

THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held on Wednesday, June 1, 1921, in the Chemical Society's Rooms, Burlington House. The President, Mr. Alfred Smetham, was in the Chair.

A certificate was read for the second time in favour of Mr. W. N. Stokoe, B.Sc., A.I.C.

Messrs. Thomas Henry Pope, B.Sc., F.I.C., and William Ellard Woolcott were elected Members of the Society.

The following papers were read: "The Composition of Egg Powder," by F. F. Beach, F. E. Needs, and Edward Russell, B.Sc., F.I.C.; "The Colorimetric Method of Determining Hydrogen-Ion Concentration: Some Uses in the Analytical Laboratory," by Norman Evers, B.Sc., F.I.C.; "The Estimation of Woody Fibre in Cattle Foods," by F. Robertson Dodd, F.I.C.; "The Spectrometric Examination of Certain Fixed Oils as a Means of Identification," by H. C. T. Gardner; and "The Joint Use of Two Indicators in the Titration of Acids and Bases," by J. L. Lizius, B.Sc., A.I.C.



OBITUARY NOTICE.

BERTRAM BLOUNT.

BERTRAM BLOUNT was born at the end of 1866 in London, and as a child was physically weak, and, indeed, through the whole of his life was never robust, though his indomitable will enabled him to conquer Nature's handicap, and even to attain some success as a cyclist. Educated at King's College School, he passed to King's College, and formed one of the band trained under the late Professor Bloxam; at college he was distinguished by his accuracy and painstaking capacity, as well as by his clearness of thought and expression. At nineteen he joined Mr. W. H. Stanger, a consulting engineer, who held the appointment of Consultant to the Crown Agents or the Colonies, and it is no exaggeration to say that Blount there founded the profession of Engineering Chemist; first as Mr. Stanger's assistant, and then as partner, he forced on engineers and contractors the view that the chemistry of engineering was of prime importance. On Stanger's death, Blount continued the

chemical side of the practice on his own account, and quickly became one of the recognised leaders of his profession ; perhaps he is best known as the leading authority on cement, though his knowledge of electro-chemistry and its practical applications was perhaps equally great, and there was scarcely a branch of inorganic chemistry of which he was not a master.

Few men had a greater power of getting to the root of a problem, and he had the peculiar gift of conveying his thoughts clearly and forcibly, occasionally very forcibly, and he inspired confidence. His contributions to chemical literature were not very numerous ; while still a student he published a paper on calcium borate in the *Journal of the Chemical Society*, followed by one on explosive pyrites ; and his first paper in the ANALYST was on a sample of navy green paint. His later communications included "The Estimation of Copper by Ignition in Hydrogen," "The Use of Physics in Analytical Methods," and "The Proposed Standardisation of Methods of Chemical Analysis." With A. G. Bloxam he wrote "Chemistry for Engineers," and was the author of "Practical Electro-Chemistry," and his lecture on "Cement" before the Institute of Chemistry also appeared in book form.

Blount was elected a Fellow of the Institute of Chemistry in 1891, and was a Member of the Council on two occasions, whilst he served as examiner in 1907-1911.

He was always interested in the affairs of our Society. On three occasions he served on the Council, and twice as Vice-President. He was for many years an abstractor for the ANALYST, and was subsequently a member of the Publication Committee.

During the war he was strenuous in his demand that the Government should make cotton contraband of war, and in season and out of season he devoted his whole energy to this, and had he been listened to, the war would have been shortened materially and countless lives saved ; the strain on his health probably hastened his end.

Always active, always interesting, never really unkind, though often polemical and sarcastic, he was a true friend and a trusted companion, and his early death on April 9, leaves a gap which can never be filled. H. DROOP RICHMOND.



NOTES ON THE SO-CALLED ACTION OF WATER ON LEAD.

By JOHN C. THRESH, M.D., D.Sc., F.I.C., ETC.

(*Read at the Meeting, April 6, 1921.*)

THE historical part of this subject was so fully dealt with by Mr. Heap in a paper read before the Society of Chemical Industry (*J. Soc. Chem. Ind.*, 1913, **32**, 771, 811, 847), that anyone interested in this history can easily refer thereto. It will be found that the statements made by different observers are very conflicting, and that there are many anomalies which require explanation.

At my laboratory there are notes, extending over a period of twenty years, on waters which acted upon lead, and when recently a series of waters had to be

examined these records were looked up. Amongst others were notes of the action of samples of distilled water prepared in the laboratory, and some were recorded as "eroding" lead, some as exerting a "solvent" action, some which both "eroded" and "dissolved" lead, and some which apparently did neither. Different fractions from the same distillation had different effects, and it was quite obvious that ammonia-free distilled water must vary considerably in its character. That such was the case was easily demonstrated by examining a number of such waters by the determination of the electric conductivity. The most carefully distilled water had at 20° C. a conductivity of 2, but most gave 3 to 4, and one had a conductivity as high as 14. Certain waters yielded a distillate containing the merest trace of carbon dioxide, others yielded distillates containing considerable quantities, and the degree of oxygenation also differed considerably. It seemed probable, therefore, that these variations accounted for the differences recorded in the action of distilled waters on lead.

The examination of the natural waters above referred to raised other points. One sample was of a river water which, when filtered, contained no lead, whereas, unfiltered and acidulated, it yielded an appreciable colour with hydrogen sulphide. (Lead in large quantities was found in the flocculent sediment in the river, and the drinking of this water by cattle had caused lead poisoning.) Another water, rain water collected in a large concrete-lined tank, and having a long leaden suction pipe to the pump, gave the following perplexing results: Lead per 100 c.c. in water, no acid added, 0.10 mgrm.; after acidifying, 0.25 mgrm.; decanted after standing twenty-four hours, 0.12 mgrm.; after centrifugalisation, 0.10 mgrm.; after filtration through paper, 0.025 mgrm.; and after filtration through Gooch and Pasteur filter, *nil*.

EFFECT OF FILTRATION ON LEAD IN WATER.—To ascertain the effect of filtration, two solutions were made of neutral lead acetate, one with distilled water nearly free from carbon dioxide, and the other with a rain water containing some carbon dioxide and a trace of carbonate. The former solution was quite clear, and the latter faintly turbid. After standing twenty-four hours, successive 50 c.c. were removed by means of a pipette and filtered. (The original solutions contained 0.2 mgrm. of lead in 50 c.c., and the first 50 c.c. of each were examined without filtration.)

	Solution in Distilled Water. Lead found.	Solution in Rain Water. Lead found.
1st 50 c.c. not filtered	Mgrm. 0.20	Mgrm. 0.125
2nd " filtered through paper ...	0.06	0.04
3rd " " " " ...	0.08	0.065
4th " " " " ...	0.14	0.10
5th " filtered through asbestos ...	0.025	0.01
6th " " " " ...	0.085	0.03
7th " " " " ...	0.13	0.04
8th " filtered through porcelain ...	0.00	0.00
9th " " " " ...	0.025	0.00
10th " " " " ...	0.08	0.02

The cylinders in which the waters had stood appeared hazy, as though some deposit was on the glass. This proved to be the case, as, after rinsing, and then adding 50 c.c. of slightly acidified water, both yielded solutions containing lead. The distilled water cylinder yielded 0.375 mgrm., and the rain water 0.30 mgrm. In another experiment with a solution of lead acetate in distilled water (2 mgrms. Pb per 100 c.c.), a minute fragment of sodium was added to give an alkaline reaction. Fifty c.c. of this passed through a filter-paper yielded 0.2 mgrm. of lead, and 50 c.c. passed through a Pasteur filter was free from lead. In another experiment lead foil was placed in a litre of specially distilled water containing the merest trace of carbon dioxide, but saturated with air. The water was contained in a bottle completely filled and stoppered so as to exclude air. After two days the lead was removed, and the liquid poured off was found to contain about 12 mgrms. of lead in 100 c.c. It was diluted so that each 50 c.c. contained 2 mgrms. This liquid was alkaline to naphtholphthalein, and became turbid upon addition of a trace of sodium carbonate. Filtered through the finest filter-paper obtainable, the lead in the filtrate did not exceed 0.005 mgrm., and that passed through a Gooch asbestos filter and a Pasteur filter was quite free from lead. The remainder was passed in successive 50 c.c. through a coarser filter-paper. The first 50 c.c. contained 0.07 mgrm., the second 0.10 mgrm., and the amount passed gradually increased to 0.35 mgrm. in the thirteenth portion, after which the filter practically ceased to pass the water, the pores being choked.

