PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 172.   Session 1896–97.

Dec. 17th, 1896.   Mr. A. G. Vernon Harcourt, President, in the
Chair.

Messrs. Alexander Scott, Frederick B. Power, W. W. Cobb, and
Claude M. Thompson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alfred
Cartmell, Alexandra Road, Burton-on-Trent; William Diamond, Pye
Bridge, Alfreton; William Buckland Edwards, 5, Garlinge Road,
Brondesbury, N.W.; Vaughan Harley, M.D., 25, Harley Street, W.;
Fred Ibbotson, B.Sc., 9, Melbourn Road, Spring Vale, Sheffield;
David Smiles Jerdan, M.A., B.Sc., 68, Union Street, Greenock;
Edward Rosling, Melbourne, Chelmsford; Henry Potter Stevens,
B.A., 14, Lower Sloane Street, Chelsea, S.W.; Harry Thompson,
Walton House, West Parade, Anlaby Road, Hull.

The certificate of the following candidate, recommended by the
Council, under Bye-law I, par. 3, was also read:—

Jyoti Bhusan Bhaduri, Presidency College, Calcutta.

Of the following papers those marked * were read.

***165. "On the experimental methods employed in the examination of
the products of starch-hydrolysis by diastase." By Horace T.
Brown, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar.**

The paper is divided into the following sections: (1) the deter-
mination of solids from solution-density; (2) determination of
specific rotatory power; (3) the relation of $[\alpha]_J$ to $[\alpha]_D$; (4) de-
termination of cupric reducing power; (5) limits of accuracy of
the methods.

The authors state that this account is a preface to a series of papers dealing with the question of starch-hydrolysis, and is a critical review of the experimental methods which have been employed by different observers who have approached this subject. An attempt has also been made to remove the misunderstanding which still exists as to the relations of the different systems of notation.

The determination of the total solids from the density of the solution by the employment of the "divisor" method admits of great accuracy if the solution-densities of the pure substance have been previously determined.

The " divisors " at varying concentration have been determined for cane sugar, maltose, dextrose, levulose, soluble starch, and the mixed products of starch-hydrolysis of various grades, and the results have been plotted out in the form of curves whose equation is given in each case. The pure substances used in constructing these curves were dried in a vacuum over phosphoric pentoxide at temperatures from $100°$ to $130°$.

For mixed starch hydrolytic products, the divisor for equal concentrations increases with the specific rotatory power, and in such a regular manner that when the value of R is known, the divisor at any given concentration can be calculated. From the relation which this divisor bears to the divisor of the apparent maltose present in the mixed hydrolytic products, it is deducible that the divisor for the amylin constituent is constant for equal concentrations, even in starch products of very different grades of hydrolysis.

In the section on specific rotatory power, the methods of exact determination are discussed, and the relations of $[\alpha]_J$, $[\alpha]_{J3\cdot86}$, and $[\alpha]_D$ are defined for substances of equal dispersive power. As the dispersive power of cane sugar is sensibly different from that of dextrose and starch-hydrolytic products obtained by diastase, the factors for the conversion of $[\alpha]_J$ into $[\alpha]_D$ are not identical in these cases. Much confusion of these relations has also been introduced by the unrecognised fact that $[\alpha]_J$ has been referred to two distinct rays in the yellow of different refrangibility.

The cupric-reduction of maltose and of the products of starch-transformation is constant only when the conditions of experiment are identical. These are exactly defined for the authors' method of procedure, and the reducing values are given in tabular form, and are compared with those of other observers.

*166. " On the specific rotation of maltose and of soluble starch." By Horace T. Brown, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar.

The authors' determinations of the specific rotatory power of maltose at a temperature of $15\cdot5°$ do not confirm the statement of

Meissl that the values of $[\alpha]_D$ vary with the concentrations between 2 and 20 per cent., but confirm the general statement of Ost that between these limits the specific rotatory power is constant. At higher concentrations than 20 per cent., the specific rotatory power diminishes slightly.

The actual results point to a value of $[\alpha]_D = 137.93°$, which is sensibly greater than Ost's value of $137.46°$ at $15.5°$.

