country in consequence of the new Patent Law. Referring to the future development of the coal-tar colour industry in this country, he said that, according to the latest German statistics, the export of indigo and other tar colours, reached, in round figures, 9½ millions sterling. This showed what amount of business might be recovered in this country. In the paper it was stated that there was no mention of this process made in Beilstein; but he might add that even in special works, such as Schultz's book, a description of this process could not be found.

Dr. J. C. CAIN said he had seen the plant used by Mr. Friswell for this process. The stirrer consisted of a central axle fitted with wings which were rapidly revolved. From an engineering point of view he would suggest that the vessel be raised considerably higher, so that the pipes might lead directly into the filter press, which would tend to prevent the solid material settling in the bend. The modern process of separating *ortho*- and *para*-toluidine was already carried on at the nitro-toluene stage by fractional distillation under diminished pressure.

Dr. G. T. MORGAN said the paper had an important bearing on the theory of ammonium bases, as it showed that at least one aromatic base, *p*-toluidine, had the property of combining with water to form a compound resembling the ammonium hydroxides. Possibly other benzenoid amines were capable of yielding hydrates which, however, were only stable at lower temperatures. In those works where arsenic acid was available this acid might be employed to separate *p*-toluidine from *o*-toluidine by taking advantage of the difference in solubility of their arsenates instead of using the phosphates as in Levy's process.

Dr. R. LESSING drew attention to the analogy of *p*-toluidine with phenol. In the manufacture of carboic acid a certain percentage of water was desirable for obtaining crystallised phenol from the mixture of the tar acids. Here, as in the case of *p*-toluidine, a hydrate was formed which, by its crystallising properties, was distinguished from the liquid hydrates of the cresols.

THE CHLORAMINE REACTION OF THE PROTEINS, AND TECHNICAL APPLICATIONS.

BY C. F. CROSS, E. J. BEVAN, AND J. F. BRIGGS.

The interactions of the simpler amines and the halogens have been studied by numerous observers. One of these reactions of particular interest, for reasons which we hope to make evident by the present communication, is that which leads to the production of monochloramin, NH_2Cl . This compound is readily obtained in solution by the interaction of chlorine (water) and ammonia, but more conveniently by substituting a hypochlorite for the free halogen. In a brief account of this reaction by F. Raschig (Ber., 1907, 40, 4586) it is shown that it takes place according to the equation: $\text{NH}_3 + \text{M}^\circ\text{OCl} = \text{NH}_2\text{Cl} + \text{M}^\circ\text{OH}$. The product reacts with iodides similarly to the hypochlorites, thus, $\text{NH}_2\text{Cl} + 2\text{HI} = \text{NH}_3 + \text{HCl} + \text{I}_2$; that is, using the terminology of "bleaching" chemistry, the "active chlorine" is double the actual combined chlorine. But the chloramin is in other respects markedly different in chemical activity from the hypochlorites, notably in the extreme feebleness of its bleaching actions. Although unstable and readily decomposing according to the equation, $3\text{NH}_2\text{Cl} = \text{N}_2 + \text{NH}_3 + 3\text{HCl}$, under certain conditions it undergoes the characteristic synthetic transformation to hydrazine—thus: $\text{NH}_2\text{Cl} + \text{NH}_3 = \text{H}_2\text{N.NH}_2.\text{HCl}$. The conditions specified by Raschig are, to heat together 200 c.c. aqueous ammonia (20 per cent. NH_3) with 100 c.c. of normal sodium hypochlorite in presence of a small quantity of gelatin (0.05 gm.) which he has found to favour the reaction by "raising the viscosity of the solution." The resulting hydrazine is obtained in the form of sulphate on adding sulphuric acid, or as the relatively insoluble double salt $\text{CuSO}_4.\text{N}_2\text{H}_4\text{SO}_4$ on adding a saturated solution of copper sulphate. The yield of hydrazine under the above conditions is 40–50 per cent. of the theoretical. (See also Chem. Zeit., 1907, 31, 126.) The general import of these reactions is indicated in a paper by the same author

(Zeits. angew. Chem., 1907, 20, 2065), thus:—Phenylhydrazine has been obtained from aniline. As a means of introducing the amino-group it is shown that phenol and the simple chloramine give *p*-aminophenol followed by interaction of two molecules with production of dihydroxydiphenylamine, which is directly oxidised to the indophenol. This explains the blue reaction of phenol solutions containing ammonia with hypochlorites.

The author also discusses the formation of dinitroazobenzene from *p*-nitraniline, and fully discusses the interaction of aniline and hypochlorites. These discussions are limited to bodies of the aromatic group.

We note in a paper by Knecht and Milnes (this J., 1892, 11, 131) on "The action of chlorine on wool," that the chlorinated wool was observed to retain its activity towards potassium iodide after many hours. The authors suggest that the results may be due to free chlorine or chlorinated quinone-like bodies. Other authors have dealt with the interaction of chlorine and hypochlorites with ammonia. Noyes and Lyon (J. Amer. Chem. Soc., 1901, 23, 400) have investigated the ultimate breakdown to nitrogen. J. Effront (Ber., 1904, 37, 4290) has proposed to use the interaction of hypochlorites with ammonia and proteins in drinking waters that is, under conditions of extreme dilution. He refers incidentally to the formation of nitrogen chloride (Chlorstickstoff), but regards the reactions involved as those of destructive oxidations. We shall revert to his observations on the proteins in a later communication.