It should here be added that in all cases when the lead solution was rendered faintly acid with acetic or hydrochloric acid, the liquid passed through the filters with its full complement of lead. It is fairly obvious that these neutral or alkaline solutions contain the lead compound in a colloid condition, and that the filtration effects are due to "adsorption."

When pure distilled water containing oxygen in solution acts upon lead, a soluble lead oxide or hydroxide is slowly formed. At first probably there is molecular solution, but molecular aggregates are formed, and the dispersion is then of colloid dimensions; later, larger aggregates may be formed, the dispersion becoming coarser until the liquid appears turbid. When dealing with these minute quantities, forces come into play which are of little importance when considerable masses are being dealt with, as in an ordinary analysis, but which cannot be ignored when dealing with very dilute solutions.

FACTORS AFFECTING THE COLORIMETRIC ESTIMATION OF LEAD.—In estimating quantities of lead from 0.01 to 0.4 parts per 100,000 in various kinds of water, it was observed that the colours produced with hydrogen sulphide varied not merely in depth, but in tint from a reddish-brown to a deep orange, and that frequently the addition of the reagent was rapidly followed by the production of an opalescence which entirely prevented any accurate determination of the lead contents. After a long series of comparative experiments, the conclusion arrived at was that by far the best results were obtained in the absence of a mineral acid (removed by addition of a trace of sodium acetate), and using *N* acetic acid containing as a stabiliser 0.1 per cent. of gold leaf gelatin. The quantity of free acid also affects the depth of colour of the colloidal lead sulphide. The following table shows the effects noted in one series

of experiments in which the quantity of acid used varied. The solution experimented with contained 0.2 mgrm. of lead as oxide or hydroxide in 100 c.c.

Solution : Neutral	With 1% $\frac{N}{10}$ HCl	2% $\frac{N}{10}$ HCl	4% $\frac{N}{10}$ HCl	With 1% $\frac{N}{10}$ acetic acid	2% $\frac{N}{10}$ acetic acid	4% $\frac{N}{10}$ acetic acid	1% N acetic acid
Colour with H ₂ S: 100	160	185	175	120	175	185	185

The effect due to the variation in quantity of acetic acid above a certain amount is much less than the variation with a mineral acid. The effect of gelatin is even more marked. A natural water containing lead, neutral and not acidified, gave with hydrogen sulphide a coloration of 40; acidified with acetic acid, a coloration of 60; and acidified with acetic acid containing gelatin, a coloration of 100.

The colour produced in the presence of the stabiliser is not only excellent for comparative purposes, but the liquid remains perfectly bright for considerable periods, which is a great advantage when a number of samples are being examined. In the presence of free mineral acid nitrites interfere, but in the quantities ever found in water the effect on the acetic solution is practically *nil*.

INFLUENCE OF HEAT AND AGITATION ON THE SOLUTION OF LEAD.—In making quantitative estimations of the lead taken up by water, it was found that the action was accelerated by heat, but the effect is not such as to necessitate the use of apparatus for maintaining a uniform temperature, the variations at the laboratory temperature being comparatively small, especially compared with other conditions, the chief of which is agitation. The following experiments bring out this point, and also show that the marked effect of agitation is due to the colloid condition of the lead in certain solutions; the colloid lead refuses to diffuse. A tall cylinder (150 c.c.) was filled with distilled water, and a coil of lead-foil placed at the bottom. The upper edge of the lead was opposite the 40 c.c. graduation. After standing at rest for an hour or two, a faint turbidity was noted extending up to this point. After twenty-four hours this had disappeared, but by viewing in different lights there was an obvious difference between the water above the 42 c.c. graduation and below. The upper 50 c.c. were drawn off, and contained no lead; after another twenty-four hours 25 c.c. were drawn off, and contained no lead. After sixty hours another portion of 25 c.c. was pipetted off, and was free from lead. After seventy-two hours 10 c.c. were taken off, and found to contain the merest trace of lead. Then 5 c.c. of remaining liquid were drawn off, and found to contain lead in the proportion of 10.0 mgrms. per 100 c.c., and finally the liquid remaining in the cylinder was acidified with acetic acid, and found to contain 16.5 mgrms. Pb per 100 c.c.

Time.	Agitation.	Lead acted upon by the Water.	Water.
15 minutes	In rotatory machine	2.5 mgrms. per 100 c.c.	Distilled
15 "	Shaken occasionally	2.0 " "	The same water
15 "	At complete rest	1.0 " "	" " "
4 hours	In machine	2.54 " "	A carbonated water
4 "	At rest	1.83 " "	The same carbonated water

In order to obtain uniformity of agitation, a small water-wheel was constructed with a hollow cylindrical axis in which bottles containing water could be placed. With the laboratory water-supply a rate of revolution of between 60 and 70 per minute was easily maintained. This little apparatus has been found most useful. With it the results given on page 273 were obtained.

INFLUENCE OF SURFACE AREA.—The area of lead surface exposed has a marked effect during the first few minutes, but after some hours it is very slight. The unit employed throughout was 25 sq. cms. per 100 c.c., and in all comparative experiments it is necessary to use bottles of the same shape and of approximately the same size. The effect of variation of area of lead exposed is shown in the following tabular results of one series of experiments, made with distilled water containing 0.852 mgrm. of oxygen per 100 c.c.

Unit of Lead Surface per 100 c.c.	Time.	Lead Removed.
Sq. Cm.		Mgrms.
0.5	10 minutes	0.46
1.0	10 "	0.94
1.5	10 "	2.1
2.0	10 "	2.4
0.6	15 " (rotated)	2.0
1.0	15 "	2.5
0.5	6 hours	7.25
1.0	6 "	7.9

The way in which the lead surface is cleaned has a pronounced effect upon the rate at which action commences and continues for about the first hour, but afterwards the effect is only slightly marked. Lead which has been dipped in dilute acid and then polished with a dry cloth has the greatest initial velocity, and the same lead dipped into $\frac{N}{100}$ sodium carbonate solution after treatment with $\frac{N}{10}$ hydrochloric acid had the least initial velocity, but the results were very variable. After numerous experiments, it was concluded that the most uniform results were obtained by using lead which had first been well rubbed with finely-powdered pumice and then polished with clean dry linen.

ACTION OF DISTILLED WATER.—The factors likely to affect the results having been studied, experiments were conducted with distilled water, and after many failures an apparatus was devised for distilling water and collecting the distillate without the access of air, and thus obtaining a water free from dissolved gases, especially oxygen and carbon dioxide. When such a water is obtained and the unit of lead introduced through an atmosphere free from oxygen and carbon dioxide, and the containing vessel is sealed, the water remains clear and the metal bright; and when the water is poured off quickly and tested, no trace of lead can be found in solution.

If to such a sample of water air deprived of carbon dioxide be admitted, the liquid remains clear for two or three days, after which a deposit forms on the bottom of the bottle, and when shaken the deposit exhibits a crystalline character. Under

the microscope it is seen to be very minute and acicular, single and in tufts. It settles quickly and the liquid is bright. If now ordinary air be permitted to gain entrance, the liquid soon becomes turbid from the absorption of carbon dioxide. The solution is alkaline to phenolphthalein and naphtholphthalein, and precipitates with the slightest trace of a solution of a carbonate.

