

the end of the reaction, which is indicated by the blue color being destroyed only gradually as the solution is mixed, the iodine should be added drop by drop, stirring thoroughly between each addition. The starch solution is made by working about half a gramme of wheat starch into a cream with water, pouring about 70 c. c. of boiling water over it, and filtering the solution. On no account should this solution be used without filtration, as the end reaction is never as distinct in this case. If the operator has a knowledge of quantitative analysis, he will be acquainted already with the method of making a decinormal solution of iodine; in the other case he can purchase some from any laboratory furnisher, or prepare it according to the directions contained in Thorpe's *Quantitative Analysis*, Sutton's *Volumetric Analysis*, or Mill's and North's *Quantitative Analysis*. The water used is well boiled to expel all the air (which would oxidize some of the sulphurous acid) and then allowed to cool in a bottle filled quite up to the neck and provided with a loosely fitting cork. The method of calculating the percentage of sulphurous acid can best be shown by taking an example: Sample indicated 47° Tw., equal to 1.235 specific gravity. Five cubic centimeters, equal $1.235 \times 5 = 6.175$ grammes, were made up to 500 c. c., and 25 c. c. of this solution (i. e. $\frac{1}{20}$ of it) required 15.5 c. c. of decinormal iodine solution. One cubic centimeter of decinormal iodine solution oxidizes, and consequently indicates, 0.0032 gramme of sulphur dioxide; hence the 25 c. c. of the solution used in the test contained $0.0032 \times 15.5 = 0.0496$ grammes of SO_2 . As the 25 c. c. contained — = 0.30875 gramme of the sample, the percentage of SO_2 is $0.0496 \times 100 = 16.0$ per cent.

Free Sulphurous Acid and Half of that Combined as Bisulphite of Soda.—Take 10 c. c. of the sample, place in a flask, add 200 c. c. of water and an excess of neutralized hydrogen peroxide solution, and allow to stand for a few minutes in order to oxidize the sulphurous acid and sulphites into sulphuric acid and sulphates. Commercial hydrogen peroxide is generally acid, and it should be neutralized before use, and this is best done by adding a little of an alcoholic solution of phenolphthalein and afterward adding standard soda solution from a burette until the hydrogen peroxide just takes a permanent pink color. After the bisulphite solution has stood with the peroxide a few minutes, phenolphthalein is added and then titrated with normal caustic soda solution until it just turns pink. From the data obtained the SO_2 in the free state and half of that combined as bisulphite can be calculated in the following way: Ten cubic centimeters of the sample used above weigh $1.235 \times 10 = 12.35$ grammes and they require 33.7 c. c. of normal caustic soda for neutralization. One cubic centimeter of normal soda neutralizes 0.032 gramme of SO_2 ; hence the 10 c. c. of the sample contained $0.032 \times 33.7 = 1.0784$ grammes of SO_2 in the condition named, or $\frac{12.35}{1.0784} = 8.73$ per cent. It is absolutely essential to add the hydrogen peroxide before titrating, so as to oxidize the sulphurous acid into sulphuric acid, because sulphite of soda, unlike sulphate of soda, has a slightly alkaline reaction, and would, consequently, detract from the accuracy of the test. Methyl orange is recommended by some chemists as an indicator when titrating the free sulphurous in bisulphite of soda acid, but my experience with it is that the end reaction is by no means sharp enough, whatever the dilution of the liquor, and this I find is also the experience of many analysts with whom I have come in contact.

From the figures obtained as above, the condition in which the sulphurous acid is combined in the sample can be found. The titration with iodine indicates, as stated above, the total SO_2 . Titration with caustic soda gives the SO_2 in the free state, and one-half of that existing as bisulphite, as shown by the following equation:
(a) $\text{H}_2\text{SO}_3 + 2\text{NaOH} = \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O}$
(b) $\text{NaHSO}_3 + \text{NaOH} = \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$
(Oxidation with the H_2O_2 is here disregarded, but it makes no difference in the results.)
Now by subtracting the SO_2 indicated by the caustic soda from the total SO_2 , half the amount of SO_2 combined as bisulphite, together with the whole of that combined as neutral sulphite of soda, is left. If the sample contains free SO_2 , the amount indicated by titration with caustic soda will exceed the difference between it and the total SO_2 . If it does not, then the sample contains neutral sulphite of soda. The following examples will make the calculation clear in case of the sample containing either free acid or an excess of neutral sulphite.
Example I. (sample containing free sulphurous acid)
Total SO_2 16.00 per cent. = a
 SO_2 as bisulphite and free (if any) .. 8.73 per cent. = b
Half the SO_2 as bisulphite 7.27 per cent. = c
+ any as neutral sulphite }
Since b is greater than c, free SO_2 must be present, and consequently c is half the amount of SO_2 combined as bisulphite; hence the total amount is $7.27 \times 2 = 14.54$ per cent.
The difference between this number (14.54 per cent.) and the total SO_2 indicates the free SO_2 ; hence $16.00 - 14.54 = 1.46$ per cent. of free SO_2 . Thus the sample contains:
Total SO_2 16.00 per cent.
Combined as follows:
Free SO_2 1.46 per cent.
As bisulphite of soda 14.54 per cent.
Example II. (containing neutral sulphite of soda)
Total sulphur dioxide 17.27 per cent. = a
Sulphur dioxide as bisulphite and free if any 8.07 per cent. = b
Half the SO_2 as bisulphite + any as neutral sulphite 9.20 per cent. = c
As c here is greater than b, the sample, then, must contain neutral sulphite of soda, and the amount so existing in the solution is found by subtracting b from c thus: $9.20 - 8.07 = 1.13$ per cent. of sulphur dioxide as neutral sulphite of soda. As there is no free SO_2 , b

