

was exposed to the action of the gas at a temperature of about 850°C ., we obtained a black substance intermingled with a large quantity of unaltered molybdenum, and even after repeated treatment with ammonia the conversion of the metal into its nitride was always very incomplete. Different specimens of the product were found to contain quantities of nitrogen varying from 2.4 up to 3.1 per cent., while the formula Mo_2N_3 requires 8.9 per cent. of nitrogen. Under the microscope the product was seen to be composed of black particles mixed with particles of the metal, the latter showing rounded edges. The product is not attacked by dilute hydrochloric or sulphuric acids, but it dissolves very slowly in hot concentrated sulphuric acid and it is readily oxidised by nitric acid. At lower temperatures the quantity of nitrogen fixed by the metal was less than at a red-heat. The ammonia was decomposed to a considerable extent when passed over the heated metal. Practically no nitride was formed when powdered tungsten was heated in ammonia, whether at higher or lower temperatures. The ammonia underwent some decomposition, and the appearance of the metal was altered to the extent that its particles showed rounded edges, as if it had been in a state of incipient fusion, but the product was found on analysis to contain no more than a trace of nitrogen.

Thus, as might have been expected, the behaviour of chromium towards ammonia resembles that of manganese and of iron. When the members of the chromium family are compared with one another it is seen that the resistance of the metal to the action of ammonia, or the instability of the nitride produced, becomes more marked as the atomic weights increase.

Titanium, tin, and lead.—Finely powdered titanium was heated in ammonia at a temperature of about 800°C . Much of the gas was decomposed and there was obtained a dull bronze coloured substance, which became highly lustrous when rubbed in a mortar, and which was seen under the microscope to consist of lustrous particles. A number of different specimens were prepared and analysed, but in no case did the quantity of nitrogen in the product exceed 6.8 per cent., while in some specimens it fell to 5 per cent. A bronze coloured nitride of titanium has been obtained by other methods, but this has the composition represented by the formula TiN , and contains 22.4 per cent. of nitrogen. The product which we obtained reacts very slowly, if at all, with water, and is insoluble in hydrochloric acid, but it slowly dissolves in hot concentrated sulphuric acid. It is decomposed when heated in the air, but it offers considerable resistance to the action of hydrogen at a red heat.

A number of experiments were made with tin, in the form of foil, at temperatures ranging from 160°C . to a red-heat, but no perceptible quantity of nitrogen was fixed under any conditions. Even at 170°C ., however, the appearance of the metal began to change, the lustrous surface of the foil acquiring a frosted appearance, and on examination with the microscope showing a number of minute rounded blisters or bubbles. At incipient redness a large proportion of the ammonia passed over the heated metal was decomposed, but the rate of decomposition diminished rapidly as the temperature was lowered.

The behaviour of lead we found to be very similar to that of tin, as regards both the decomposition of the ammonia and the inability of the metal to form a nitride, or the instability of the nitride produced, under the conditions of our experiments.

Zinc and cadmium.—Previous to the publication of White and Kirschbraun's paper (*loc. cit.*) we had examined in detail the interaction between zinc and ammonia at various temperatures, but as our results in the main are in agreement with those already recorded it is not necessary to do more than emphasise the statements that heated zinc readily attacks ammonia, that the most favourable temperature lies in the neighbourhood of 600°C ., and that since the temperatures of decomposition and of formation of the nitride of zinc lie close together the product always consists of a mixture of the nitride with the metal. A large proportion of the ammonia is decomposed by contact with the heated metal, and the decomposition of the gas begins at a temperature not much above 200°C .

A few experiments with cadmium showed that its behaviour is similar to that of zinc, but that it is difficult

to get more than a rather small proportion of the metal converted into a nitride. When the finely powdered metal was heated in ammonia it was partially converted into a nitride of a greenish colour, but this was mixed with a considerable quantity of the metal. The proportion of the ammonia decomposed was not so great as with zinc. When cadmium foil was heated in the gas little formation of nitride could be observed but the appearance of the foil was greatly changed, in a similar manner to that observed with other metals.