Obviously this is a solution of lead oxide or hydroxide, and the saturated solution contains about 20 mgrms. of lead in 100 c.c. Apparently the amount varies from 19.5 to 20.6 mgrms., and this may be regarded as the solubility of this compound at 8° to 12° C. With free access of carbon-dioxide-free air, the formation of the oxide or hydroxide continues, but when air is excluded, the action stops when the available oxygen is used up. This applies also to distilled water to which any acid has been added. If the acid forms a soluble lead salt, this remains in solution, whilst if the acid forms a practically insoluble lead salt, this insoluble salt is deposited as soon as the water has become saturated therewith. Carbonic acid appears to form the most insoluble salts, followed by silicic acid, then, at a distance, by phosphoric, sulphuric acid, etc. So far as the solvent action of water on lead is concerned, carbonic and silicic acids are the only ones to be considered. When the action between oxygen-laden but otherwise pure distilled water and lead takes place in stoppered bottles, quite full and protected from the access of air, it is always found: (1) That the oxygen taken up by the lead corresponds to the lead which has entered into solution as estimated by hydrogen sulphide. (2) That the loss of weight suffered by the metal is very approximately a measure of the amount of lead which has been oxidised. (3) That the amount of lead dissolved can be estimated with fair approximation by titrating the solution with $\frac{N}{10}$ acid, using methyl orange as the indicator.

(1) This requires that the oxygen contained in the water at the commencement and end of the experiment should be accurately determined, and Winkler's method has been used (save in certain cases where experiments were being made with nitrated waters, when my process was utilised). The following are the results of a series of experiments, commencing with water exhausted as far as possible by an air-pump, and concluding with water through which pure oxygen gas had been passed:

	Lead, Mgrms. per 100 c.c.																
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	Aver.
Estimated from loss of O (1 mgrm. = 12.94 Pb)	0.0	1.42	2.2	2.7	4.1	7.4	7.3	7.25	9.75	11.1	12.7	14.9	20.7	21.6	35.0	42.8	11.08
By means of H ₂ S ...	0.03	1.55	2.1	2.5	4.25	7.3	7.35	8.0	9.4	11.0	12.0	15.6	19.0	22.0	35.3	42.0	11.17

The above results show that the amount of lead chemically acted upon is determined by the amount of oxygen taken out of solution, and that the extent of this action can be accurately gauged by the amount of oxygen lost.

(2) This is more troublesome, and is of no practical use. Save with pure distilled water or acidified water the results are useless, as insoluble salts deposit upon the lead and vitiate the results. The following experiments were made with distilled water containing the merest trace of carbon dioxide:

	1.	2.	3.	4.	5.	6.	7.
Weight lost by lead foil (mgrms.)	6.2	7.5	9.0	13.2	15.0
Lead found in solution and suspension (mgrms.)	7.1	8.8	8.45	13.45	13.75
	14.5	15.0

(3) This is not of much utility, since the presence of lead salts in solution interferes with the delicacy of the end reaction, but it is worthy of notice that in distilled

waters containing only oxygen and carbon dioxide the amount of lead taken up can be approximately estimated in this way. The attempts to estimate the relative proportion of oxide and carbonate by using phenolphthalein as well as methyl orange all ended in failure.

With distilled water the velocity of the reaction between the oxygen and the lead appears to depend upon the amount of oxygen present, and the same remark applies in the presence of any free acid forming soluble lead compounds, but in the presence of acid the velocity is greater in the earlier stages. For example :

Time.	Lead acted upon—	
	Neutral Distilled Water.	Distilled Water+ 4 per Cent. $\frac{N}{10}$ HCl.
	Mgrms.	Mgrms.
$\frac{1}{2}$ hour	1.65	3.1
3 hours	4.7	8.0
5 "	7.1	9.7
24 "	11.0	12.4
48 "	12.2	13.0.

RATE OF UTILISATION OF OXYGEN.—The following gives in a little more detail information concerning a series of experiments showing the rate at which oxygen is taken up, and that action ceases when all the oxygen has been used. The bottles used all held approximately 160 c.c., and were completely filled so as to exclude air. After standing the requisite time, 5 c.c. of water were taken from the bottle, the solutions of manganese chloride added (3 c.c.), and some of the original water added again to fill the bottle. In the 5 c.c., diluted to 50 c.c., 100 c.c., or more according to circumstances, the lead was determined, and the residual oxygen was determined in the remainder of the water. The correction for oxygen in the water and chemicals added was usually so small as to be negligible. In many cases duplicate bottles of water were put on, so that the lead could be estimated in one and the residual oxygen in the other. The discrepancies which occurred when this method was used led to the discovery of the marked effect of unequal agitation.

Record of experiments made November 19 and 20, 1920. Temperature, 13° C. Oxygen in 100 c.c. of the distilled water, 1.030 mgrms. ; free CO_2 , 0.33 mgrm. :

Time.	Oxygen Left.	Oxygen Lost.	Lead Equivalent.	Lead found by H_2S .
	Mgrm.	Mgrms.	Mgrms.	Mgrms.
$\frac{1}{4}$ hour	0.95	0.08	1.03	0.6
$\frac{1}{2}$ "	0.90	0.13	1.68	1.66
1 "	0.80	0.23	2.98	2.8
2 hours	0.66	0.37	4.79	4.55
3 "	0.54	0.49	6.34	6.1
6 "	0.44	0.59	7.6	7.1
21 "	0.18	0.85	11.0	11.1
72 "	0.03	1.00	12.95	13.6

EFFECT OF CARBON DIOXIDE.—Carbon dioxide produces very insoluble lead salts; yet it is capable of dissolving a small quantity of lead when it is present in unusual amounts. It is a most important factor in the action of water on lead, since the so-called "erosive" action is entirely due to it. It does not prevent the action of the oxygen dissolved in the water, but it enters into combination with the oxide formed. If the amount of carbon dioxide does not greatly exceed 1 part per 100,000 of water, when lead is inserted action is distinctly visible within a few minutes. The formation of an insoluble lead carbonate can be seen at the surface of the metal, and this glides down and forms a turbid layer at the bottom of the bottle. As the action proceeds, the turbid layer increases in thickness until it just covers the upper surface of the lead. After this, if unshaken, the suspended matter slowly deposits and the water again becomes clear.

When the carbon dioxide exceeds 1.5 parts per 100,000 this turbidity is not produced, the water remains perfectly clear and bright, some lead is taken into solution if sufficient carbon dioxide be present, but a very insoluble carbonate is deposited on the metal, which assumes a dark grey colour. The amount of lead acted upon can be easily ascertained from the oxygen loss. It is very difficult in many cases to determine it directly by hydrogen sulphide, since a considerable amount of strong acid must be added to dissolve the deposit, and if much oxygen is left in the water the action of this acid has to be allowed for. When action has proceeded until nearly all the dissolved oxygen has been used up, the determination is easy, but when much oxygen remains a correction must be made for the amount of lead affected by the acid added. This is best done by taking duplicate samples, which are prepared and kept under identical conditions, and at the expiration of the required time one bottle is used for estimating the residual oxygen, and into the second is introduced 1 per cent. of 99 per cent. acetic acid and the bottle shaken until all the deposit is dissolved off the lead. This usually takes two to five minutes. Now 5 c.c. of the acid water are removed for the determination of the lead by means of hydrogen sulphide, and the remainder is used for the estimation of the residual oxygen. The difference between the two oxygen determinations is the measure of the lead acted upon by the acid, and affords the necessary correction. The following table is explanatory:

Time.	Oxygen in 100 c.c. of Water used.	Oxygen Lost.	Lead Equivalent.	Lead found by H ₂ S.
	Mgrms.	Mgrm.	Mgrms.	Mgrms.
3½ days	1.103	0.52	6.75	—
3½ "	1.103	0.63	8.1	8.0 - 1.35 = 6.65
4 "	1.106	0.21	2.75	4.0 - 1.7 = 2.3
6 "	1.106	0.495	6.3	8.4 - 1.6 = 6.8
7 "	0.515	0.135	1.75	3.15 - 1.6 = 1.55

In the following table the results obtained with oxygenated water containing various quantities of free carbon dioxide are recorded. In the cases where the free

carbon dioxide was less than 1 part per 100,000 the liquid was turbid; where it contained 1.15 parts it was dull; in all the others the water remained clear.