We are concerned at the moment with the widely diversified group of such derivatives, *viz.*, the nitrogenous colloids which we shall refer to under the group designation of proteins, used in the general sense, and without reference to the special classifications of the most recent literature of this vast field.*

These bodies react with chlorine and the hypochlorites to form chloramine derivatives. Our observation of these reactions and their products have satisfied us that they take place in constant and characteristic quantitative proportions, and that the derivatives are simply related to the original substance, that is, are formed without destructive actions. Hence, these reactions may be made the basis of a number of quantitative methods which prove useful in the province of technical investigations. But further, such reactions occur in a number of industrial operations the significance of which will be found to be further elucidated by reference to the fundamental facts established for the simplest chloramine derivatives.

It will perhaps facilitate the exposition of our theme, as a contribution to industrial chemistry, if we approach it through the subject of flax bleaching.

Chloramine reactions in flax bleaching processes.—Raw flax as is well known retains a proportion of the nitrogenous constituents of the plant, derived from the cortical parenchyma which surrounds the bast fibres. In the full "linen bleach," the product of which is the pure flax cellulose, these residues are progressively eliminated together with the residues of the lignocellulose or wood. In various grades of partial bleaching to which both flax cloths and yarns are subjected (creaming—half-bleach—three-quarter bleach) these residues survive in considerable proportion, being whitened or decolourised by the processes of alkaline hydrolysis and hypochlorite oxidation which, while of the same character as those employed in the "cellulose bleach" are limited in intensity to produce the maximum of decolorisation consistent with the minimum removal of the non-cellulose constituents of the fibre.

It is to the production of chloramine derivatives in the hypochlorite baths that we have to call attention. These bodies when formed on the fibre are remarkably stable, they resist protracted washing; they resist the acid treatments (souring), which usually follow, and they do not yield to the exhaustive washing which again supervenes. As follows inferentially from our account of the properties of the simplest chloramine, the chloramine group is characterised by "active chlorine," and

* Kossel, *ibid.*, 1901, 34, 5214. E. Fischer, *ibid.*, 1904, 38, 530.

its presence is brought to evidence by the ordinary reagent, potassium iodide. Also the iodine set free may be estimated by titration with an alkaline arsenite—translated in calculating into its equivalent of "active chlorine."

We may state here, that in standard trade samples of "creamed" linen yarns, we have found such "active chlorine" to amount to as much as 0.1 per cent. We shall revert to the consequences of this defective practice after a more definite proof of the fundamental relationships involved, *i.e.*, of the reaction of the flax proteids with hypochlorite chlorine. The maximum fixation of active chlorine, we may note, is determined by reaction with the pure halogen; further, this maximum is for particular cases invariable.

The following quantitative observations were made upon a series of specimens of a sample "green" yarn damask, *viz.*, (a) the original untreated cloth; (b) after line boiling, sour and wash; (c) after a further lye boil (caustic soda) sour, and wash. The total nitrogen was estimated in these specimens and found to be:—(a) 0.5 per cent.; (b) 0.2 per cent.; (c) 0.05 per cent. Portions were then, after weighing, wetted out in boiling water, squeezed through rollers, and exposed in one case to 1 per cent. "bleach" solution, and in another to an atmosphere of chlorine gas, each series in one vessel. They were then well washed to remove any soluble inorganic chloroxygen compounds; then covered separately, with *N*/10 sodium arsenite solution, and titrated back with *N*/10 iodine. The percentages of active chlorine fixed were as follows:—

	(a)	(b)	(c)
	Per cent.	Per cent.	Per cent.
From 1 per cent. "bleach".	0.049	0.024	0.007
From chlorine gas	0.250	0.066	0.019

The relation between the two series of numbers is so far convincing.

We may mention incidentally that the chlorination of the lignone residues to lignone chlorides has been ascertained, by experiment with typical nitrogen-free lignocelluloses, not to contribute to the result. Nor does the flax cellulose treated under these conditions show any fixation of active chlorine (or oxygen).

We have now to mention an observation which has a particular technical interest, as well as furnishing another link in the chain of evidence connecting the fixation of "active chlorine" with the amino constituents of the flax. In the reactions of the ordinary "steeps" or bleaching baths, which are dilute solutions, generally slightly basic, of the hypo-chlorites, there is a partial breaking down of the chloramine compounds to soluble derivatives, which are by no means unstable; consequently they tend to accumulate in the standing liquors of the bleach works. This accumulation, however, is opposed by their tendency to "work out" of solution and fix themselves upon cellulose after the manner of colloidal mordanting oxides, or of dyestuffs. If a pure cotton cellulose be steeped in one of these "old" liquors for some hours, and thereafter exhaustively washed, it will be found to show the reactions of these chloramine derivatives. In order to establish again the relations of nitrogen to "active chlorine" in such a case we carried out quantitative observations as follows:—

Nitrogen in 500 c.c. of old filtered bleach liquors (by Kjeldahl and Nessler tests) *N*=4.2 mgrms. 16 grms. of mercerised cotton steeped 24 hours in 500 c.c. of this liquor, washed, and corrected by blank steeped in fresh bleach liquor (Kjeldahl and Nessler tests), *N*=4.2–1.6 mgrms. =2.6 mgrms. fixed. This cotton showed the characteristic active chlorine after exhaustive washing. We also fixed chloramines on pure cotton by steeping in bleach liquors after reaction with the proteins of wheat (flour) as of barley (wort), the liquors being filtered clear before use.