This discrepancy is due to the fact that Ost employed weighed quantities of hydrated maltose which had been dried in a desiccator over sulphuric acid. The authors find that even after six weeks' drying in this manner, hydrated maltose contains 0.46 per cent. more water than corresponds to $C_{12}H_{22}O_{11} \cdot H_2O$. If Ost's numbers are corrected for this they give values, up to 20 per cent. concentrations, of $[\alpha]_D = 138.12°$ at $15.5°$, a result almost exactly identical with that of the authors.

The specific rotatory power of soluble starch for concentrations of 2.5 to 4.5 per cent. is, at $15.5°$, $[\alpha]_D = 202.0°$.

*167. "On the relation of the specific rotatory and cupric-reducing powers of the products of starch-hydrolysis by diastase." By Horace T. Brown, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar.

When starch is transformed by diastase, a certain relation is always found to subsist between the cupric-reduction and specific rotatory power of the hydrolytic products. This relation can be expressed in such a manner as to be entirely independent of any view we may hold as to the true nature of the transformation products, and it is of so exact a nature that if one property is known the other can be predicted with certainty. This is true not only for the mixed hydrolytic products, but for any fractionated portion of them.

The authors regard this fact as lying at the root of the whole question of starch-hydrolysis, and, as it is still not admitted by most continental workers, they bring forward a large amount of fresh evidence which they regard as absolutely conclusive.

The results of the examination of 70 different starch transformations are given, some of them mixed products, others fractionated products, the specific rotatory and cupric-reducing powers being given in the various notations in use. When the experimental results are plotted on a system of rectangular co-ordinates, the degrees of specific rotation between soluble starch and maltose being represented on the line of ordinates, and the cupric-reducing powers from soluble starch to maltose on the line of abscissæ, the values all fall practically on a straight line joining the points of intersection of the co-ordinates corresponding to the optical and reducing properties of soluble starch and of maltose respectively.

The properties of soluble starch being $R = 0$, $[\alpha]_D = 202°$, and of maltose, $R = 100$ and $[\alpha]_D = 138·0°$, then the relation of specific rotation and cupric reduction for any mixture or fractionation of the starch-hydrolytic products will be expressed by $[\alpha]_D = 202 - 0·64 R$.

The differences in the calculated and observed values for the 70 cases of hydrolysis examined are given, and are shown to be very small indeed.

The authors have examined the published results of C. J. Lintner and of Ost, both of whom have denied the existence of any relation between $[\alpha]_D$ and R, and find that, when rightly interpreted, they, for the most part, strictly conform to the law of relation expressed above.

DISCUSSION.

Dr. ARMSTRONG, after commenting on the value of the information brought under the notice of the Society by Mr. Horace Brown and his co-workers, and on the remarkable accuracy with which starch could now be estimated, expressed the hope that it would be possible ere long to determine what really took place when starch was hydrolysed; he thought it was time that we should no longer be content merely to determine certain analytical factors; we ought rather to seek for chemical methods which would render it possible to separate and isolate the products.

Mr. A. R. LING asked what value the authors found for the cupric reducing power of maltose when Wein's method was used.

Dr. G. H. MORRIS, in reply, said that they found that Wein's tables give results about 5 per cent. too low when the cupric reduction of maltose is estimated by Wein's method, and the copper obtained calculated into maltose by the table; in other words, perfectly pure maltose gives $R = 95$—96 instead of 100.

*168. "The action of hydrogen peroxide and other oxidising agents on cobaltous salts in presence of alkali bicarbonates." By R. G. Durrant, M.A.

Similar green solutions may be obtained by adding hydrogen peroxide, sodium hypochlorite, chlorine, bromine, or ozone to cobaltous salts in presence of alkali bicarbonates—or by adding a cobaltous salt to the anode of previously electrolysed potassium carbonate.

The green colour is not destroyed by excess of cold acetic acid, but is rendered rather bluer in tint. This acetic solution is reduced by hydrogen peroxide.