Oxygen in Original Water per 100 c.c.	Free Carbon Dioxide. Parts per 100,000.	Total Lead acted upon calculated from O lost and by H ₂ S.	Lead in Clear poured-off Liquid.	Lead in Filtrate.	
				Pasteur.	Paper.
Mgrms. 0.70	0.75	Mgrms. 7.0	Mgrms. 0.20	Mgrm. 0.00	Mgrm. —
1.053	1.15	11.65	0.275	—	0.03
1.053	2.65	12.7	0.25	0.03	—
1.031	3.0	13.3	0.30	0.00	—
1.045	4.0	10.7	0.40	0.00	—
1.045	7.9	10.9	1.9	0.00	—
1.045	14.3	9.45	2.85	0.00	0.60

INFLUENCE OF CARBONATES.—When bicarbonates are present action is retarded, and calcium carbonate in carbon dioxide solution has a much greater retarding action than the sodium salt. Of the hundreds of experiments made, a few only can be quoted here. These show that when small quantities of carbonates only are present, the lead when immersed in the water causes more or less turbidity, but when the amount of calcium carbonate present exceeds about 1 part per 100,000 the water remains clear. A larger quantity of sodium bicarbonate is usually necessary to produce this effect.

Time.	Amount of Salt Present, Calculated on Bicarbonate.	Free CO ₂ .	Oxygen Lost.	Lead Equivalent.	Lead by H ₂ S.	Notes.
1 day	(CaC ₂ O ₅) 0.4	0.0	0.51	6.6	—	Turbid. No lead in solution.
"	" 0.9	0.0	0.18	2.3	—	Less turbid. Ditto
"	" 1.35	0.0	0.20	2.6	—	Clear and bright. Ditto
2 days	" 0.5	0.15	0.73	9.45	10.5	Turbid. Trace Pb in solution
"	" 1.0	0.3	—	—	4.8	Clear and bright. No Pb in sol.
"	" 1.45	0.45	0.59	7.65	8.0	" " "
"	" 1.7	0.5	0.22	2.85	2.85	" " "
4 days	" 19.0	0.55	0.22	2.85	2.8	" " "
2 days	(NaHCO ₃) 0.5	0.0	0.77	10.2	10.15	Turbid. No Pb in solution
"	" 1.0	0.0	0.44	5.7	—	Clear and bright. Ditto
"	" 2.0	0.0	0.36	4.65	—	" " "
"	" 5.0	0.0	—	—	—	" " "

When water containing carbonate is kept in constant motion whilst in contact with lead, the water becomes turbid, or at least dull, and if poured off and acidified lead is found to be present. The following experimental results show how markedly the results may be affected by agitation. The water used was a pure chalk water of over 20° hardness.

Time.	Agitation.	Oxygen Present.	Free CO ₂ .	O used.	Lead Equivalent.	Notes.
3 hours	Rotated	1.030	0.0	0.10	1.3	Water dull, but does not deposit
24 hours	At rest	1.030	0.0	0.363	4.7	Water bright. No lead in poured-off liquid

The rotated water gave the following results :

50 c.c. poured off and treated with hydrogen sulphide without acidification : lead absent.

50 c.c. poured off and treated with hydrogen sulphide after acidification : 0.32 mgrm. Pb per 100 c.c.

50 c.c. poured off and filtered through paper after acidification : 0.10 mgrm. Pb per 100 c.c.

GENERAL CONCLUSIONS.—The effect of numerous salts has been studied, but the results must be reserved for another occasion. The experiments above recorded prove that water has no action whatever on lead ; that it is the foreign matters dissolved in water which affect the metal, the oxygen combining with it to form a soluble oxide or hydroxide, which remains in solution (to the point of saturation) in the absence of other substances capable of combining with it. This solution is of a colloidal nature and of such coarse degree of dispersion or so liable to adsorption that it will not pass through a Pasteur filter, and may not even pass a fine paper filter. In the presence of acids forming soluble lead salts, such salts are formed and will pass through any filter. If the acid forms insoluble salts, these are thrown down, and may be deposited on the metal in such a way as to prevent any further action. Any soluble salts present in the water may likewise act upon the lead hydroxide. Water is merely an inert medium, by means of which these foreign substances are enabled to act upon each other, the water itself taking no part other than that of a solvent.

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THE COMPOSITION OF EGG POWDER.

By F. F. BEACH, M.A., F.I.C., F. E. NEEDS, A.I.C., AND EDWARD
RUSSELL, B.Sc., F.I.C.

(*Read at the Meeting, June 1, 1921.*)

THE examination of a substance bearing the name "egg powder" was occasionally undertaken in the City Laboratories, Bristol, and it was generally recognised that it was similar to baking powder, as the table on p. 282, taken from two consecutive years, will show.

Rice starch was the common organic constituent, and the only real difference between these substances was one of colour, effected by the introduction into the

BEACH, NEEDS, AND RUSSELL :

	Liquid Egg. 1.	Dried Egg. 2.	Dried Eggs. 3.	Dried Eggs. 4.	Egg Powder. 5.	Egg Powder (Guaranteed to contain Eggs). 6.	Egg Substitute—		Egg Powder. 9.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	7.	8.	Per Cent.
Loss at 100° C. (moisture, etc.)	72.8	4.8	9.05	8.0					14.5
Ash	0.95	3.71	3.17	3.24	7.63	12.72	23.3	8.66	25.16
Calcium sulphate	0.22	0.62	1.35	0.21	0.79
CaSO ₄ in ash	2.9	4.9	5.8	2.4	3.1
Ethereal extract	13.65	50.61	40.09	39.07	0.34	0.99	0.19	0.30	0.30
Refraction (Zeiss) at 35° C.	67.5	65.0	64.0	67.0					
Nitrogen	...	6.97	7.04	7.45	0.96	0.97	0.92	0.55	0.74
Protein	...	43.5	44.0	46.5	6.02	6.06	5.75	3.44	4.62
Organic phosphorus (P ₂ O ₅)	11.8	1.28	1.20	1.27	0.0095	0.025	0.0043	0.0088	0.016
Arsenic (grains per pound)					$\frac{1}{300}$	$\frac{1}{150}$	$\frac{1}{300}$	$\frac{1}{250}$	$\frac{1}{155}$
Cold water extract					Colourless	Yellow	Deep yellow	Light yellow	Yellow
Tartrates	+	Trace	+	+	-
Insoluble matter, phosphates	Trace	+	+	-	+
Microscope	Rice. Turmeric.	Rice. stained yellow. Granular particles of egg protein.	Rice and some maize; some stained yellow.	Potato. Rice. Maize. Turmeric.	Rice masses, some stained.

THE COMPOSITION OF EGG POWDER

	Egg Substitute --		Egg Powder.		Egg Substitute--				Rice.	Rice +1 per Cent. Dried Egg. 18.	Rice +10 per Cent. Dried Egg. 19.
	10.	11.	12.	13.	14.	15.	16.	17.	Per Cent. 12-87	Per Cent. 12-98	Per Cent. 12-11
Loss at 100° C. (moisture, etc.)	Per Cent. 10-0	Per Cent. 10-6	Per Cent. 9-97	Per Cent. 11-3	Per Cent. 12-5	Per Cent. 10-08	Per Cent. 11-1	Per Cent. 12-87	Per Cent. 12-98	Per Cent. 12-11	
Ash	18-33	11-43	9-3	23-15	20-1	13-06	10-8	0-35			
Calcium sulphate	0-62	0-24	0-27	1-37	0-091	0-27	0-59				
CaSO ₄ in ash	3-4	2-1	2-9	5-9	0-45	2-2	5-4				
Ethereal extract	0-27	1-18	0-80	0-19	0-61	1-15	0-69				
Refraction (Zeiss) at 35° C.											
Nitrogen ...	0-58	0-80	0-90	0-72	0-87	1-13	1-42	1-12	1-22	1-63	
Protein ...	3-62	5-0	5-62	4-5	5-43	7-06	8-87	7-0	7-62	10-18	
Organic phosphorus (P ₂ O ₅)	0-007	0-017	0-0127			0-0059		0-022	0-053	0-141	
Arsenic (grams per pound) ...	3-00	3-00	1-000	3-30	3-00	1-000	1-000				
Cold water extract	Light yellow	Colourless	Colourless	Yellow	Colourless	Yellow	Deep yellow				
Tartrates ...	+	+	+	-	-	+	-				
Insoluble matter, phosphates	+	-	-	+	+	-	+				
Microscope ...	Wheat and rice masses, stained and unstained. Maize, Turmeric.	Rice masses and grains. Turmeric.	Rice masses and grains. Turmeric.	Rice masses, stained yellow.	Rice masses. Turmeric.	Maize, some stained. Parenchyma. Spiral vessels and pigment cells.	Wheat. Rice masses. Some wheat stained yellow.	Rice masses and grains.			