Aluminium.—Our experiments with aluminium were discontinued after the publication of the paper already referred to. We had found, however, that reaction does take place between the metal and ammonia, but that—at least under the conditions of the experiments—only a small proportion of the metal can be permanently converted into the nitride in this way. The rest of the metal is changed in physical properties in a similar manner to the other metals which do not readily form nitrides by interaction with ammonia, and as usual much of the gas was decomposed.

Palladium.—In view of the results formerly obtained with platinum, some comparative experiments with palladium were carried out. The metal was used in the form of a very fine powder. No formation of nitride was observed in any of the experiments, which were made at different temperatures up to bright redness, but on inspection under the microscope the metallic powder was found to contain a number of rounded particles which had the appearance of having been in a semi-fused state. The decomposition of the ammonia was very considerable.

It is known that the alkali and the alkaline earth metals interact with dry ammonia when heated in the gas, yielding amides or nitrides respectively according to the conditions of the experiment. Therefore, taking into consideration the fact that the metals examined by us include representatives of all the groups of these elements, there are grounds for reaffirming our former conclusion that in all probability a reaction of some sort takes place between every metal and ammonia at a suitably high temperature. We incline to the belief that a nitride of the metal is produced, at least transitorily, even though no nitrogen remain permanently in combination with the metal, because it has been proved that frequently the temperature at which a metallic nitride is formed and that at which it is decomposed lie very close together. It is, moreover, difficult to account otherwise for the very marked alterations in the physical character of those metals which do not appear capable of forming comparatively stable nitrides.

THE AMYLOLYTIC AND PROTEOLYTIC FERMENTS OF WHEATEN FLOURS, AND THEIR RELATION TO "BAKING VALUE."

BY JOHN S. FORD AND JOHN M. GUTHRIE.

PART I.

When an attempt is made to determine the activity of the amylolytic ferment, which is well known to be present, to some extent, in wheaten flours, a limited experience shows that the operation is not simply a question of extracting the flour with water and measuring the activity of the extract, by allowing it to act on soluble starch, in the customary manner. Before recording the reasons for this assertion we may state that the actual activity determinations of the various extracts, mentioned hereafter, were made in the manner and with the precautions described by us in previous publications (this J., 1904, 414; J. Inst. Brew., 1905, 206), using soluble starch of R 1.0 as the hydrolyte. The results are in all cases expressed as the grams of maltose produced by the filtered extract of 1 gm. of the substance acting on excess of soluble starch for 1 hour at 40°C .

The first point to be ascertained in connection with the estimation was the influence of the duration of extraction.

Experiments were carried out, with two wheaten flours of different origin, as follows:—

TABLE 1.—*Influence of duration of extraction.*
20 grms. flour, $\frac{1}{2}$ litre water at 18°.

Time of extraction. Minutes.	Grms. maltose per 1 gm. flour.	
	No. 1.	No. 2.
10	8.88	12.88
30	8.03	13.58
60	5.38	13.05
90	3.48	11.41
120	3.00	9.31

These extractions were made by means of a shaking machine described by us (*J. Inst. Brew., loc cit.*).