The evidence so far obtained shows (1) that the cobalt is in the "cobaltic state." This is proved by the results of three

245

volumetric methods—in which standard sodium hypochlorite, hydrogen peroxide, and sodium sulphite are respectively employed—green precipitates, produced from the green solutions, gave results showing that the available oxygen closely approximates to that to be expected from cobaltic hydrate.

(2) That the green colour of the solutions and of the precipitates appears not to be due to a particular alkali, since (i) identical tints were obtained with the five different alkali bicarbonates, (ii) potassio-cobaltic nitrite gives no green colour with bicarbonates, (iii) green precipitates washed free from all alkali, and digested with cold weak acetic acid give green filtrates.

(3) That carbon dioxide is necessary both for the formation and preservation of the green colour. The green colour of the acetic solution remains only so long as carbon dioxide is present. The green precipitates (free from alkali) retain carbon dioxide so long as they remain green, and lose it when they become brown. It is, therefore, possible that the green cobaltic compound is of the nature of a carbonate.

DISCUSSION.

Several speakers, including the PRESIDENT, expressed the view that whilst the author had made it clear that the green substance was a cobaltic compound, further proof was needed of the suggestion that the salt formed was a cobaltic carbonate.

Dr. RIDEAL mentioned that sodium peroxide, as well as hydrogen peroxide, gave rise to the green colour, provided that an alkali bicarbontate was also present.

Dr. ARMSTRONG said that he would like to give expression to the opinion that the time was come to determine what should be their course of action with regard to the publication of the discussions that took place at the meetings; of late there had been an almost entire absence from the Proceedings of reports of the remarks made in the room, although these had often been of a nature which made it desirable that they should be brought under the notice of the Fellows generally. If the Secretaries could not undertake the work, steps should be taken to procure a proper report. Personally he had had no difficulty in obtaining reports during the nine years in which he had charge of the Proceedings, and he did not believe that there would be any difficulty. Without such reports the Proceedings were of little value.

Professor DUNSTAN said that Fellows attending the meetings were aware that it was not often that a comprehensive discussion followed

the reading of an ordinary paper. All important remarks and suggestions made at the meetings had been recorded in the Proceedings, and although no attempt had been made to record everything, and there might occasionally be room for difference of opinion as to what was important, he was always glad to receive from speakers, after the meeting, reports of their remarks, which he believed had been in nearly every case inserted in the Proceedings. He had, however, not thought it desirable to print Dr. Armstrong's remarks, of the omission of which Dr. Armstrong now complained, made on two recent occasions proposing to record the time occupied by readers of papers. The method adopted by the speaker's predecessor in office in reporting discussions had given rise to much dissatisfaction. If the present plan was not thought sufficient, then a shorthand report of the discussions could be taken. As a matter of fact, however, the main value of the Proceedings lies in its being the means of bringing at an early date under the notice of the Fellows, not merely remarks and suggestions made at the meetings, but concise abstracts of the papers read, the full publication of which could not take place in the Journal until much later.

The PRESIDENT remarked that if a full report of the proceedings were considered desirable, its preparation could not be included in the duties of the Honorary Secretaries. He was disposed to think, however, that if it were generally known that the Secretaries were ready to receive from speakers after the meeting a few sentences giving the substance of their remarks, that this would meet the case in nearly every instance.

169. "Electrical conductivity of diethylammonium chloride in aqueous alcohol." By James Walker, Ph.D., D.Sc., and F. J. Hambly, F.I.C.

The authors have determined the conductivity of diethylammonium chloride dissolved in pure water, and in $10\cdot1$, $30\cdot7$, $49\cdot2$, $72\cdot0$, $90\cdot3$, and $99\cdot0$ per cent. alcohol, by volume, at dilutions ranging from 10 litres to 8000 litres. Tables and curves have been constructed, showing the variation of the molecular conductivity and the degree of dissociation with varying dilution and varying proportions of alcohol.

170. "Formation of substituted oxytriazoles frcm phenylsemicarbazide." By George Young, Ph.D., and Henry Annable.