egg powder of a few grains of turmeric, or, in some cases, a few grains of coloured maize starch. The examinations of baking powders predominated, but a sufficient number of the egg powders were examined to justify the conclusion that egg powder is merely coloured baking powder.

	Baking Powder.			Egg Powder.		
	1.	2.	3.	1.	2.	3.
Ash, per cent.	28.8	14.1	8.6	26.2	20.1	8.95
Calcium sulphate, per cent.	0.78	0.62	0.35	0.7	0.89	0.30
Calcium sulphate as percentage of ash ...	2.7	4.4	4.1	2.7	4.4	3.4

Where, then, is the justification for the use of the word "egg" in this substance? That there was probably some such idea in the public mind suggested itself to some trader, as a sample was recently brought into these laboratories bearing a small covering label with the seductive suggestion that it contained "the actual egg." For the purpose of testing the accuracy of this statement and obtaining information to see if it would be possible to separate this substance from baking powder and really standardise it, a series of analyses of the various brands sold here was made and compared with the analytical results obtained from the examination of "desiccated egg," both purchased and prepared.

The following analytical figures were determined for both "desiccated egg" and egg powders, some of which were described as egg substitute—an equally unsatisfactory name, as a coloured baking powder is no satisfactory substitute for "eggs": Moisture, ash, calcium sulphate, ethereal extract, nitrogen expressed as protein, organic phosphorus, and microscopical character.

The appended table shows the results obtained in the case of three samples of desiccated egg and fourteen samples of egg powder and substitute. A comparison of these figures shows how widely these substances differ in all essential features, there being no evidence of egg whatever in any egg powders except that stated to contain actual egg, and then the evidence is limited to microscopical detection, the increase in ether extract, protein and organic phosphorus being so small as to be negligible. "It is quite clear that in any revision of values this substance would have no place; for a real claim to the use of the word 'egg' in this connection should mean a definite figure for ether extract, protein and organic phosphorus." With regard to the latter figures, in a recent paper in the *J. Amer. Chem. Soc.*, 1920, 42, 2238, Messrs. Brauns and MacLaughlin have shown that lecithin and cephalin can be extracted from organic substances and examined; but as the process suggested would involve too great a labour, the extraction by means of hot alcohol of these substances, their saponification in the alcoholic solution, and the estimation of the total phosphorus would appear adequate, and by this means a standard could be laid down for a minimum percentage of actual egg. In the last column of the table the effect of mixing dried eggs with the usual base of egg powder, the cereal

rice, is studied, and we would suggest that the figures of this last column provide a suitable basis for a standard.

DISCUSSION.

Mr. G. RUDD THOMPSON said that it was a very open question whether so-called "egg powders" were not a very grave infringement of the Food and Drugs Act. Action had already been taken where there was a specific declaration of "egg powder" or "containing the active principle of the egg," but that, as a rule, manufacturers did not give this loophole; they used instead such a phrase as "A perfect substitute for egg." He considered that a thorough report should be made on all these substances put on the market, as so many of them were mere frauds, being composed of nothing more than coloured starch, or baking powder, to which methyl orange had been added.

Dr. DYER said that for a great number of years there was no such thing as egg powder in the literal sense, and during that time (when it could not possibly have been misleading) the term "egg powder" had come to be applied to baking powder coloured yellow. More recently, powdered egg had become possible, which had led to a certain amount of ambiguity between egg powder and powdered egg, and it was difficult to say that it was not of the nature under which it was sold. He did not think the authorities were slack. But there was doubt as to whether the long continuance of the term "egg powder," as applied to coloured baking powder, might not legally be held to have established something in the nature of a commercial "right of user" of this title.

Dr. VOELCKER alluded to a case he had come across lately of a material which appeared to consist of genuine egg powder, and which, though unsuitable for human use, was sold to farmers as a food for poultry. It was perfectly genuine, consisting of egg powder giving an ether extract of 39 per cent., and albuminoids 43 per cent., was sold at a reasonable price, and was a good food for poultry. He would welcome anything which could be done to establish a firm understanding on this matter.

Mr. MORE said it was well known commercially that an egg powder was not an "egg" powder, but a baking powder coloured with a small quantity of aniline dye. He considered that some powers were required in the new Food Bill to ensure that such materials were properly and correctly named.



NOTES.

The Editor desires to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A SIMPLE METHOD FOR TESTING GLUE.

MANY methods for testing glue have been suggested, and most of them are unsatisfactory or give results which are difficult to interpret.

The following simple method involving the use of the machine for testing the tensile strength of cement has been devised, and is claimed to be a useful addition to the tests already in use.

The method is as follows: Briquettes of pitch pine of the same dimensions as those used in testing the tensile strength of cement (*cf.* British Standard Specification for Cement) are made, the grain running longways. These are then sawn across the middle at right angles to the axis, care being taken that the operation is done with great exactitude, and the cut surfaces smoothed down with sand-paper so that they fit absolutely when placed together.

Twenty-five grms. of glue are allowed to stand in 100 c.c. of water for twenty-four hours. This is then heated on a water-bath until all the glue has dissolved, the evaporated water replaced, and the solution cooled to 50° C. A quantity of the solution is then removed by a small pipette specially made from a thin glass tube delivering exactly 0.3 c.c., which is found to be the amount required to cover the sq. inch section of the briquette. This amount is run out on to the flat surface of one of the half-briquettes, the other half is put immediately on top of it, and the two halves are held in position by a 2-inch rubber band. After twenty-four hours the briquette is placed in the cement testing machine and broken in the ordinary way.

The cross-section of the middle of the briquette being exactly 1 sq. inch, the tensile strength of the glue can be given in pounds per sq. inch. Several briquettes should be used for each sample, and the mean results taken.

The following are the results obtained from ten samples of glue. The figures marked * are considered abnormal and not included in the means.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	
Pounds per Square Inch.										
410	300	60	400	*500	400	40	370	100	450	
445	180	0	280	190	250	60	328	120	410	
575	180	115	380	175	265	120	315	105	300	
440	220	75	255	280	305	90	450	140	470	
*275	220	110	430	220	*605		380		450	
550	365	110	446	215	*175					
480	270	50	285	170	400					
440	280	60	380	210	405					
Mean :	477	246	72	356	207	338	78	369	124	416

In order to classify the glues for general purposes, the following standards were made :

Quality.		Tensile Strength. Pounds per Square Inch.	
A. Good	More than	300
B. Medium	„	150 and less than 300
C. Poor	Less than	150

CONCLUSIONS.—1. From the above results it will be seen that there is an occasional abnormal briquette; obviously this should be omitted from the mean of the series.

2. That by the above method anyone can fix his own standards, using whatever wood or strength of glue be most suitable.

3. It is suggested that for each series six briquettes be made.

4. That a really fair estimate of the strength of different glues can be obtained by this method.

D. R. FRAZER.

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CAIRO.