As it is obvious from these results that destruction* of the enzyme takes place with varying rapidity, dependent on certain characteristics of the flours, we are at once confronted with a difficulty, that of time of extraction. Quite apart from this rapid destruction of amylase, the degree of which varies with the ratio of flour to water, there are other difficulties, for it was found that an aqueous extract added simultaneously to different preparations of soluble starch gave different results, dependent to some extent on the salt concentration of the starches or probably, speaking more accurately, on the resulting hydron concentration of the solutions. It was also observed that the filtered solutions obtained by limited extractions, when retested after standing several hours gave different values. In some instances an increase and in others a decrease of activity was recorded, the results depending on the time of extraction and the nature of the flour. We need not give the experimental details of these observations as they cannot yet be generalised. Now, as sample No. 1 was acid in reaction and No. 2 very faintly alkaline, to rosolic acid, it seemed probable that we had to deal with destruction of amylase by hydrogen or hydroxyl ions, consequently an evident inference was to extract the flours with a solution of an ampholyte known to have no specific influence on amylolytic action. Various substances suggest themselves for this purpose and were tried, but we need only record a few of our experiments. In the first place an attempt was made to adjust the "neutrality" of the aqueous extraction by the addition of 2 grms. of potassium di-hydrogen phosphate plus 0.2 gm. of di-sodium hydrogen phosphate per $\frac{1}{2}$ litre of water. When No. 1 flour was extracted thus for $\frac{1}{2}$ hour, the value obtained was 14.28 as against 8.03 grms. of maltose formed in the case of simple aqueous extraction. The addition of the same proportion of mixed phosphates to the starch used for the aqueous extract conversion did not appreciably alter the value. Extraction with solutions of other ampholytes, as glycine, gelatine, certain proteoses, etc., gave similar increased values. In the case of extraction with mixed phosphates the increased amylolytic activity is not necessarily a proof simply of adjustment of "neutrality" and consequent preservation of amylase, as it might be due partly to increased solution of the enzyme; the differentiation of these actions is not easy. It seemed of interest to see how far the addition of a neutral salt, such as potassium chloride, would affect the amount of active enzyme in solution. The use of this salt is however tantamount to concurrent addition of amphoteric bodies owing to the increased solution of certain proteins of the flours. The results of such an experiment are tabulated below, as even though they are the measure of a composite effect, they are of considerable interest.

TABLE 2.—*Influence of potassium chloride on solution and activity of the amylolytic ferment of wheaten flours.*

	Grms. maltose per 1 gm. flour.	
	Extraction 1 hour 18°	Digestion 3 hours 30°.
Water alone.....	3.22	2.80
Water plus 10 grms. potassium chloride per $\frac{1}{2}$ litre	13.72	17.36

An extension of these experiments was made thus:—1 gm. of flour was digested for 18 hours at 30° with 50 c.c. water and with potassium chloride solutions as under:—

TABLE 3.

	Pot. chloride per 100 c.c.	Grms. maltose per 1 gm. flour.
Flour with water alone		4.06
" " " plus	0.02 gm.	6.10
" " " "	0.20 "	11.76
" " " "	0.40 "	13.70
" " " "	1.00 "	17.36
" " " "	2.00 "	18.62
" " " "	4.00 "	18.90
" " " "	8.00 "	18.20
" " " "	12.00 "	15.40
" " " "	16.00 "	13.72
" " " "	20.00 "	12.04

The flour with water alone yielded salts to solution equal to 0.007 gm. per 100 c.c. Toluene was used as an antiseptic in the above digestions.

The solution obtained by aqueous digestion above, when added to starch solutions containing potassium chloride equal in amount to that added by the volumes of the saline extracts used in the starch conversions, gave a maximum value of 4.62. These experiments were carried out at an early stage in this investigation, before we were cognisant of the great destruction of amylase which takes place during aqueous extraction or digestion, and were considered at that time to represent simply increased solution of the enzyme; we now see that this is not the case, the major portion of the increased activity being due to conservation of the enzyme by solution of protecting bodies. Reference to a recently published paper (Contributions to the Bio-chemistry of Barley, *Jour. Inst. Brew.*, 1908, 61; this *J.*, 1908, 239), in which we describe certain methods for the estimation of the amylase of resting barley, will provide reasons for this opinion. In connection with the investigation on barley, just mentioned, some comparative experiments were made with wheaten flours, an extension of which we record here. In making these comparisons it was not our intention to subject wheaten flours to exhaustive examination, but these whilst exhibiting a marked resemblance to barley flours in certain directions, also show such wide differences in the behaviour of their amylase in other respects, that we have felt compelled to carry the inquiry somewhat further, more particularly as our results seem to have some bearing on the problem of the strength or baking value of flours, a subject with which, we hasten to mention, we do not pretend to be familiar. In the paper referred to, it was demonstrated that barley contains a very large and hitherto unsuspected amount of amylase, which may be rendered soluble and extracted under conditions which preserve its activity, by the use of a suitable proteolyst. A full description of the mode of using this "solvent" is given in the paper mentioned and to it, for details, we must refer those interested. It is sufficient to state here that the proteolyst papain was found most suitable for use

