyceric acid and the alcohol in question with hydrogen chloride gas, and then fractioning under reduced pressure. This method was also adopted in the case of isobutylic glycerate, although this compound could also, doubtless, have been satisfactorily prepared by the sealed tube method. It was found that the facility of etherification was much greater in the case of the primary than in that of the secondary alcohols, whilst in the case of the tertiary butyl alcohol (the only tertiary alcohol experimented with) it was not found possible to obtain an ethereal salt.

In preparing the isopropylic and secondary butylic salts, a considerable quantity of a white substance was formed which was found to be an anhydride of glyceric acid, whilst in the attempt to prepare the tertiary butylic salts, this anhydride appeared to be the sole product.

The active ethylic glycerate was prepared by both the sealed tube and hydrogen chloride methods, and the resulting products were found to have the same rotatory power, thus showing that the activity is in no way impaired by the high temperature ( $180^{\circ}$  C.) employed in the sealed tube method.

Attention is directed to the relationship between the molecular rotations of the several glyceric ethereal salts experimented with. This rotation increases almost quite regularly from methylic to ethylic, to normal propylic glycerate. Isopropylic glycerate has a somewhat lower rotation than the normal propylic compound, but the isobutylic glycerate lies much more nearly on the "main line" of molecular rotatory increase than either the normal or secondary butylic compounds, the rotations of which correspond closely with that of the isopropylic glycerate. It is pointed out that the addition of  $\text{CH}_2$  to the alkyl group increases the molecular rotation by 6.54 in the case of methylic and ethylic, and of 6.85 in the case of the ethylic and normal

propylic glycerates, whilst the increase is only 5.56 in the case of the isopropylic and isobutylic glycerates. These values for  $\text{CH}_2$  are very similar to those which can be deduced in the case of ethereal salts of tartaric acid, in which, also, the rotatory value of  $\text{CH}_2$  is less in the case of the isothan of the normal compounds.

In reviewing the rotatory power of these active glyceric ethereal salts in relation to the recently advanced theories of Guye and of Crum Brown, they are of opinion that, although in the first three terms of the series, the increase in rotation follows the increase in the weighting of one of the groups attached to the asymmetric carbon atom, yet that by a consideration of the rotatory powers of the higher terms, as well as by a comparison of the rotations of ethylic glycerate and ethylic lactate (the only active lactic ethereal salt hitherto prepared), it is obvious that the molecular rotation is affected by the qualitative nature of the groups as well as by the relative magnitude of their masses.

127. "Formation of the ketone 2:6-dimethyl-1-ketohexaphane from dimethylpimelic acid." By F. Stanley Kipping, Ph.D., D.Sc.

In a recent paper by the author and Mackenzie (*C.S. Trans.*, 1891, 569), it was stated that "when dimethylpimelic acid is heated with phosphoric anhydride at a moderately high temperature, it yields an oil having a strong turpentine-like odour; this reaction will be further investigated by one of us."

Although, on continuing the experiments, only a very small quantity of the oil was obtained in the manner indicated, owing to the formation of resinous products, the investigation was not relinquished as it seemed probable that the product would prove to be a dimethyl-ketohexamethylene (2:6-dimethyl-1-ketohexaphane, *cf.* these Proceedings, 1892)  $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 \cdot \text{CHMe} \end{smallmatrix} > \text{CO}$ , the formation of which in this way would be of considerable interest, not only on account of the nature of the product, but also as showing that dicarboxylic acids are capable of undergoing a change similar to that already studied in the case of the fatty acids (*Trans.*, 1890, 532, 980).

Ultimately, by distilling the calcium salt of dimethylpimelic acid with soda lime under reduced pressure, an oil was obtained which, after agitation with soda solution, was distilled, and the portion boiling at about  $180^\circ$  collected separately; this fraction contained a ketone of the composition  $\text{C}_8\text{H}_{14}\text{O}$  (found,  $\text{C} = 76.5$ ,  $\text{H} = 11.1$  per cent.; calculated,  $\text{C} = 76.2$ ,  $\text{H} = 11.1$  per cent.), capable of interacting with hydroxylamine, forming a *hydroxime* of the composition  $\text{C}_8\text{H}_{14}\text{NOH}$ , crystallising from light petroleum in colourless prisms melting at about  $112^\circ$ ; the hydroxime had an odour very similar to that of camphor hydroxime.