Having regard to these observations, it was of interest to devise a plan of analysis of "old" bleach liquors, to determine the presence of soluble chloramines. This plan follows from a characteristic differentiation of the

chloramines from the hypochlorites, in their resistance to hydrogen peroxide. The latter is added in slight excess to destroy hypochlorites, the solution is then acidified, and the excess of peroxide destroyed by adding dilute permanganate till the solution is faintly pink. On then adding a soluble iodide, the chloramine is brought into reaction, and may be estimated by thiosulphate solution. We need not elaborate the details of this method, necessary to eliminate the errors due to the possible presence of other oxidising compounds. It will be modified by observers to meet the requirements of particular cases. We may observe that we have also found it of considerable use in studying chloramine reactions in solution with amino compounds of known constitution. We also think it would serve no useful purpose to multiply records of our observations. Those we have cited are typical; we have made many series of determinations for the purpose of convincing ourselves, but we may well leave it to those interested to make their own observations.

We may conclude this section of our subject by stating our own conclusions in general form:—

(1) No flax fabrics washed from hypochlorite treatment can be safely assumed to be free from "active chlorine," however thorough the washing.

(2) The fixation of chlorine as "active chlorine" is in general in direct proportion to the nitrogen contents of the fabric. It is probably actually proportionate to the amino-groups of the protein constituents. It therefore progressively diminishes as these are removed through the various stages of bleaching.

The reaction conversely is a test of the purity of a bleach, and will be found of use in comparing one bleach with another.

Low-bleached damasks when treated with chlorine gas will be found to have a marked chloramine reaction, and it is important to note that the nitrogenous bodies thus reacting are the most resistant of the non-cellulose impurities, and are the last to be eliminated in the cellulose bleach.

(3) A hypochlorite liquor which has been used upon flax goods may contain some form of dissolved chloramine chlorine, which is not only devoid of bleaching action, but may influence prejudicially the action of the bleaching bath.

These conclusions are of direct import to the flax bleacher, and follow immediately from our experimental results and actual observations of the industrial processes and their products. In so far as they have not entered into consideration in the conduct of flax bleaching, they afford a new basis of experimental observation and control of the processes. But by control we must understand as chemists the regulation of processes to bring about particular results. If, for instance, it is recognised that to the more obvious functions of the hypochlorite bleaching liquors, which are those of hydrolysis and oxidation, we must add that of chloramine production, it becomes necessary to re-investigate the processes in relation to this function. We make this suggestion to those interested directly or indirectly in the industry. But as the lines to be followed in such an investigation will be obvious to every chemist, it is unnecessary to develop the matter in detail.

Application to histological investigations.—We have to pass on to a further application of the reaction originating in the same field of investigation, but suggesting extensions in many other directions. It is a matter of interest to localise the fibre constituents giving this characteristic reaction. If the flax in any form is treated with mercerising soda (15 per cent. NaOH) the "pectic" constituents of the fibre are considerably attacked, and on washing are removed in solution. The fibre thus treated is chlorinated and washed, and then treated with iodide solution. The distribution of the reaction is seen to be local, and on subjecting the fibre to microscopic examination, it is easy to resolve the strongly reacting regions into a complex of non-reacting fibres (cellulose), and more or less intensely coloured cellular masses, either still adherent to the fibres, or detached as a result of the mercerising treatment. We shall pursue this investigation as a development of histological method, by observations upon growing flax of this season's crop.

It will be seen from the quantitative observations upon gelatin (*infra*) that the quantity of chlorine fixed under maximum conditions is very large, when calculated in terms of the protein under reaction, an important point in respect of microchemical reactions that is for visual demonstration. Further the presence of lignocellulose does not vitiate or obscure the observations. These latter constituents have specific relationship to chlorine in virtue of their quinonoid character, and as will be remembered, after chlorination the particular reaction is localised by a careful application of sulphite of soda. (Cellulose, Cross and Bevan, p. 134.) Thus it is easy to differentiate these reactions for the purpose of localising their source, and by examining sections of raw flax after chlorination, we have detected the layer of proteid bearing cells situated between the cuticular tissue and the bast fibres proper.

It is obvious that this reaction has a general value in histological research. It can be graduated to any required intensity by using more or less dilute solutions of hypochlorous acid, or where considerable intensity of reaction is required, the pure halogen. We need not go into details of manipulation of histological objects, whether in their original form or in the form of sections.