* A decrease of activity, though to a much less degree, may sometimes be observed in the extraction (under similar conditions) of ground barley, when this is prolonged beyond two or three hours.

in this connection with barley, and the same is in the main true in the case of wheaten flours. These however differ in certain respects from entire barley meals and barley flours, and the conditions for the use of papain in estimating the amount of amylolytic ferment are not quite so simple, nor are the results quite so concordant, still much valuable information may be obtained by the application of this method, even though it is far from ideal.

When wheaten flours are digested for a few hours with active papain, the filtered extracts so obtained are found to exhibit a very high amylolytic activity. In the case of the Hungarian flour used for the experiments in Table 3 the activity corresponded to the production of 27.4 grms. of maltose per 1 gram. of dry flour. This is by no means a high value as even in our somewhat limited experience high grade Canadian flours have given as great a figure as 48 grams maltose. The mode of operation we adopted provisionally for the determination of this value (which for convenience we shall term "total amylase") is as follows:—2 grams of the flour are digested with 50 c.c. of a 1 per cent. solution of active papain for 18 hours at 30°, the solution is then filtered and $\frac{1}{2}$ c.c. of this is added to 70 c.c. of starch solution (containing 2 grms. of starch) at 40°, after 30 minutes the action is stopped by the addition of 5 c.c. of soda solution (10 grms. per litre). These conditions give concordant results, but it is preferable to dilute 25 c.c. of the filtered solution to 100 c.c., to use 1 c.c. of this and to allow the action to proceed for 1 hour. The same values are obtained by either manner of working, but it is obvious that with the more concentrated solution greater precision of measurement of extract and of time is necessary; with a suitable pipette and a stopwatch this precision is a simple matter. Departure from the conditions of dilution, i.e., ratio of flour to solvent, is not admissible and we are not prepared to say that the values obtained are the maximum. Doubling the amount of active papain does not alter the value, but the addition of a small quantity of a neutral salt (potassium chloride) slightly augments it. The increases, however, practically fall within the limits of experimental error. The amylase of wheat, like highly purified preparations of amylolytic enzymes from other sources (see J. Chem. Soc., 1906, 78; this J., 1906, 228) does not exhibit its full hydrolytic activity except in presence of a certain salt concentration. As the amount of salts (soluble) in wheaten flours though not great, varies considerably it seems advisable to add a quantity of a neutral salt (e.g., potassium chloride) to the papain solution and also to the soluble starch. A tentative explanation of this influence of neutral salts is given in our paper on barley (*loc. cit.* p. 74). Suitable quantities to employ, are for the papain 0.5 gram., and for the soluble starch 0.25 gram., per 100 c.c. These amounts regulate variations of salt content of the wheats, papain, and starch preparations, and tend to ensure uniformity of results. The function of the active papain is a dual one; it apparently liberates a certain amount of amylase which is present in an insoluble form as part of a molecular complex, and also prevents its destruction as well as that of the soluble portion of the ferment. A comparison of the amylolytic activities obtained by treatment with active and passive papain shows that the amount of "insoluble" amylase is very variable, ranging from 20 to 60 per cent. of the total. The passive papain figure is however somewhat indeterminate, the addition of small amounts of neutral salts either to the starch or the papain solution increasing the value. For the purpose of a simple comparison between the active and passive proteolyst values, for a given sample, this is not of much moment as the salt concentration can be kept constant, but when we attempt to utilise these values i.e. the ratio of soluble to total enzyme, as a means of differentiation between flours of diverse origin, this variation with the salt content introduces a possibility of error which however can only be slight in amount if potassium chloride is added as we have suggested. Before discussing the papain values further, we may refer to another attempt made to find a basis for differentiation, this was an autodigestion of the flours at 30°. The two samples Nos. 1 and 2, of Table 1, when digested with water at 30° (with addition of nitrobenzene as an antiseptic) behaved as follows:—

TABLE 4.—"Autodigestion" of wheaten flours.
20 grms. per $\frac{1}{2}$ litre.