indicates the amount of SO_2 as bisulphite of soda, the total amount is $8.07 \times 2 = 16.14$ per cent.
This sample has the following composition:
Total sulphur dioxide 17.27 per cent.
combined as under
As bisulphite of soda 16.14 per cent.
As sulphite of soda 1.13 per cent.
Commercial bisulphite of soda generally contains an excess of sulphur dioxide or of alkali. For most of the uses to which it is put by dyers and calico printers, an excess of sulphur dioxide is preferable to an excess of alkali.

CHEMICAL EXAMINATION OF WRITING INKS.

By A. ROBERTSON and J. HOFMANN.

THE authors draw lines across the letters or figures with quill pens dipped in the following reagents, and observe the changes where the ink and the reagent meet, using, if needful, a magnifying power of 100 diameters. The reagents are: (1) A 3 per cent. solution of oxalic acid; (2) a 10 per cent. solution of tartaric acid; (3) a 2 per cent. solution of chloride of lime; (4) solution of 1 part stannous chloride in 1 part hydrochloric acid and 10 parts of water; (5) sulphuric acid at 15 per cent.; (6) hydrochloric acid at 10 per cent.; (7) nitric at 20 per cent.; (8) saturated solution of sulphur dioxide; (9) 4 per cent. solution of gold chloride; (10) solution of 1 part potassium ferrocyanide in 1 part hydrochloric acid and 10 parts water; (11) solution of 1 part sodium thiosulphate (hyposulphite) in 1 part ammonia and 10 parts water; (12) 4 per cent. soda lye.

Reagents.	Iron and gall ink.	Logwood with—		Nigrosine.	Vanadium ink.	Resorcin ink.
		Potassium chromate.	Copper sulphate.			
Oxalic acid.....	Disappears.	Violet.	Orange.	No change.	Turns pale and runs a little.	Bright red.
Citric acid.....	Turns pale.	Violet.	Orange.	Runs dark blue.	Turns pale and runs.	Disappears.
HCl.....	Disappears, but leaves a yellow.	Purple red.	Blood red.	Little change.	Slightly paler and runs slightly.	Light rose.
Sulphuric acid.....	Disappears.	Red.	Purple red.	No change.	Slightly paler.	Bright red.
Nitric acid.....	Disappears.	Red.	Purple red.	Runs slightly.	Slightly paler.	Light rose.
Stannous chloride.....	Disappears.	Red.	Magenta.	No change.	Slightly paler.	Disappears.
Sulphurous acid.....	Turns pale.	Violet gray.	Red.	No change.	Slightly paler and runs.	Turns paler.
Gold chloride.....	Slightly paler.	Red brown.	Brown.	No change.	No change.	Runs brown.
Sodium thiosulphate and NH.....	Dark red.	No change.	Dark blue.	Dark violet, runs.	Runs much.	Brown.
Ferrocyanide and HCl.....	Blue.	Red.	Brick red.	No change.	No change.	Rose.
Sodium hydroxide.....	Dark red.	Brown.	Dark red, runs.	Dark violet, runs.	Dirty brown, runs.	No change.
Chloride of lime.....	Disappears.	Disappears.	Disappears leaving a yellow stain.	Brown.	No change.	Brown.

The subjoined table shows the results. The results with tartaric acid are not tabulated.—*Chemiker Zeitung*.

THE ACTIVE ALBUMEN IN PLANTS.*

By O. LOEW.

ONE of the most important chemical functions of plant cells is that synthesis of albuminous matter which serves for the formation of protoplasm. The living protoplasm, however, is composed of proteids entirely different from the ordinary soluble proteids, as well as from the proteids of dead protoplasm. In other words, if living protoplasm dies, the albuminous constituents change their chemical character. We observe that in the living state a faculty of autoxidation (respiration) exists which is wanting in the dead condition; and Pfuger, in 1875, drew from this the conclusion that in protoplasm the chemical constitution of the living proteids changes at the moment of death.

Various other considerations force us to accept this logical conclusion. Chemical changes readily occur in all those organic compounds that are of a labile character. There exist so-called labile atom constellations that are in lively motion, and are thus prone to undergo change, the atoms falling into new arrangements which present more stable constellations. We do not doubt that vital force is a mode of motion due to the presence of atoms in labile positions in the albuminous substance. The motion ceases when there occurs a migration of the labile atoms to some stable position. The aldehydes give us fine illustrations of labile combinations and stable rearrangements in other allied substances.