Reverting in conclusion, to the question of flax, the distribution of these nitrogenous bodies may be altered by the processes of alkaline preparation. Generally, these bodies are extremely resistant, and they are only gradually broken down by the successive alkaline boils. As the result of progressive hydrolysis we have to reckon with the absorption of the dissolved products at all events in traces, by the cellulose of the fabric, as shown above in the case of pure cotton, and the problem of obtaining absolute purity of the flax cellulose is thereby complicated. Further, on placing pure cotton cellulose (bleached) in contact with flax goods, (a) in the lime boil, and (b) in the lye boil (caustic soda) which follows, it is found that the cotton cellulose is permanently stained by taking up the products of the action of the alkali upon the flax constituents. These resist washing and then on exposing to chlorine or acid hypochlorite and exhaustive washing, the characteristic fixation of the chloramine chlorine is noted by the relative intensity of the potassium iodide and starch reaction, the colour developed in (a) being stronger than that developed in (b). This, of course, is a point of some practical importance, and affords a basis of critical study of the processes which are a necessary preparation for the ordinary bleaching operations.

We have observed that the "active chlorine" of chloramines is possessed of an inferior oxidising power as compared with the active chlorine of hypochlorites, and that it has no direct bleaching actions upon colouring matters and dyestuffs. This is an important consideration when it is remembered that "creamed" flax yarns containing "active chlorine" are "blued" by the addition of sensitive dyestuffs such as Methyl Violet. Whether the blue resists the chloramine during a period of storage is not so certain, but the possible discharge of the dyestuff should not be overlooked. We have made experiments with reduced leuco-derivatives of triphenylmethane dyestuffs which show that the oxidising power of the chloramine existing on creamed flax yarns is sufficiently pronounced to restore the colour and dye the yarn. In reply to the question whether the active chlorine of the chloramine is sufficiently powerful to transform the cellulose into oxycellulose, the evidence is not conclusive. But we must lay stress on one danger of the presence of chloramine in these yarns, that is, the generally simultaneous presence of free acid. The decomposition of the chloramine which takes place gradually in the course of time, is accompanied by the formation of hydrochloric acid. If, as is often the case, the bleach works possess a supply of very soft water, the basic matters absorbed by the finished yarns are not sufficient to neutralise this acid, with the result that nearly all the yarns which show the presence of active chlorine, also show the presence of free acid when tested with methyl orange. In their destructive action on cellulose, acids are catalytic in their functions, their action is progressive and cumulative, and therein lies the danger of flax chloramine.

About a year ago we recorded (Zeits. angew. Chem.,

1907, 20, 570) the presence of active oxygen and acidity in a sample of bleached cotton cloth which had been thoroughly washed. On the evidence available we attributed the phenomenon to the formation of a cellulose "peroxide," but we were unable to reproduce the conditions on any pure cotton fabrics by the use of hypochlorites in the laboratory. We are now able to give an explanation of those reactions which brought about this exceptional condition of the cotton, which will at once be understood when we state that the cloth in question had been bleached in a hypochlorite liquor which had previously been employed on flax goods. The cotton had absorbed from the bleach liquors the protein chloramines which had diffused from the flax. It is to be noted that the results as regards peroxidation of cellulose are confirmed by Ditz (Chem. Zeit., 1907, No. 68), who obtained such products by the action of persulphates on pure cellulose. The products which we examined were characterised by a permanent acidity not removable by washing with distilled water, and it still remains therefore an open question whether the cellulose had merely combined with the chloramine, or as a result of the combination had itself undergone peroxidation on long standing at the expense of the chloramine.

Quantitative observations on protein-chloramine reactions.—Gelatin.—It is of course a matter of importance to determine the relationship of the fixation of chlorine to the nitrogen groups of particular proteins. At present we have to be satisfied with the general proportion of chlorine to total nitrogen, though we have little doubt that this reaction may be extended to throw a light on the actual proximate constitution of the proteins. Before we consider these reactions we may mention two facts of importance. First, that the gelatin chloramine formed by interaction of chlorine gas and the hydrated substance is extremely stable. A preparation which we made in December last, which was washed, dehydrated with alcohol and dried and found to contain 0.6 per cent. of active chlorine was examined on the 24th February and found to contain 0.2 per cent. Secondly, the chloramine is sensitive to the reagents known as antichlors, and a gelatin chloramine treated with sulphurous acid reverts to the original condition, which is shown by a full reaction with chlorine. These, of course, are constitutional facts which will have their application in research.

We now have to deal with the technical application of the reaction.

Chlorine and gelatin.—The interaction of these bodies may be made to give results which are sufficiently constant to afford a quantitative method of determination of the protein. In order to secure these results we have first to reckon with the fact that a mass of gelatin is only attacked superficially. If a sheet of dry gelatin of convenient thickness be immersed in a solution of hypochlorite for some hours, the gelatin will be found to have swollen almost normally, but the surface will have a hard feel which suggests its insolubility. After exhaustive washing of the swollen sheet, sections of same when placed in potassium iodide solution, are found to show the chloramine reaction in superficial layers of varying thickness. If the section be boiled with water the interior portion is found to be perfectly soluble, but the two surfaces remain in the liquid as insoluble films. Thus we may say that hypochlorites have a "tanning" action on gelatin in converting it into its chloramine, and that the product constitutes a semi-permeable membrane, which permits the passage of water, but prevents the diffusion of the hypochlorite. To secure a general attack we have found it necessary to use chlorine gas, and to diffuse the gelatin through a mass of inert material presenting an indefinitely large surface, for which purposes cotton yarn is very convenient. Cotton yarn was impregnated with known quantities of gelatin solution containing aluminium sulphate, and then dried. Weighed quantities of this yarn containing a known weight of gelatin were steeped in cold water to hydrate the gelatin, they were then squeezed out and exposed to an atmosphere of chlorine for one hour. Exhaustive washing of the chlorinated product gave variable final results, because soluble products presumably formed by hydrolysis of