	Grms. maltose per 1 gram. flour.	
	No. 1.	No. 2.
After 1 hour.....	2.87	11.83
" 3 "	2.87	11.90
" 4 "	2.80	11.69
" 5 "	2.66	11.34
" 26 "	2.52	12.74

It will be noticed that sample No. 1 falls in value whereas No. 2 shows an increase after 5 hours. From this behaviour we surmised that No. 2 flour contained a proteolytic enzyme, on fuller investigation this was found to be the case, but we shall return to the question of this proteolyst later. Now in such a method of "autodigestion" it would appear at first sight, from the differences exhibited by the above flours, that the equilibrium attained under constant conditions of time and dilution, might prove of service as a differential test. This is true to some extent provided the starch used is also a constant. That is to say concordant results representing a composite something—a balance of solution and destruction—can be obtained, but such extracts containing destroyed, partially destroyed, and active amylase yield results which depend to some degree on the salt concentration of the starch preparation used for the hydrolysis, hence the method is not applicable for general employment.

As it seemed possible that the diastatic powers revealed by proteolysis with papain, represented an approach to absolute values, it was thought desirable to extend the examination to various flours. It is generally admitted that one important factor of the strength of wheat in bread making is the capacity of gas formation (see Humphries, Brit. Assoc. Rep., 1907), and as it is apparent that the greater part of the carbon dioxide liberated in panary fermentation must be derived from the starch of the flour by the intervention of diastatic action, it seemed likely that flours with the greatest amount of amylase would, other things being equal, stand highest in baking value. A slight calculation shows that the pre-existent sugars in wheaten flour can only account for a small proportion of the carbonic acid formed. Taking as an example a N. Manitoba flour which when fermented in the usual way with yeast, yielded some 350 c.c. of gas per 20 grms.: this corresponds roughly with the fermentation of 1.3 gram. of sugar or $6\frac{1}{2}$ per cent. on the flour. This flour was found when extracted with water, after destruction of the amylase in the manner described by one of us (Analyst, 1904, 277; this J., 1904, 953), to contain 0.82 per cent. of sucrose and 0.1 per cent. of a reducing sugar. Manifestly then, amylolytic action plays a prominent part in providing sugar for the fermentation. Direct experiment by the conventional fermentation test did not yield values in complete accord with the amylase results, this however is only to be expected, for the amylase is not the sole governing factor; such conditions as the state of the starch, nature of the soluble matters of the flours, their bacterial contamination and that of the yeast as well as its type, have also a large influence on the rapidity and amount of gas production. In order to find how far the amylase values corresponded to baking quality, we communicated with Mr. A. E. Humphries, Ex-President of The National Association of Millers of Great Britain and Ireland, who kindly sent us five samples, of "baking value" known to him. These samples which were marked as under, gave the following results as regards total amylase.

Sample.	Grms. maltose per 1 gram. dry flour.
A	26.8
B	29.2
C	43.2
D	34.3
E	35.8

The flour "D" was found, in the manner indicated, to contain an active proteolytic enzyme. Now as a few experiments showed us that this enzyme had an extremely detrimental influence on the tenacity of the gluten and hence on the property of gas retention, we placed this flour last as regards baking value and the others in the order of their amylase content thus:—C, E, B, A, and D. Mr. Humphries informed us, on receipt of this classification, that it was correct as regards the order of baking value. This result looked rather hopeful, but the number of samples examined was hardly sufficient to warrant over-confidence in a classification by two factors, consequently Mr. Humphries kindly sent other seven flours of different origin which when tested in a similar manner gave total amylase as follows:—

Sample.	Grms. maltose per 1 gm. dry flour.
F	46.8
G	25.4
H	32.3
I	31.7
J	38.8
K	29.6
L	22.1

The sample "L" contained an active proteolyst in even greater amount than "D," it was consequently on this account as well as owing to its low amylase figure, placed last and the others arranged in the order of their "activities" thus F, J, H, I, K, G, and L, or combining both lots the order became F, C, J, E, H, I, K, B, A, G, D, L. On communicating with Mr. Humphries he informed us that actual baking trials yielded the following results:—

TABLE 5.