THE ESTIMATION OF SMALL AMOUNTS OF CHROMIUM IN STEELS.*

Since the publication of my paper on the estimation of small quantities of chromium in steel (ANALYST, 1921, 38), my attention has been drawn to the sensitive colour reaction of chromic acid with diphenyl-semicarbazide described by Cazeneuve (ANALYST, 1900, 25, 331). This indicator gives an intense "permanganate" colour with chromic acid, visible at far greater dilutions than the colour of the chromic acid itself. It was thought worth while to try the chromium process, using this indicator in the colour matching, and to carry it to greater dilutions, to find out if the separation of the chromium from the iron is as complete as it appears to be.

Samples containing a small but measurable quantity of chromium gave identical results, whether the chromium was estimated in the ordinary way by direct matching of the chromic acid colour, allowing for the blank, or whether the indicator was added to the two tubes and the purple colour matched (if necessary diluting and taking an aliquot part).

The details of the experiments, with percentages of chromium too low to be estimated by matching the chromic acid colour, are as follows :

$\frac{N}{1000}$ $K_2Cr_2O_7$ added to 4 Grms.	Cr added.	$\frac{N}{1000}$ $K_2Cr_2O_7$ re- quired for 100 c.c.	$\frac{N}{1000}$ $K_2Cr_2O_7$ re- quired for 4 Grms.	Cr found.
c.c.	Per Cent.	c.c.	c.c.	Per Cent.
Blank	—	Less than 1 drop	—	—
1.00	0.00043	0.15	0.75	0.00032
2.00	0.00087	0.35	1.75	0.00076
3.00	0.00130	0.55	2.75	0.00120
4.00	0.00174	0.70	3.50	0.00152

In each case 4 grms. of electrolytic iron were used, and the separation carried out in the original experiments.

These results prove that the oxidation and separation of the chromium from the iron are complete.

The indicator is made up by dissolving 1 grm. of diphenyl-semicarbazide in 10 c.c. glacial acetic acid, and making up the solution to 1,000 c.c. with water; 5 c.c. are added to each tube, and 10 c.c. of 1 : 3 sulphuric acid are used instead of the original 20 c.c.

B. S. EVANS.

RESEARCH DEPARTMENT,
WOOLWICH.



ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Colorimetric Estimation of Lactose in Milk. R. G. Owen and R. Gregg. (*J. Lab. Clinical Medicine*, 1921, 6, 220-221; *Chem. Abstracts*, 1921, 15, 1033.)—The method described is a modification of that employed by Folin for the estimation of sugar in blood (*ANALYST*, 1920, 45, 227). Two standard solutions of pure lactose are prepared containing 0.25 and 0.35 mgrm. per c.c. To 1 c.c. of milk 2 c.c. of sodium tungstate solution and 2 c.c. of $\frac{2}{3}$ -N sulphuric acid are added, and the mixture allowed to stand for five minutes, diluted to 100 c.c., and filtered. One c.c. of the filtrate is run into a special sugar tube, 1 c.c. of water being added. Into two similar tubes 2 c.c. of each of the standard solutions are run, and 2 c.c. of alkaline copper solution are added to the three tubes, which are then immersed for six minutes in a boiling water-bath. Two c.c. of Folin's molybdate-phosphate solution are introduced, and the mixtures are diluted to 25 c.c. The colour of the solution under examination is then compared in a colorimeter with the standard to which it most closely approximates.

T. J. W.

"Rice" Beans (*Phaseolus calcaratus*). (*Bull. Imp. Inst.*, 1920, 18, 476-478.)—*Phaseolus calcaratus* is widely cultivated in India, where it is known as the "rice" bean. Five samples of beans of different varieties gave the following results: Moisture, 9.0 to 10.6; crude proteins, 20.8 to 25.3; fat, 0.5 to 1.0; carbohydrates, 54.7 to 60.3; fibre, 4.8 to 5.4; ash, 3.8 to 4.6 per cent.; nutrient ratio, 1 : 2.9 to 1 : 2.2; food units, 113 to 119. All the samples were free from hydrocyanic acid. These beans are similar in composition to "black gram" (*Phaseolus Mungo*) and cow-peas (*Vigna Catjang*), and would be readily saleable in the United Kingdom as a feeding-stuff.

R. G. P.

Adulteration of Rice Bran. (*U.S. Dept. Agriculture. Service and Regulatory Announcements. Suppl. N.J. 8,431, March 10, 1921.*)—Two shipments of rice bran had the following composition: Moisture, 8.48 and 7.83; ether extract, 12.03 and 13.04; crude fibre, 16.70 and 17.52; crude protein, 10.66 and 10.88; ash, 12.33 and 12.15; and ash insoluble in acid, 7.40 and 7.32 per cent. These analyses indicating the presence of added rice hulls, proceedings were taken, and a conviction obtained.

Hydrocyanic Acid as a Sterilising Agent for Flour. Marchadier and Goujon. (*J. Pharm. Chim.*, 1921, **23**, 417-420.)—Whilst recognising the value of gaseous hydrocyanic acid as a disinfectant for fabrics and clothing, the authors contend that it is unsuitable for farinaceous foodstuffs on account of the possible retention of small quantities of the cyanide, and the fact that flour so sterilised does not make good bread. They have examined a sample of wheat flour having a distinct smell of almonds, which persisted even in foods prepared from it. The sample gave a strong Guignard reaction with sodium picrate paper, and showed the presence of 82 mgrms. of hydrogen cyanide per kilo. Such quantity is dangerous to the consumer, and treatment of flour in this way should be prohibited. H. E. C.

Use of Dyes in the Microscopical Examination of Bread, Flour, Feeding Stuffs, etc. P. P. Fechner. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **41**, 170-172.)—A dye reagent, termed "Violet," is recommended as being useful for the ready identification of the various constituents of bread, flour, etc.; when treated with this reagent, the cellulose tissue is coloured blue-green to blue-violet, the proteins violet or red, the oil yellow or brown, whilst the starch remains white or colourless. Another reagent, also prepared by the author, colours the cellulose tissue red, and differentiates to some extent between the different varieties of starch; rye, wheat, barley, oat, rice, maize, millet, and buckwheat starches are coloured black or brown, whilst sago, banana, potato, acorn, chestnut and leguminous starches remain white in colour. W. P. S.

Cassava Flour. C. Grimme. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **41**, 172-175.)—Bitter cassava (*Manihot utilissima*), when dried, is ground to form cassava flour; further preparation yields starch (tapioca) and alcohol. Cassava flour contains: Water, 12.73; proteins, 0.65; fat, 0.11; starch, 88.84; crude fibre, 1.81; and ash, 1.12 per cent. The ash contains about 33 per cent. of K_2O and 20 per cent. of P_2O_5 . W. P. S.

Estimation of Carbohydrates in Vegetable Foods. V. C. Myers and H. M. Croll. (*J. Biol. Chem.*, 1921, **46**, 537-551.)—*Soluble sugars*: The vegetable is finely chopped, well mixed, and ground in a mortar with sand and a measured volume of water. A portion of the mixture is saturated in the cold with pure picric acid and filtered. Two 3 c.c. portions of the filtrate are measured into test-tubes, and 1 c.c. of 22 per cent. sodium carbonate solution is added to one of them, both tubes being then heated in a boiling water-bath for ten minutes. One c.c. of sodium carbonate solution is run into the second tube, and the heating of both tubes continued for a further twenty minutes, when they are cooled and diluted to 10, 15, or 20 c.c. to match approximately a standard prepared by heating for twenty minutes 3 c.c. of 0.02 per cent. pure dextrose solution with 1 c.c. of sodium carbonate solution, cooling the liquid, and diluting it to 10 c.c. The colours are matched in a colorimeter, and any increase shown in the solution hydrolysed by heating with picric acid represents the sucrose present. *Total available carbohydrate*: The ground vegetable is weighed out accurately into a graduated flask, and

boiled with 100 c.c. of water for one and a half hours under a reflux condenser, then ground to a paste, and rinsed back into the flask with water to give a total volume of about 200 c.c. A plug of cotton-wool is inserted in the neck of the flask, and the contents are heated to boiling and cooled to 40° C., after which 5 c.c. of a 1 per cent. solution of taka diastase and a few c.c. of toluene are added, and after its contents have been mixed the flask is kept at 37° C. for eighteen hours. The mixture is then cooled, diluted to 250 or 300 c.c., and filtered after thorough shaking, after which 20 c.c. of the filtrate are heated with 1.4 c.c. of concentrated hydrochloric acid in a boiling water-bath for one or two hours. After cooling, the liquid is almost neutralised with strong sodium hydroxide solution, diluted to 25 c.c., and saturated with picric acid, the subsequent procedure being as described above for soluble sugars. A correction must be made by means of a blank estimation for the sugar produced by hydrolysis of the taka diastase solution. Results obtained by this method with a variety of fruits and vegetables are given.