the chloramin appeared to diffuse indefinitely and the results in terms of chlorine decreased as the time of washing was prolonged. We were able to arrive at a fixed point by suspending the yarn without washing in a current of air from a small fan, until perfectly dry. The yarn was then placed in an excess of *N*/10 sodium arsenite solution (diluted) about one hour being allowed for complete penetration, and the excess of arsenite was titrated back with *N*/10 iodine. It might be presumed that the proportion of active chlorine fixed would be a measure of the quality of the gelatin, but we find that such is not the case, and that three samples of skin gelatin of very different qualities gave approximately identical results. As the mean of a large number of determinations we have fixed the proportion of active chlorine taken up by gelatin under these conditions at 15.4 per cent. of its air dry weight. This number is not appreciably changed if the gelatin be previously combined with formaldehyde. Further if the chloramine be immediately destroyed by sulphurous acid and washed, the gelatin will again take up the same amount of active chlorine on a second treatment with the gas.

From this work we have evolved a method for the detection and estimation of gelatin in tub-sized papers. The qualitative test possesses the advantage that any number of samples may be tested simultaneously, and that a very small fragment of each sample is sufficient. We have to bear in mind that iron compounds which are present in traces in the majority of papers would interfere with the test. In order to eliminate this error, and to arrive at a rapid result, we place the moist fragments after chlorination in a bath of 2 per cent. solution of sodium phosphate, previously heated to 45° C. and leave them for exactly five minutes. This reduces the otherwise inconvenient delicacy of the reaction, and ensures that only papers containing proteid matter will show a positive result. The fragments are removed from the bath and tested with potassium iodide and starch. Papers containing only 0.5 per cent. of gelatin still show a strong coloration. It should be noted that the presence of large quantities of mechanical wood pulp in a paper will produce a faint chloramine reaction owing to traces of proteid matter contained in raw wood. For the quantitative determination we suspend the sheets of paper after chlorination in front of the fan and expose to a full blast of air for at least 1½ hour. We find that exposure for only ¾ hour gives too high results owing to the greater density of paper as compared with cotton yarn, whilst exposure for 2½ hours gives the same result as for 1½ hour. The paper is then torn up, placed in *N*/100 arsenite for a considerable time (at least 1 hour), and the excess titrated with iodine. If these conditions be followed the divisor 15.4 noted above gives the quantity of gelatin in the paper as shown by the following examples:—

Paper.	Percentage of gelatin by Kjeldahl (air dry weight) $N\% \times 6.53$.	Percentage of gelatin by chlorine (air dry weight).
Ordinary note paper (air dried vellum).....	7.1	7.1 7.25 7.4 7.3
Typewriting paper (cheap quality).....	2.62	2.8 3.0
Hand-made ledger paper (Itayal).....	*8.15	7.7 7.7

* This number has been corrected for ammonia alum, which was used in the size in the proportion of 15 per cent. on the gelatin.

Silk and chlorine.—We have selected silk as a convenient type of protein for the quantitative investigation of the relations between the active chlorine of the chloramine and the total chlorine fixed by this and other groups of the molecule (e.g., unsaturated and quinonic groups). We have not succeeded in obtaining constant results, possibly because the reagents do not penetrate the substance of the fibre, but the relative results possess a certain interest. In determining these relations, exhaustive washing, which is very difficult to attain, is necessary; the total chlorine is then determined by heating with nitric acid and

silver nitrate. In the first place, silk, like the flax and gelatin, shows much lower results for active chlorine when treated with hypochlorite solutions than when exposed to chlorine gas, and in the latter case the result appears to increase with the time of exposure; this may be a question of penetration or of proteolytic hydrolysis. The following results may be recorded:—

Boiled-out silk. (Air-dried weights.)

Conditions.	Active chlorine.	Total chlorine.
	Per cent.	Per cent.
Silk and 0.5 per cent. neutral hypochlorite (washed).....	1.2	—
Silk and chlorine gas ½ hour (washed).....	3.01—3.04	6.01
" " 1 hour.....	5.46	7.24
" " (blown off).....	6.40	—
" " (sulphurous acid and washed).....	nil	3.38

(Acidity produced during chlorination, 11 per cent. of hydrochloric acid.)

Titration of nitrogenous substances in solution.—We are not prepared to propose a finished method for the rapid titration of nitrogenous bodies in solution, however desirable such a method would be for many technical purposes, but we believe that the chloramine reaction will ultimately lead to such a process. In this case it will be necessary to ascertain whether the chloramine reaction is a measure of the total amino-groups present, or only of amino-groups in a certain state of freedom. (Compare the nitrous acid process of H. T. Brown for determination of the amino-acid index.)