Sample flour.	Strength Bakers' marks.	Value Total amylase.	Arrangement by	
			Baking.	Amylase.
A	68	26.8	C	F
B	70	29.2	J	C
C	96	33.2	K	J
D	40	34.3	F	E
E	70 to 80*	35.8	H	H
F	88	46.8	I	I
G	68	25.4	E	K
H	85	32.3	B	B
I	85	31.7	G	A
J	92	38.8	A	G
K	90	29.6	D	D
L	35	22.1	L	L

* A notable increase of strength with age. B might therefore be placed above H in the order of "baking value."

For convenience of reference, the amylase values and classification by these are included in the above table. The results of the examination of this more extended set of samples shows, not greatly to our surprise, that potential gas producing power, as measured by the total amylase of the flours, qualified by the presence or absence of an active proteolyst is not sufficient to assess their baking value. It however indicates that in developing a method of evaluation the total amylase is one important factor, also that the presence of a proteolytic ferment is another and possibly more valuable, consideration. Now though we all along recognised that the capacity of gas retention must of necessity be another of the factors to be considered, we preferred to attempt a classification on the basis of amylase alone on the chance that such might comote proportionately the condition or amount of the "gluten," but apparently it does not do so. The question of the amount of gluten has received attention from many workers and its condition as affected by salts, etc., has recently been raised and investigated by T. B. Wood (Jour. Agric. Sci., 1907, 267; this J., 1908, 175), and into this aspect of the question of baking strength we are therefore unable to enter to any extent. We have however made a slightly extended examination of the sample "F" which by its amylase value is so

misplaced in the series. This flour Mr. Humphries informs us "gives an extraordinary amount of gas, but the dough does not hold it." From this it is evident that if the "gluten" factor were considered the flour would be differently placed. Now this sample though it does not contain an active proteolyst shows more resemblance to the sample "D" in respects to its soluble nitrogenous constituents* than it does to sample "C." The salts and soluble matters are also high and it is therefore probable that in the original grain the metabolism of the endosperm has not attained the stage of maturity characteristic of the wheat from which "C" was milled. This notwithstanding the possibility of similarity of climatic conditions under which these two wheats were grown. It would be interesting to know how far post-maturation (such as is brought about by kiln drying and subsequent storage of barleys) might induce advantageous changes in wheats which do not yield flour of satisfactory quality when milled newly thrashed.

Another point which might repay investigation, is the influence of the salt (sodium chloride) used as a condiment in bread making. It is evident, from our results, that very small amounts of saline substances are capable of greatly augmenting the solution, conservation and activity of the amylase, and the salt so used may thus (leaving out of account other possibilities) indirectly increase gas production. The employment of such adjuncts as yeast foods or malt extracts containing amphoteric substances may also give rise (quite apart from any specific influence due to sugars or amylolytic ferments contained in them) to a like effect.

The protease.—The presence of an active proteolyst in wheaton flours does not seem to have been demonstrated yet by other workers. As we have already stated, it is possible by a combination of amylase determinations to deduce its presence; the method, however, is much too troublesome to merit employment, especially as the presence of the enzyme may readily be detected by a modification of the usual gelatine test. For this purpose we add 5 grms. of the flour to 50 c.c. of 1.5 per cent. gelatin (pure) solution saturated with nitrobenzene, the mixture is digested at 35° for at least 48 hours. By this test such samples as "D" and "L" show obvious liquefaction. A concentrated aqueous extract of the flour plus gelatine to 1.5 per cent. may also be used, in which case a satisfactory passive control with an equal volume of boiled extract can be carried out. As little is known about the conditions of extraction of this protease, we prefer to test the solid flour,† using as a control another flour known to be free from a proteolyst. The gelatin method in this application is unfortunately not quantitative; we have tried to render it so, by determination of the resulting viscosities, but without success. We have also endeavoured to employ the method proposed by Sörenson (Compt. rend. Carlsberg, 1907, 7, 1), but the amount of enzyme present is too small for the successful application of this elegant device. The use of polypeptides after Abderhalden was also inadequate, and failure attended other processes devised by ourselves, as for example the determination of the amount of change in the nature of the nitrogenous matter in extracts of the wheats, etc.