T. J. W.

Inversion and Estimation of Cane Sugar. A. R. Rose. (*J. Biol. Chem.*, 1921, **46**, 529-535.)—The solution containing less than 5 per cent. of cane sugar is mixed with twice its volume of saturated picric acid solution and heated in a boiling water-bath for ten minutes. After cooling, the solution may be diluted to a definite volume and a polarimetric reading taken, or a volume of 20 per cent. sodium carbonate solution equal to that of the sugar solution taken may be run in, the mixture heated in the water-bath for thirty minutes, and the red colour produced compared in a colorimeter with that given by a standard solution of pure sugar (Dehn and Hartman, *J. Amer. Chem. Soc.*, 1914, **36**, 403). Should dextrose or laevulose be present in the original solution, the cane sugar may be estimated by polarimetric readings taken before and after the picric acid inversion. For the estimation of sugars in food products, from 1 to 10 grms. of the sample are triturated in a mortar with 100 c.c. of water and 0.5 gm. of solid picric acid. The mixture is centrifuged or filtered, and 1 c.c. of the clear solution is transferred to a test-tube containing 2 c.c. of saturated picric acid and 1 c.c. of 20 per cent. sodium carbonate solution, and heated in a boiling water-bath for thirty minutes, when the red colour produced is proportional to the amounts of dextrose and laevulose present. A similar volume of the solution is hydrolysed by heating for ten minutes with the picric acid before the addition of the sodium carbonate, when the colour produced by reduction will be proportional to the original dextrose and laevulose, together with the invert sugar derived from the sucrose present. Dextrin and maltose, if present, should be removed or allowed for. The results given show that the method yields a high degree of accuracy.

T. J. W.

Grape-Seed Oils. É. André. (*Comptes rend.*, 1921, **172**, 1296-1298.)—Eleven samples of grape-seed oil, obtained in some cases by pressing the seeds and in others by extraction with petroleum spirit, have been examined. The limiting values found for the various constants are as follows: Sp. gr. at 20°/0° C., 0.9170 to 0.9334; n_D^{20} , 1.4708 to 1.4772; saponification value, 171.0 to 191.1; iodine value, 94.3 to 135.0; saponification value of the acetylated oil, 189.7 to 231.8; acetyl value, 13.3 to 49.3.

T. H. P.

Perilla Seed from Cyprus. (*Bull. Imp. Inst.*, 1920, 18, 479-481.)—Perilla seed (*Perilla ocymoides*), grown experimentally in Cyprus from seed of Japanese origin, contained 6.3 per cent. of moisture and 43.1 per cent. of oil. The oil had the following values: Sp. gr. at 15°/15°, 0.9298; $[n]_D^{20}$, 1.472; saponification value, 190.5; and iodine value, 185. The sp. gr. is lower than that previously recorded for perilla oil—viz., 0.9318 to 0.9372; otherwise the figures closely resemble those recorded previously. The residual meal gave the following results calculated on a basis of 7.0 per cent. of fat: Moisture, 9.0; crude proteins, 35.6; fat, 7.0; carbohydrates, 19.4; fibre, 18.9; ash, 10.1 per cent.; nutrient ratio, 1 : 1.0; food units, 126. The meal therefore contains rather less fibre and considerably more protein than undecorticated cotton-seed cake, and, if found to be non-injurious to animals, would form a valuable feeding-stuff.

R. G. P.

Oil of "Maroola" Nuts (*Sclerocarya Caffra*). (*Bull. Imp. Inst.*, 1920, 18, 481-483.)—The kernels of *Sclerocarya Caffra* (N.O. *Anacardiaceæ*), a small tree found only in Natal and the Transvaal, contained 5 per cent. of moisture and 56.2 per cent. of a clear, pale, yellowish-brown oil with the following values: Sp. gr. at 15°/15°, 0.9167; $[n]_D^{20}$, 1.460; m.-pt. of fatty acids, 25.0° C.; acid value, 3.7; saponification value, 193.5; iodine value, 76.6; soluble volatile acids equivalent to 0.1 c.c. $\frac{N}{10}$ alkali; insoluble volatile acids, 0.45 c.c. $\frac{N}{10}$ alkali per 5 grms.; and unsaponifiable matter, 0.6 per cent. As the nuts are difficult to crack, and only contain 10 per cent. by weight of kernel, they are unlikely to be of commercial value as a source of oil.

R. G. P.

Analyses of Chicory and Other Coffee Substitutes. J. Pritzker and R. Jungkunz. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, 41, 145-169.)—Analyses are recorded of some fifty-six samples of chicory, roasted beans and cereals, fig coffee, dandelion coffee, etc. In estimating the amount of chicory in a coffee-chicory mixture, use is made of the water-soluble extract of the substances: 10 grms. of the sample are mixed with 200 c.c. of water, weighed, and boiled for five minutes. After cooling, the original weight of the mixture is restored by the addition of water, the solution is filtered, and the specific gravity of the filtrate is determined. The percentage of water-soluble substance (TS) is calculated by the formula $TS = (S - 1) \times 5160$, where S is the sp. gr. of the 5 per cent. decoction. The average amount of water-soluble substances yielded by thirty-nine samples of chicory was 60.68 per cent.; coffee gave from 23.2 to 25.2 per cent. Since $\frac{N}{20}$ iodine solution has practically the same colour as that of a 5 per cent. decoction of normal chicory, the author suggests the use of this iodine solution as a standard in comparing the colour of chicory extracts, the colorations being made after suitable dilution. Two samples of dried dandelion root yielded the following results: Water, 10.02, 3.85; ash, 2.02, 5.13; water-soluble substances, 50.00, 36.20 per cent.; and sp. gr. of the 5 per cent. decoction, 1.0097, 1.0070.

W. P. S.

Volatile Oil from the Leaves of the "Wild Pimento" of Jamaica. O. D. Roberts. (*J. Soc. Chem. Ind.*, 1921, 40, 94-96r.)—From the distillation of the

leaves of *Amomis* (= *Pimenta*) *jamaicensis* about 0.49 per cent. of volatile oil of pale yellow colour, having an odour resembling lavender, was obtained, which had the following constants: Sp. gr. at 15°/15° C., 0.8895; $[\alpha]_D^{25} = -6^\circ 0'$; $n_D^{20} = 1.471$; acid value, 2.4; ester value before acetylation, 4.2; and ester value after acetylation, 129.4. The oil is soluble in 2.5 volumes of 70 per cent. alcohol, and becomes cloudy again with six volumes. The composition of the oil was: Terpenes, including α -phellandrene and dipentene, 17.0; cineol, 15.0; aldehydes, 0.1; alcohols (*l*-linalool and geraniol), 38.3; esters as linalyl acetate, 1.5; phenols, 0.1; acids (acetic and caproic), 0.2; and residue containing sesquiterpenes, 27.8 per cent. H. E. C.

Essential Oil from *Perilla Nankinensis*. S. Furukawa and Z. Tomizawa. (*J. Chem. Ind. Tokyo*, 1920, **23**, 342; *J. Pharm. Chim.*, 1921, **23**, 426.)