The ketone is, in all probability, a dimethylketoexamethylene; it has a peppermint-like odour, which seems to be characteristic of the cyclic ketones of this class, ketopentamethylene (Wislicenus and Hentschel), methylketopentamethylene (Semmler, (*Ber.*, **25**, 3517) and suberone, which is probably a methylketoexamethylene (compare Kipping and Perkin, *Trans.*, 1891, 217), being all described as having this particular odour.

The publication of this note at present time seems to be desirable in view of the fact that in the last number of the *Berichte* (p. 231) von Baeyer has described a ketone, obtained by the distillation of calcium pimelate with soda lime, which is doubtless a homologue of the compound prepared by the author. The investigation is being continued.

**128. "Note on the interactions of alkali-metal haloids and lead haloids and of alkali-metal haloids and bismuth haloids." By Eleanor Field, Assistant-Demonstrator in Chemistry, Newnham College, Cambridge.**

By boiling potassium or ammonium iodide with lead iodide, chloride, bromide or fluoride and water in the ratio of 30 parts of the former to 1 part of the lead compound to 75 parts of water, pale yellow, needle-like crystals were obtained, having the composition  $3\text{PbI}_2 \cdot 4\text{KI}$  or  $3\text{PbI}_2 \cdot 4\text{NH}_4\text{I}$ .

By boiling potassium or ammonium chloride, or bromide, with lead iodide and water in the ratio of 6 parts of the former to 1 part of the lead compound to 50 parts of water, lead iodochloride,  $\text{PbICl}$ , was obtained.

By boiling potassium or ammonium iodide with lead chloride and water, in the ratio of 1 part alkali of the former to 5 parts lead chloride to 250 parts water, iodochlorides of lead of the composition  $\text{PbI}_2 \cdot 3\text{PbCl}_2$  and  $\text{PbI}_2 \cdot 5\text{PbCl}_2$  were obtained; when lead bromide was used in place of lead iodide, the product was an iodobromide of lead,  $\text{PbI}_2 \cdot 2\text{PbBr}_2$ .

These results show that when a large excess of potassium or ammonium iodide is used, the whole of the lead haloid is transformed into iodide, if the lead compound was not iodide to start with, and that the lead iodide thus formed combines with the potassium or ammonium iodide to form a double salt; but that if less alkali-metal haloid be used in proportion to the amount of lead haloid employed, the product contains the halogen of the two haloids, and it is free from alkali-metal. The composition of the products of the interaction depends more on the relative quantities of the interacting haloids than on the nature of the metals and the halogens of the salts employed.

The results obtained by the interactions of alkali-metal and bis-

muth haloids differed from those obtained with lead haloids. The compound  $\text{BiBrCl}_4\text{K}_2$  was obtained by dissolving bismuth chloride in solution of potassium bromide used in the ratio  $\text{BiCl}_3 : \text{KBr}$ . The compound  $\text{BiClBr}_4\text{K}_2$  was obtained when bismuth bromide was dissolved in solution of potassium chloride in the ratio  $\text{BiBr}_3 : \text{KCl}$ . But when bismuth chloride and ammonium bromide interacted in the ratio  $\text{BiCl}_3 : \text{NH}_4\text{Br}$ , the same substance was obtained as when bismuth bromide interacted with ammonium chloride in the ratio of equal numbers of molecules, viz.,  $\text{BiCl}_3\text{Br}_3(\text{NH}_4)_3$ . This compound is similar to the  $\text{SbCl}_3\text{Br}_3\text{K}_3$  obtained by Atkinson (*C.S. Trans.*, 1883, p. 289) by the interaction of antimony and potassium haloids, either in the ratio  $\text{SbCl}_3 : 3\text{KBr}$  or in the ratio  $\text{SbBr}_3 : 3\text{KCl}$ .

These results indicate that the composition of the products of change is dependent, not only on the relative masses of the interacting haloids, but also on the nature and relative affinities of the halogens and also of the metals of the interacting haloids.

129. "An isomeric form of benzylphenylbenzylthiourea." By Augustus E. Dixon, M.D.