It seemed advisable to establish by direct experiment on a practical scale, how very detrimental an active proteolyst is to the gas retaining capacity of "gluten," and for this purpose we sent Mr. Humphries a preparation of protease equal in activity to about five times that present in "D." Mr. Humphries kindly carried out baking trials with the active, and an equal amount of passive proteolyst and a control without addition, all with the same high-class flour. He reported that there was no difference between the passive batch and the

* We would point out that the work of H. A. Guess (J. Amer. Chem. Soc., 1906, 283; this J., 1906, 695) shows that though the ratios of the various proteins do not indicate the true "baking value" of a flour they have some intimate connection with it.

† The use of solid flour in the manner suggested is convenient as a preliminary test. It is advisable, however, to confirm positive indications by the examination of active and passive aqueous extracts, as it has been shown by Batre and Floresco (Compt. rend., 1895, 121, 615) that long continued heating of gelatin solution in presence of certain salts gives rise to loss of its property of solidifying.

control, but that within a quarter of an hour the dough of the active showed most conclusively that something very abnormal was taking place. The final loaf was quite useless. "It had practically failed to 'rise' at all and the crumb was devoid of tenacity." Subsequently we sent Mr. Humphries about one-fifth the amount of enzyme, actually 0.5 grm. of a crude preparation, which he added to a baking of 12 lb. of flour. A control with passive enzyme and also one without was carried out. The results were as follows:—

	Bakers' marks.
Control	90
Active	85
Passive	94

Mr. Humphries remarks that, "the active had a depreciating effect, but not to a very great extent; however, it was a real effect that would quickly be appreciated by a miller or baker." He also adds that by other tests he proved to his satisfaction that, "it was gas retention and not gas making which this proteolytic enzyme had affected."

The above experiments suggest a reason why certain preparations of malt extract prove unsuitable for use as baking adjuncts; they also provide one explanation for the cause of what is known as "rotten gluten," and show conclusively why certain classes of wheats give flours of low baking value, quite apart from other considerations. It is interesting to note that the flour "L," previously mentioned was made from English wheat grown on Plot 10, Rothamstead, a plot which has been manured continuously for about 60 years with ammonium salts.

How far the presence of a proteolyst in wheaten flours is due to racial, climatic, or soil influences is a subject for future investigation.

In concluding we have much pleasure in acknowledging our indebtedness to Mr. Humphries for kindly supplying us with many samples and much information.

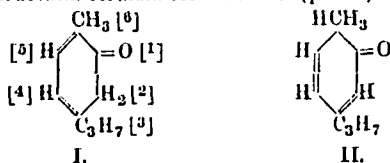
THE IODINE VALUES OF THE PHENOLS.

BY ERNEST WAKE AND HARRY INGLE.

(This J., April 15, 1908, pp. 315—316.)

ERRATA.

The structural formula for carvacrol (p. 316) should be



Yorkshire Section.

Meeting held at the University of Sheffield on Wednesday, March 18, 1908.

MR. F. W. BRANSON IN THE CHAIR.

THE RECOVERY OF CYANOGEN COMPOUNDS IN THE DRY DISTILLATION OF COAL, AND THE DISPOSAL OF EFFLUENTS FROM AMMONIA STILL.

BY DR. J. GROSSMANN.