The question now arises, can we chemically demonstrate that the albuminous substance formed by synthesis in plants is—even before it has become protoplasm—different from ordinary albumen? It was known long ago that the juice of plants—that is the aqueous solution in the vacuoles of the cells—contains albumen, but it was thought to be ordinary albumen. It is easy to prove that this is not the case.

On treating living plant cells with dilute solutions of ammonia or organic bases or their salts, remarkable changes are observed. These consist either in the formation of numerous minute granules, as is the case on the application of most of the bases, or in the production of little globules flowing together to make relatively large drops of a substance of high refractory power, as is the case on the application of weak bases like caffeine or antipyrine. These latter two bases in weak solution do not injuriously affect the protoplasm itself, since the cells will keep alive for a number of days in a 0.5 per cent. solution of these bases; the cells are, how-

ever, soon killed by other bases and their salts. The granules and globules formed in the living cells by the action of caffeine have been called by Bokorny and myself *proteosomes*. They give the principal reactions of albuminous bodies, but contain in most cases an admixture of small quantities of lecithin and tannin. These admixtures, however, can be removed by cultivating the objects (the alga, spirogyra, for instance) in solutions rich in nitrates.

If now by such cultivation the tannin has been removed and the proteosomes then produced by treatment with caffeine, we can observe that these albuminous proteosomes are capable of reducing silver from even highly diluted alkaline solutions. This property is lost after treatment with dilute acids as well as after the death of the cells.* In these cases the proteosomes become hollow and turbid, their substance appearing to coagulate and shrink.

There are thus experimental grounds for the conclusion that not only the organized albumen of the living protoplasm, but also the albumen dissolved in the vacuoles—the unorganized albumen—is a different substance from the ordinary albumen, which is present in dead cells. We may sum up the line of argument as follows:

1. Bases act upon the albumen of living cells; not, however, upon that of dead cells, nor upon ordinary dissolved albumen.

2. The action may be observed microscopically to take place in the case of various vegetable objects, in the liquid portion of the protoplasm itself as well as in the vacuoles. This can be especially well observed with the alga spirogyra when treated with caffeine.

3. The granules and globules into which the active

albumen aggregates by the action of bases—called by us *proteosomes*—have the property of reducing dilute silver solutions in the absence of light, and lose this property by the action of acids.

4. The active albumen in its most unchanged condition can be made visible by caffeine or antipyrine, two bases that do not act as serious poisons to the cells. Living cells containing proteosomes, brought out by caffeine, when placed in distilled water regain their original condition, the proteosomes become gradually dissolved again (rapidly at 25° C.), and a new application of caffeine will now make them reappear.

5. If proteosomes are produced by caffeine or antipyrine, and the death of the cells is then caused by ether vapor, etc., it may be easily observed that soon after the death of the protoplasm the proteosomes of the vacuoles are also changed in their optical and chemical properties; they become turbid and hollow, they coagulate, and they lose their property of being resolvable in distilled water.

CHEMISTRY OF DIGESTION.

DR. A. L. GILLESPIE points out that, though hydrochloric acid is a powerful antiseptic and capable, in dilutions of 0.1 to 0.2 per cent., of inhibiting or destroying most minute organisms, the addition of proteid matter to it, and formation of what he terms proteid-hydrochlorides in the process of digestion, allows the same organisms to flourish luxuriantly, though the strength in acidity be maintained. After a meal consisting largely of proteids, generally an hour elapses before the advent of free hydrochloric acid, and the gastric juice is therefore much less antiseptic than after a meal of carbohydrate material. It is suggested accordingly that, since a typhoid or other pathogenic bacillus ingested during a heavy dinner has a more favorable opportunity for development than if it were taken with such food as porridge, it would be well if there were any danger of poisoning by disease germs to take nothing with a proteid meal except it had been thoroughly cooked, or, as alternatives, to live chiefly on carbohydrates, or to take some dilute hydrochloric acid after each meal.—*Medical Magazine*.

CHEMISTRY AND PALÆONTOLOGY.

A NOVEL application of chemical analysis was recently explained by A. Carnot, at the Paris Academy of Sciences. He has endeavored to fix the age of prehistoric human remains by noting the progressive diminution of fluorine in the fossil bones of successive geological ages. Representing the proportion found in the oldest specimens by 1, that of the tertiary remains would be indicated by 0.64, of the quaternary by 0.35, and of the more recent bones by 0.5 or 0.6. An

* Paper read before the Liege meeting of the International Congress of Physiologists.—Reprinted from *Nature*.

† O. Loew and Th. Bokorny, *Biolog. Centralblatt*, xi., 1.

‡ These globules closely resemble the aggregated masses that Darwin observed after irritation of leaves of *Drosera*.

* The proteosomes produced by ammonia and various other bases preserve this property for a much longer time after the death of the cell than those produced by caffeine or antipyrine.