The action which takes place when a mixture of phenylsemicarbazide and benzaldehyde is oxidised, has been reinvestigated, and the views expressed by one of the authors in a previous paper (Trans., 1895, **67**, 1063) have been confirmed. The following aldehydes yield

oxytriazoles by this action : metanitrobenzaldehyde, paranitrobenz-aldehyde, metatoluic aldehyde, terephthalic aldehyde, cinnamic aldehyde.

The authors have failed to obtain oxytriazoles from formaldehyde, acetaldehyde, paraldehyde, isobutyric aldehyde.

171. "α-Bromocamphorsulpholactone." By C. Revis and F. Stanley Kipping, Ph.D., D.Sc.

When α-bromocamphor is treated with anhydrosulphuric acid, or with chlorosulphonic acid, it is converted into α-bromocamphor-sulphonic acid (Trans., 1893, **63**, 548). In the course of some experiments on the preparation of this sulphonic acid, it was found that when 70 per cent. anhydrosulphuric acid is added to a solution of α-bromocamphor in chloroform, the product consists, to some extent, of a crystalline compound which is insoluble in water.

This substance has the composition $C_{10}H_{13}BrSO_4$ (found C = 38·8, H = 4·3, Br = 25·1, S = 9·7 per cent.; calculated C = 39·0, H = 4·2, Br = 25·8, S = 10·3 per cent.). It appears to be a bromo-camphorsulpholactone, and its formation is doubtless due to the oxidation of hydrogen to hydroxyl accompanying sulphonation, water being then eliminated from the hydroxysulphonic acid; it is, probably, closely related to the dibromocamphorsulpholactone, $C_{10}H_{12}Br_2SO_4$, recently described (Lapworth and Kipping, Proc., 1896, **12**, 77), and it resembles the latter in ordinary properties. It crystallises from chloroform and ethylic acetate in lustrous, transparent plates or prisms, melts at about 290°, and is moderately easily soluble in boiling acetic acid, chloroform, and ethylic acetate. It is very stable, and separates, unchanged, from a solution in nitric acid (sp. gr. 1·4), even after heating for some time ; it seems not to be attacked by cold potash (sp. gr. 1·3), and, even on boiling, it is only slowly dissolved.

Dr. Lapworth has, independently, observed the formation of this lactone from α-bromocamphor and anhydrosulphuric acid.

172. "Dimethylketohexamethylene." By F. Stanley Kipping, Ph.D., D.Sc.

In a recent paper on camphoric acid (*Amer. Chem. J.*, 1896, **18**, 685), Noyes describes the preparation, from dihydrocampholytic acid, of a ketone which forms an oxime melting at 112—113°, and possesses an odour similar to that of camphoroxime. On comparing the melting point of this oxime with that of the isomeric oxime of dimethyl-ketohexamethylene, he found that, for the latter, the author had given the melting point 114—115° (Trans., 1895, **67**, 349), whereas Zelinsky had given it as 104—105° (*Ber.*, 1895, **28**, 781). Noyes

himself then prepared dimethylketohexamethylene oxime, and found the melting point to be 120—122°.

The possible identity of the two oximes in question being a matter of great importance—for, if their identity were established, much light would be thrown on the constitution of camphor—the author has prepared dimethylketohexamethylene by the improved method recently described (Kipping and Edwards, Proc., 1896, **12**, 188), and has made further experiments with this substance.

The oxime, prepared in the usual manner, is at first very oily, apparently from the presence of unchanged ketone, but it soon becomes a semi-solid crystalline mass; when freed from oil and recrystallised once or twice, it melts quite sharply at about 114°, but further purification raises the melting point to 117·5° (uncorr.), at which point it remains, even after six successive crystallisations from different solvents. This melting point and that previously recorded were taken with an ordinary standard thermometer; observations made with a short thermometer, the thread of which was entirely immersed, gave a m. p. of 118·5—119°. Noyes does not state whether the m. p., 120—122°, is corrected, nor how the observation was made, and the range of 2° would seem to indicate that the substance did not melt sharply; he also leaves the identity of his dimethylketohexamethylene oxime with the oxime of the ketone which he obtained from camphor an open question.