The process which I published two years ago (this J., 1906, 411) aimed chiefly at the avoidance of noxious effluents in the manufacture of ammonium sulphate, which frequently, when once formed, are difficult to dispose of. It is, however, not every gas or coke works which has difficulties in that direction, and the question of the

recovery of cyanogen compounds and that of the disposal of the effluents from the ammonia stills need, therefore, not go hand in hand.

For the last thirty years various processes have been proposed dealing with the problem of extracting cyanogen compounds from the crude coal gases, chiefly in the manufacture of illuminating gas, generally with a view to producing ferrocyanide compounds in an insoluble form. The best known of these processes are those of Foulis, Bueb, etc. They require considerable alteration in plant, and the working up of the cyanogen compounds into commercial ferrocyanide is complicated by the presence of ammonia in the crude products and requires skilled supervision. Within recent years, chiefly in consequence of a new outlet for sulphocyanides, inventors have aimed at obtaining the latter from the crude gas. But as cyanogen in the shape of ferrocyanide has more than double the value of cyanogen in the shape of sulphocyanide, it is evident, apart from other reasons, that it is more advantageous to aim at the production of ferrocyanides.

Although the presumption has been strong that all the cyanogen in crude coal gas is originally present in the state of hydrocyanic acid or ammonium cyanide, the fact that such is indisputably the case has only lately been proved by the work of R. Forbes Carpenter and Linder, and which is recorded in the Annual Reports on Alkali, etc., Works presented to the Local Government Board. Their researches show that the crude gas contains cyanogen only as hydrocyanic acid or ammonium cyanide, and that, in the absence of air during or after condensation, ammonia liquors contain all the cyanogen as ammonium cyanide, so that whatever sulphocyanide or ferrocyanide may be found in these liquors, is due to secondary action. The sulphocyanide is due to the presence of ammonium bisulphide or polysulphide which acts on ammonium cyanide according to the equation: $\text{NH}_4\text{CN} + (\text{NH}_4)_2\text{S}_2 = \text{NH}_4\text{CNS} + (\text{NH}_4)_2\text{S}$. But the ammonium bisulphide is a secondary product, which has been formed from the ammonium sulphide by oxidation due to the presence of air: $2(\text{NH}_4)_2\text{S} + \text{O} = (\text{NH}_4)_2\text{S}_2 + 2\text{NH}_3 + \text{H}_2\text{O}$. In like manner ammonium cyanide has no strong action on metallic iron; but if the iron of the vessels containing the crude ammonia liquors, or of other parts of the apparatus coming into contact with them, has become oxidised, ferrocyanide is freely formed.

It is thus evident that the cyanogen may be recovered from crude ammonia liquors either altogether as ferrocyanide or as sulphocyanide so long as care be taken to perform the necessary operations within a short time after the liquors have been produced, and particularly before their composition has been changed by access of air; and as sulphocyanides, as stated before, are of less commercial value than ferrocyanides the problem before me was how the conversion of ammonium cyanide into ferrocyanide could be best effected. It is well known that the alkali ferrocyanides, including ammonium ferrocyanide as such, are easily soluble; and that they form double compounds which in some cases are insoluble in other cases difficultly soluble. The difficulty which presented itself at the outset of my experiments was that on agitating ammonia liquors with an excess of ferrous oxide or carbonate, I generally obtained part of the ferrocyanide formed in solution and part as an insoluble or difficultly soluble precipitate. As the quantity of cyanide present in crude ammonia liquors varies considerably it is necessary, in order to render any method aiming at the production of ferrocyanide practicable, to use a large excess of the iron compounds; it will also be expedient to obtain the ferrocyanide of ammonia completely as such in solution, free from insoluble ammonium ferrocyanides; for the recovery operations in the case of insoluble double compounds with ammonia become complicated. I have found that these conditions are fulfilled, if the action of an iron compound on ammonium cyanide takes place in the presence of a sufficient excess of ammonium sulphide. Under such conditions only soluble ammonium ferrocyanide is produced.

The most suitable iron compound for the purpose is evidently ferrous sulphide. As previously stated it is necessary to use a considerable excess of ferrous sulphide,