We have made a few preliminary experiments on gelatin solutions using the hydrogen peroxide and potassium permanganate method noted above. We found that it was necessary to employ slightly alkaline solutions of the hypochlorite, because in presence of acid other groups of the proteid are chlorinated and precipitates are formed. The difficulty of these titrations lay in the tendency to spontaneous decomposition of the chloramine, but by limiting the time of action of the hypochlorite to about 1 hour the results were fairly constant. Ten c.c. of a 1 per cent. gelatin solution were placed in a flask with 50 c.c. of water, and 5 c.c. of normal caustic soda solution. An excess of hypochlorite was then added and allowed to act for one hour, a slight excess of hydrogen peroxide solution was then added, the solution acidified, and titrated back with permanganate. The chloramine was titrated by *N*/10 thiosulphate after addition of potassium iodide. For periods ranging from ½ to 1½ hour, the results were sufficiently constant, and showed 12.0 to 12.4 per cent. of active chlorine on the air dry gelatin. No difference could be detected between a very good sample of gelatin and a very poor sample. We hope that this titration may be considerably simplified, and perhaps standardised by taking advantage of the fact that hypochlorite chlorine will bleach a solution of indigo-carmin, whilst chloramine chlorine has no action on the dyestuff; we put forward this suggestion for the benefit of those who are interested.

In conclusion we observe that in this communication we limit ourselves intentionally to the positive experimental results of our investigations. We would only mention one matter of rather theoretical or speculative interest, that is the application of this reaction to the investigation of the colloidal state. There can be no doubt that the reaction with the nitrogenous colloids is well defined, and is available for solving constitutional problems as regards the constituent groups actually reacting. But the colloid is the proximate complex, and the chloramine reaction taking place in such large quantitative ratio, without, so far as we can see, breaking down the complex, i.e., the colloid itself, as measured by its characteristic physical properties, it becomes an important pioneer reaction, comparable with the quinone-chloride reaction of the lignocelluloses, which has proved of great utility in the investigation of the fibre colloids.

DISCUSSION.

The CHAIRMAN said the experiments which had been shown were of extreme importance, as they furnished a new key for unlocking the chemistry of the proteins and the organic colloids in general. They were also of great practical value in helping to solve the difficulties which beset the path of the bleacher. For it would seem that boys need now only go about the works and test whether each "boil" had been accomplished successfully, in that it destroyed all those proteins which in the "bleaching" process formed the chloramines.

The Chairman then referred at length to the views of Raschig on catalysis (this J., 1907, 1108), and which found a corollary in the papers by Pope and Barlow—which had led him to add glue to the solution of hypochlorite and ammonia in order so to influence the chemical change that the yield of hydrazine, which was at first only a few per cent., was brought up to a percentage of 40 or 60. Indeed, Raschig gave a very practical proof of what could thereby be achieved in that he now manufactured hydrazine at a very low price. Raschig's hypothesis that the shape of the molecules was altered by making the solution more viscous through the addition of glue (gelatin), casein and proteins in general, would seem to become untenable in the light of the facts brought forward by the authors of this paper. For they proved that the formation of chloramines from proteins and chlorine took place in stoichiometrical proportions. This opened up a new vista of investigation which would require an army of chemists to work out thoroughly. The authors had now put the action of chlorine of proteins on a line with ordinary chemical reactions, amenable to the laws of the atomic theory. Reverting to Raschig's views he (the Chairman) pointed out that Raschig had also obtained favourable results by introducing glycerin, sugar, and starch into the solution of hypochlorite and ammonia. As these substances were characterised by hydroxyl groups he would like to ask the authors whether, in their opinion, the hydroxyl groups were perhaps attacked in a similar manner as were the amino groups of the proteins by chlorine.

Dr. S. RIDEAL referred to some previous work by himself and Mr. Bevan on the action of electrolytic chlorine in bleaching. They found that the Hermite process gave quantities of available chlorine in excess of the theory, and after much discussion the explanation was not quite cleared up. It would seem that this combination with nitrogenous substances present might offer some further solution to the peculiar behaviour of electrolytic chlorine both in bleaching and in sewage treatment. He (Dr. Rideal) recently had had a good deal to do with the sterilisation of sewage effluents by electrolytic chlorine, and found that ammonia and amino-compounds influenced the germicidal action. These unstable amino-chlorides explained this phenomenon. The authors had overlooked a paper by himself and Mr. Stewart, in the Analyst, 1897, p. 228, in which they had described a method for the determination of proteins by chlorine in which they showed that gelatin and allied proteins gave an insoluble chlorine compound which could be dried and weighed, or the nitrogen estimated by Kjeldahl's process. Bromine behaved similarly, and Allen and Searle (Analyst, 1897, p. 258) later worked out an analytical process using the latter reagent. In the course of that work he found that Mulder (Berzelius, Jahresb., 19, 734) and others as far back as 1840 had prepared several of these bodies, "protein chlorous acid" and chlorite of albumin being the names ascribed to those from gelatin and albumin.

Mr. J. L. BAKER, in reference to the statement that proteins formed substituted chloramines, asked if that would also apply to proteolytic degradation products. Would peptones form such compounds? It would be of interest particularly in showing the differential distribution of proteins in seeds, etc. How would the authors proceed to examine a barleycorn for the distribution of proteins? Was it necessary to remove the starch?