Noyes suggests that the several preparations of the oxime obtained respectively by Zelinsky, by himself, and by the author, may be mixtures of stereoisomerides, and the latter has therefore directed attention to this possibility ; there are certainly indications of the presence of more than one substance in the crude oxime, as a few crystals, melting not sharply at about 75°, have been separated; nevertheless, the only crystalline product which has yet been isolated in any quantity is that which melts sharply and constantly at 118·5—119° (corr.).

This oxime crystallises from a mixture of chloroform and light petroleum in lustrous, transparent prisms, which have been examined by Mr. Pope. " The crystals consist of monosymmetric prisms, which show the forms {100}, {001}, {110}, and {111} ; the plane of symmetry is the optic axial plane, and an optic axis emerges normally to the face (100). Some faces give good reflections, but parallel faces do not give images at 180° to one another, a behaviour which is frequently observed in the case of mixtures." This indication that the oxime may be a mixture, in spite of its constant melting point, must be borne in mind, and if confirmed, the different melting points of the various preparations would be accounted for.

In order to facilitate the identification of dimethylketohexamethyl-

ene, the author has prepared the semicarbazone; this compound slowly separates in crystals on warming the ketone with a solution of semicarbazone hydrochloride and sodium acetate in dilute alcohol. After recrystallisation it melts at about 196°, and further treatment does not seem to change its melting point. A sample dried at 100° gave C = 59·26, H = 9·36 per cent.; calculated for $C_9H_{17}N_3O$, C = 59·02, H = 9·29 per cent.

Dimethylketohexamethylene semicarbazone is fairly soluble in cold chloroform but less so in cold benzene and ethylic acetate, and crystallises best from methyl alcohol in the form of small, translucent, well-defined prisms. Heated slowly from about 175°, and using a short thermometer, it begins to sinter at about 190°, and melts completely at about 200—201°, effervescing, but not darkening; the m. p. depends on the size of the crystals and on the rate of heating. The crude semicarbazone seemed to be homogeneous, and the yield appeared to be good, but as, on recrystallising the preparation from boiling acetic acid, most of it suffered decomposition, further experiments are necessary to prove that only one semicarbazone exists.

173. " The localisation of deliquescence in chloral hydrate crystals." By William Jackson Pope.

Chloral hydrate crystallises from solution in large monosymmetric plates, showing the forms {100}, {011}, and {$\bar{1}11$}, and having the axial ratios $a : b : c = 1·6369 : 1 : 1·3951$, $\beta = 59° 5'$; these crystals consist of the same modification of chloral hydrate as was obtained in previous experiments (Pope, Proc., 1896, **12**, 142), and described as the biaxial modification, stable at ordinary temperatures. The crystals deliquesce in the air, but in a peculiar manner; the forms {011} and {$\bar{1}11$} rapidly absorb water vapour, and after a few minutes' exposure become covered with a layer of solution, whilst the faces of the form {100} remain perfectly bright during a considerable time. The attraction for moisture exercised by the pinacoïd {100} is thus much less than that exhibited by the other two forms.

It is consequently concluded that crystal deliquescence, like crystal solubility and other properties, varies with the direction in the crystal perpendicular to which its intensity is measured.

174. " Enantiomorphism." By William Jackson Pope and Frederic Stanley Kipping.

Crystals of the two enantiomorphous forms of a substance which exhibits circular polarisation only in the crystalline state, and in which the circular polarisation is an inherent property of the crystal structure, *i.e.*, of a substance belonging to Class 2*b* (Pope, Trans.,

1896, **69**, 971), should be deposited from the optically inactive solution in equal numbers, unless any disturbing factor is operative favouring the deposition of crystals of one particular enantiomorphous form, as, for example, contact of the slightly supersaturated solution with a crystal of that form. The truth of this statement can be demonstrated from our present knowledge of crystal structure, and is also evident from a consideration of the recent work of Landolt (*Ber.*, 1896, **29**, 2404), who showed that the crystalline powder of sodium chlorate, which rapidly separates from aqueous solution, consists of almost equal quantities of dextro- and lævo-rotatory crystals. The authors have extended these observations, and by taking a number of different crops of the large crystals deposited by spontaneous evaporation of sodium chlorate solution, have ascertained that the average numbers of dextro- and lævo-crystals deposited are the same, in absence of any disturbing factor.