Phenylthiocarbimide and dibenzylamine interact, forming the compound  $\text{C}_6\text{H}_5\text{N}:\text{C}(\text{SH})\cdot\text{N}(\text{C}_6\text{H}_5)_2$ , isomeric with the thiourea  $\text{C}_7\text{H}_7\text{N}:\text{C}(\text{SH})\cdot\text{NC}_6\text{H}_5\cdot\text{C}_6\text{H}_5$  (m. p.  $103^\circ$ ), previously obtained by the author (*Trans.*, 1891, 567) from benzylthiocarbimide and benzylaniline; it crystallises in vitreous prisms, insoluble in water, rather sparingly soluble in ether and alcohol, and melting at  $145\text{--}146^\circ$  (uncorr.); it is converted by the action of alcoholic ammonia at  $100\text{--}110^\circ$  into phenylthiourea and dibenzylamine.

130. "A new atomic diagram and periodic table of the elements." By R. M. Deeley.

After a reference to Lothar Meyer's diagram of atomic volumes and Mendeleeff's periodic table of the elements, a diagram is described in which the ordinates are "volume heats" and "volume atoms" instead of atomic volumes; a table of the elements is also given, in which the elements are arranged periodically, in accordance with their positions on the diagram.

The volume heats are obtained by multiplying specific heat by relative density, and the volume atoms by dividing relative density by atomic weight.

## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

Grundzüge der theoretischen Chemie, von L. Meyer. **Zweite Auflage.** Leipzig 1893. From the Author.

Carl Wilhelm Scheele, Pharmacist and Chemist. **A Brief Account of his Life and Work, 1742—1786.** (Reprinted from the *Pharmaceutical Journal*) London 1893. From the Pharmaceutical Society.

The Year-Book of Science, edited for 1892 by T. G. Bonney. London, Paris and Melbourne 1893. From the Publishers.

### II. *By Purchase.*

Mikroskopische Physiographie der Mineralien und Gesteine, von H. Rosenbusch. Band I. Stuttgart 1892.

Organische Reaktionen und Reagentien, von E. Seelig. Stuttgart 1892.

Guide pratique pour l'analyse quantitative, par C. Graebe. Genève et Paris 1892.

Berzelius und Liebig; ihre Briefe von 1831—1845, herausgegeben von J. Carrière. München und Leipzig 1892.

Handbuch der physiologisch- und pathologisch-chemischen Analyse, von F. Hoppe-Seyler. Sechste Auflage neu bearbeitet von F. Hoppe-Seyler and H. Thierfelder. Berlin 1893.

The First Principles of Chemistry, by W. Nicholson. Third edition. London 1796.

Chemistry of the Organic Dye-stuffs, by R. Nietzki. Translated, with additions, by A. Collin and W. Richardson. London 1892.

Odorographia; a Natural History of Raw Materials and Drugs used in the Perfume Industry, by J. C. Sawer. London 1892.

Quantitative Chemical Analysis by Electrolysis, by A. Classen. Translated from the 2nd German Edition by W. H. Herrick. New York 1888.

Manual of Bacteriology, by E. M. Crookshank. Third Edition. London 1890.

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## HOFMANN MEMORIAL LECTURE.

An extra meeting of the Society will be held on Friday, May 5th, 1893, the anniversary of the death of A. W. von Hofmann, when addresses will be delivered by the Right Hon. Lord Playfair, K.C.B., F.R.S., V.P.C.S.; Sir F. A. Abel, C.B., F.R.S., V.P.C.S.; Dr. W. H. Perkin, F.R.S., V.P.C.S.

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At the next meeting, on March 16th, the following papers will be read :—

“The limits of accuracy of gold-bullion assay and the losses of gold incidental to it. The volatilisation of gold.” By T. K. Rose.

“The boiling point of nitrous oxide at atmospheric pressure and the melting point of solid nitrous oxide.” By Professor Ramsay.

“The isomerism of the paraffinoid aldoximes.” By Professor Dunstan and T. S. Dymond.

“The hydroxime of formic aldehyde.” By Professor Dunstan and Dr. Bossi.

“The properties of  $\alpha$ -benzaldoxime.” By Professor Dunstan and C. M. Luxmoore, B.Sc.

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**Annual General Meeting, March 27th, at 8 p.m.**