Mr. CLAYTON BEADLE said this paper was very interesting in connection with the paper trade, as it offered a

simple method of ascertaining the amount of gelatin or casein in paper. It also appeared to throw a considerable light on problems in connection with the bleaching of celluloses. It was possible to bleach raw cottons containing 2½ to 5 per cent. of protein by means of certain accelerators very rapidly, but it required the use of about 10 per cent. of active chlorine; whereas the same cotton after treatment by boiling, which removed the bulk of this protein, would bleach with only about 1 per cent. of chlorine. This difference might be accounted for by the formation of the substituted chloramine. In connection with the bleaching of wood pulp also, the amount of chlorine consumed varied enormously with different pulps, and appeared to have no relationship with the amount of actual cellulose contained in them. Some doubt had been raised with regard to the actual chlorine consumption in the Hermite process, but, as a matter of fact, the chlorine consumption per unit of bleaching effect was estimated by three independent chemists, and he did not think there was the least difference. Three pounds of chlorine in the case of the Hermite liquor was equal in bleaching effect to five of chlorine in the case of only bleaching powder solution. The ratio of efficiency was therefore 3:5.

Mr. W. P. DREAPER drew attention to the extreme difficulty in many cases of deciding the cause of changes taking place when fabrics "tender" or develop stains on keeping. The authors had certainly thrown light on the alterations which might take place in the case of flax. In the case of wool and silk, the indications were that the matter was even more complicated. The figures given in the paper showing the different ways in which chlorine might be adsorbed, or held, by silk was interesting from the theory of dyeing side of the question.

Dr. G. T. MORGAN said he had had an opportunity of repeating Raschig's original experiments, and it certainly afforded a simple means of obtaining hydrazine. It was a very significant fact that the catalysts, gelatin, casein, or ordinary joiner's glue, which induced the formation of hydrazine from the hypochlorite and ammonia, were found by the authors to be capable themselves of forming complex chloramines. It seemed as if the presence of a substance capable of yielding complex chloramines favoured the formation of chloramine itself, and it was therefore unlikely that non-nitrogenous compounds such as glycerin would not be so efficacious. It had been known for a long time that the treatment of wool by small quantities of hypochlorite considerably modified the action of this fibre towards colouring matters, and it would be interesting to know whether the authors considered this change in the properties of wool to be due to the production of chloramines.

Mr. W. C. HANCOCK said some years ago he was engaged with Messrs. Cross and Bevan in experiments to try to obtain ammonium hypochlorite, but they failed to get a definite compound or anything which showed any characteristic reaction. It appeared on the face of it, from the reactions described to-night, that the actual ammonium hypochlorite, if formed at all, would be immediately split up into this chloramine compound and water.

Mr. Cross, in reply, said the Chairman had raised the point of catalysis in reference to the hydrazine reactions (Raschig), and Dr. Morgan had anticipated the answer that should be given. There was a catalytic action here, the gelatin holding the chloramine group more firmly than the simple amine, enabled the synthesis to take place, otherwise the conditions of reaction were almost explosive. He should not think that compounds such as the carbohydrates would act in that way. He did not think it was a question of viscosity, as suggested by Raschig, who had overlooked the chloramine reaction of the proteids, though suggesting catalysis of a certain order. Dr. Rideal had reminded them of a long stretch of ancient history, which was extremely interesting. Though the hypochlorites and proteins had been brought together *ad infinitum*, the specific chloramine reaction had been entirely overlooked as such. It was the work of Raschig's which furnished the clue to the situation,

and would, as now developed, clear up many matters of history. He agreed with Dr. Rideal that many must have observed the formation of these compounds, and it was remarkable that it required so long a time to get a clear explanation of the causes at work. He regretted that they had overlooked Dr. Rideal's communication to the Society of Public Analysts, which had an obvious and direct bearing on this particular matter. As far as he knew, it was a point of general knowledge that chlorine reacted with these proteins, and they had referred to wool and silk in this communication. The new point was the fixation of the "active" chloramine chlorine. When they came to look into Dr. Rideal's experiments no doubt they would find they had been very carefully done, and in combination with the present contribution would still further develop the examination of protein mixtures, by more exact methods of analysis. With regard to Mr. Baker's question as to the reaction becoming an index of proteolytic resolution, they had referred to the paper of Effront in the *Berichte* of 1904, who proposed to use the hypochlorite reaction for the estimation of the ammonia and proteins in drinking water. Starting with ammonia he showed that it would break up into nitrogen and hydrochloric acid; the proteins and peptones also entered into reaction with hypochlorites in constant proportions. He overlooked what was actually taking place, but his experiments bore directly on the point raised by Mr. Baker. That the series of peptones would react was undoubted, and probably in proportion to the free amino-groups. It would also be possible to correlate the chloramine reaction with Dr. Horace Brown's index, and throw a new light on the hydrolytic resolutions of the proteins. Mr. Baker also asked as to the localising of proteins in histological reactions: they would exhibit a section of potato which was a typical case. It was an extremely delicate reaction, and required graduating: the experiment with barley-corn sections could be easily carried out so that the starch did not interfere.