It seemed probable that if a substance which is optically active in solution is introduced into an aqueous solution of sodium chlorate, the presence of the former would favour the deposition of chlorate crystals of one particular enantiomorph, and experiments were consequently made to test this view. About 5 per cent. of some substance, such as dextrose, mannitol, and isodulcitol, was dissolved in a saturated sodium chlorate solution, and the crystals of the salt deposited on spontaneous evaporation examined; a great preponderance of lævo-crystals separated from the dextrose solutions whilst in the separation from the isodulcitol solutions the dextro-crystals were in excess. The mannitol solutions deposited rather more lævo- than dextro-crystals; a number of crops from each solution were collected, and similar behaviour was noticed with each crop.

This selective deposition would seem to indicate, as would, indeed, be expected, from a consideration of the equilibria possible in such systems, that the solubility of a dextro-enantiomorph of Class 2*b* (see above) in a liquid containing an optically active substance, differs from the solubility of the lævo-enantiomorph in the same solvent. Solubility determinations, and also determinations of the rates of growth of dextro- and lævo-crystals of sodium chlorate in optically active solutions are in progress.

There would seem to be no *à priori* reason why a substance optically active in solution only and possessing a high specific rotation, should exert more directive influence on the deposition of crystals of Class 2*b* than an optically active substance of very low specific rotation, the only condition necessarily favouring the deposition of crystals of a particular enantiomorph being that there should be an asymmetric compound in solution. Using methods such as those indicated above, it might, therefore, be possible to determine with ease and rapid-

251

ity whether certain substances which, although containing asymmetric carbon atoms, are optically inactive in solution, are really asymmetric compounds, the inactivity in solution being due to a compensation brought about amongst the four different groups attached to one asymmetric atom. Experiments respecting this point are in progress.

Several cases, such as that of camphorsulphonic chloride (Kipping and Pope, Trans., 1893, **63**, 560), are known in which equal quantities of optical antipodes, when crystallised together, apparently do not form a racemic compound. In the light of the foregoing results, it should be possible to effect a partial separation of such mixtures, and even of racemic compounds, by crystallising them from a solution containing an optically active substance. Experiments on the separation of a number of racemic compounds, and of inactive mixtures of optical antipodes by methods based on the above considerations, have been commenced, but the results are not yet sufficiently conclusive to warrant any definite statements respecting them.

Premising the truth of the considerations stated above, Eakle's observation (*Zeit. f. Kryst.*, 1896, **26**, 562) that a sodium periodate solution containing sodium nitrate deposits more lævo- than dextro-crystals of the periodate, is quite incomprehensible.

IMPORTANT NOTICE TO AUTHORS OF PAPERS.

The attention of authors is directed to the following resolution of the Council.

"No title shall be included in the list of titles of papers to be brought before a Meeting of the Society, unless the paper and an abstract of it are in the hands of the Secretaries at least three days before the date of the Meeting; and no announcement of titles can be made in the Proceedings until the papers have been received by the Secretaries."

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in January. Applications for grants, accompanied by full particulars, should be sent to the Secretaries on January 15.

At the next meeting, on January 21st, the following papers will be received. The authors of those marked with an asterisk have announced their intention of being present :—

*" Studies of the properties of highly purified substances. I. The influence of moisture on the production of ozone from oxygen and on the stability of ozone. II. The behaviour of chlorine, bromine, and iodine with mercury. III. The behaviour of chlorine under the influence of the silent discharge of electricity, and in sunlight." By W. A. Shenstone.

*" Action of diastase on starch." Part III. By A. R. Ling and J. L. Baker.

*" The solution-density and cupric reducing power of dextrose, levulose, and invert-sugar. By Horace T. Brown, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar.

" Derivatives of Maclurin." Part II. By A. G. Perkin.