Dr. Rideal and Mr. Beadle particularly raised the question of electrolytic oxidation under conditions which they examined many years ago. They did certainly admit that probably chlorine might have got locked up in this particular way, especially as in certain of the bleaches investigated nitrogenous compounds were involved, and chloramines would undoubtedly be formed. Of course, in dealing with sewage and disinfectant reactions they had a whole line of new investigations opened out.* He had no doubt they must assume that the bacteria themselves would be chloraminated by this process, but how they would behave under those modified conditions remained to be shown. Mr. Dreaper had mentioned the application of this reaction in connection with the theory of dyeing. He was welcome to look at the numbers they had obtained for silk. No doubt the application of this reaction would enable them to investigate a number of problems which previously were not open because they had no means of quantitatively modifying the proteins, as, for instance, they could do with cellulose to form cellulose esters and other derivatives; in the case of nitrogenous colloids they had to make their observations on the substances which nature presented to them. Now they had the means of definitely modifying them. He had already made use of Dr. Morgan's suggestion in accounting for what he suggested was catalysis in regard to Raschig's use of a protein in promoting the hydrazine reaction. He might say that in this paper they had carefully limited themselves to what they had actually done. It was not fair in a matter of this wide application that they should attempt to anticipate a great deal of work which each specialist was entitled to bring forward himself. They had not thrown out a number of speculations as to the extensions which might be made, but he would recommend all those who had not come across Raschig's papers to take them into consideration, for it was quite clear that a large extension of investigation would result.

* Dr. Raschig, in a private communication (March 5) suggests that the particular and persistent odour, raised in the human skin in contact with hypochlorite solution may be due to chloramine reactions. We have made observations which confirm this suggestion (March 9).

New York Section

Meeting held at Chemists' Club on Friday, Jan. 24, 1908.

MR. GEO. C. STONE IN THE CHAIR.

PRESENTATION OF THE PERKIN MEDAL TO MR. J. B. FRANCIS HERRESHOFF.

(ABSTRACT OF PROCEEDINGS.)

After a few introductory remarks by the chairman, in which he emphasized the importance of stimulating research by proper recognition, and drew attention to the work of Perkin, who not only discovered a new product, and developed the method of using it, but sold it, the Secretary, Dr. Hugo Schweitzer, read the report of the Medal Committee, and gave a history of Perkin's life work, quoting thus Adolf von Bayer: "The key to the knowledge of the nature of aniline colours lies in the basic properties of the carbon atom. The aniline colours which delight the eyes have thus attained more importance to science. Their rays are the torch which enlightens the path of the explorer in the dark regions of the interior of the molecule, and the man who has lit the torch is William Henry Perkin." Dr. Schweitzer observed that the discovery of mauve by the youthful Perkin led to the development of one of the most wonderful and scientific of human achievements, the coal tar industry. It exercised a predominant influence on all branches of chemical technology and had given employment, comfort, and health to millions. Dyestuffs innumerable have been and are still being evolved from coal tar giving a "rainbow" range of colours complying with every demand of taste and fashion, equalling in beauty, brilliance, stability and fastness to time, light and chemicals those supplied by Nature from plants and animals.

A host of therapeutic agents for the treatment of most diverse maladies has been and still is produced from coal tar. Anesthetics and the active principles of animal glands and even a remedy for the African "sleeping sickness" are synthetically produced from this source.

Artificial "sweeteners," 550 times sweeter than sugar; artificial oils of almond and musk; odours of wintergreen, violets, roses, jasmin, and heliotrope are produced. Photographic developers and colour photography; "safety" explosives, smokeless powders; preservatives, alike against the destroyers of the forest and the bacteria in foods are all derived from the same source. Yet what do all these signify compared with von Bayer's encomium on Perkin's work: "It lit the torch enlightening the path of the explorer into the dark regions of the molecule."

Dr. Schweitzer recalled the celebrations of the 50th anniversary of the foundation of the coal tar industry—in London on July 26th; in America in October, 1906,* in honour of Sir William H. Perkin. On these occasions the chief scientific and technical societies of the civilised world and many universities congratulated him and accentuated his marvellous work and personal worth. The American celebration was in hands of a Committee.† This Committee collected funds for a chemical library—to be placed in the Chemists' Club and to be called the "Perkin Library." On the happy suggestion of Mr. H. A. Metz, a sum was set aside to provide for the award of a gold medal—to be called the "Perkin Medal"—to that chemist residing in the United States who had accomplished the most valuable work in applied chemistry during his career, whether this had proved successful at the time of execution or publication, or had subsequently become valuable in the development of industry. The

* This J., Vol. XXV., 1906, pp. 783-6 and 1207-8.

† The Committee was constituted as follows:—G. C. Stone, H. Schweitzer, C. P. Chandler, W. H. Nichols, T. J. Parker, Clifford Richardson, V. Coblenz, R. W. Moore, Maximilian Toch, and F. C. R. Hemingway (representing the New York Section of the Society of Chemical Industry); W. McMurtrie, S. P. Sadtler, W. H. Walker, C. B. Dudley, H. C. Sherman, F. J. Pond and G. M. Joyce (representing the American Chemical Society); E. F. Roerber, S. A. Tucker, C. O. Mallouk, and A. von Jaekovic (representing the American Electro-Chemical Society).