—The oil distilled from the fresh plants in different stages of growth shows a gradual increase in content of aldehydes and diminution of esters by the action of an enzyme, whilst the oil obtained from the dried plants changes in the converse way. The oil has the following percentage composition: *l*-limonene, 20 to 30; perillaldehyde, 44 to 57; and a trace of α -pinene. Perillaldehyde has b.-pt., 237°; sp. gr. at 15°/15° C., 0.9675; $n_D = -145.8^\circ$ *, yields an exceedingly sweet α -antialdoxime (m.-pt. 102°) and a β -synaldoxime (m.-pt. 129°) which is not sweet. It also gives a crystalline phenylhydrazone and semicarbazone. Perillonitrile ($C_9H_{13}CN$) is a liquid, as sweet as saccharin, of b.-pt. 123° (15 mm.) and sp. gr. at 15° C. 0.9488 to 0.9490; and perilla alcohol is described as of b.-pt. 118° to 121° C. (11 mm.), and sp. gr. 0.9690.

H. E. C.

Bromometric Estimation of Salicylic Acid. I. M. Kolthoff. (*Pharm. Weekblad*, 1921, **58**, 699-702.)—In an investigation of the bromometric method for estimating salicylic acid, 25 c.c. of $\frac{N}{10}$ potassium bromate were mixed with 1 gm. of sodium bromide and 25 c.c. of the salicylic acid solution, and varying amounts of 4 *N*-hydrochloric acid were added. After standing for five minutes in a stoppered flask, 5 c.c. of *N*-potassium iodide were introduced into the mixture, and it was then titrated with $\frac{N}{10}$ thiosulphate solution. The results indicated that the accuracy of the method is largely dependent on the amount of hydrochloric acid added. With quantities between 6.5 and 15 c.c. the error was -1.3 to -14 per cent.; dilution with water before addition of potassium iodide decreased the error, but accurate results were only obtained with 2 to 6 c.c. of acid. Only a slight excess of bromate is essential; 27 per cent. was found to be sufficient.

Fresenius and Grunhüt's method (*Zeitsch. anal. Chem.*, 1899, **38**, 298) of liberating bromine before adding the salicylic acid is not to be recommended, as too much bromine becomes volatilised. In the estimation of very small amounts of salicylic acid—*e.g.*, in foodstuffs—the amount of hydrochloric acid is of less importance than with stronger solutions; thus, with 10 c.c. 4 *N*-HCl added to 25 c.c. of a 0.001 mol. solution the error was only -2.3 to -2.7 per cent. The following method gives accurate results: Twenty-five c.c. of $\frac{N}{10}$ potassium bromate, 1 gm. of sodium bromide, and not more than 5 c.c. of hydrochloric acid, are added to 25 c.c. of salicylic acid in

* Temperature not given.

0.012 to 0.008 mol. solution. After the mixture has stood for five to ten minutes in a stoppered flask, 5 c.c. of *N*-potassium iodide are rapidly added, and the liquid is titrated with $\frac{N}{10}$ thiosulphate, starch being added only towards the end of the titration. The addition of alcohol, as in the bromometric estimation of phenol, may be omitted.

W. J. W.

Necessity for the Physiological Control of Adrenaline and Suprarenal Preparations. M. Tiffeneau. (*J. Pharm. Chim.*, 1921, [vii.], 23, 313-317, 366-375.)—Six samples of adrenaline of various origins have been examined, with the following results: (1) Synthetic origin, $[\alpha]_D^* = -52^\circ 30'$, physiological activity 100; (2) natural, $[\alpha]_D = 53^\circ 36'$, physiological activity 100; (3) unknown origin, $[\alpha]_D = -38^\circ 33'$, physiological activity 60; (4) synthetic, $[\alpha]_D 0$, physiological activity 51; (5) synthetic, $[\alpha]_D 0$, physiological activity 46; (6) unknown origin, $[\alpha]_D = -24^\circ 17'$, physiological activity 42. Thus, for *laevo*-rotatory adrenalines, the results of the physiological test correspond well with the optical rotations, whilst for the racemic compounds this is no longer the case. Suprarenal preparations lose in physiological activity if kept under unsuitable conditions, and should be tested before use.

T. H. P.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Lathyrism or Poisoning caused by Vetch Seeds. M. Mirande. (*Comptes rend.*, 1921, 172, 1142-1143. Cf. Hughes, *ANALYST*, 1895, 20, 169.)—The author has investigated the cause of lathyrism, the poisoning produced in man and animals by ingestion of certain vetch seeds, notably those of *Lathyrus sativus* and *L. cicera*. The cotyledons are found to contain a substance which readily undergoes auto-fermentation, with liberation of carbon dioxide and hydrogen sulphide in considerable proportions. Water removes this substance from the crushed seeds, but careful washing is necessary to render the extraction complete. Incipient germination makes the seeds incapable of yielding hydrogen sulphide when subsequently pounded and moistened. The fermentation of the substance is scarcely appreciable at 35° C., but is very active between 35° and 40° C., and ceases only at temperatures above about 60° C., which is the average coagulating temperature of the proteins.

T. H. P.

Occurrence of Catalase in Fish. P. C. Stockstad. (*Tids. Kem.*, 1920, 17, 181-187; *Chem. Abstracts*, 1921, 15, 691.)—Ten species of fish were found to give positive reactions for catalase, those containing the highest content of fat and esterase yielding the highest catalase constant. Tests were made with P_{H} 7.07 and at a temperature of 15° C., and the constants determined by titration with potassium permanganate before and after enzymic digestion. The values obtained ranged between 1.19 and 4.8, and in all cases the reaction was monomolecular, but with herring the results were abnormal, owing to the effect of some undetermined factor.

T. J. W.

* Temperature not given.

Oxidising Enzymes of Fruits. M. W. Onslow. (*Biochem. J.*, 1921, 15, 113-117.)—This work is a continuation of that described previously by the author (*Biochem. J.*, 1920, 14, 541-547). The fresh tissues, neutralised aqueous extracts, residues and filtrates from cold alcoholic extracts, and hot alcoholic extracts were purified by precipitation with lead acetate, decomposition of the precipitate with dilute sulphuric acid, and removal of organic acids and tannins by treatment with alcoholic calcium chloride and gelatin, and tested with benzidine, α -naphthol, and guaiacum, each with the addition of hydrogen peroxide, and with catechol and guaiacum. The following fruits were shown to contain the components of an oxidase: Cherry, peach, apricot, medlar, strawberry, grape, fig, and mulberry; whilst a peroxidase only was detected in blackberry, red currant, black currant, gooseberry, grape fruit, pomegranate, pineapple, melon, and tomato. Although the fruits contain no oxidase, this class of enzyme is present in blackberry and tomato leaves. Details are given of the reactions obtained with the tissues and the various extracts obtained from the fruits. T. J. W.

Antiscorbutic Capacity of Milk Powders. E. B. Hart, H. Steenbock, and N. R. Ellis. (*J. Biol. Chem.*, 1921, 46, 309-318.)—Experimental work on the feeding of scorbutic guinea-pigs upon a basal diet to which had been added dried milk prepared by different methods has shown that the original antiscorbutic property of the milk is destroyed by certain methods. The diet was composed of heated alfalfa flour, rolled oats, casein, and salt, the casein being replaced by the milk powder under examination to the extent of 40 per cent. of the mixture. The methods giving a product without antiscorbutic properties were the Merrell-Soule spray process and the uncondensed spray process employed by the California Central Creameries. The Just process, in which the milk is dried on heated rolls, yielded a powder possessing excellent antiscorbutic properties, whether prepared from summer milk or winter milk obtained from cows rationed with roots and tubers. T. J. W.

"Black Spot" of Chilled and Frozen Meat. F. T. Brooks and M. N. Kidd. (*Dept. Scientific and Ind. Research, Food Investigation Board. Special Report*, No. 6, 1921, 6 pp.)—The "black spot" fungus has been found on New Zealand mutton and lamb, Australian mutton and rabbits, and upon beef from the Argentine and South Africa. When isolated and grown in pure culture, it proved to be one of the many forms of the mould *Cladosporium herbarum*, which is common on dead vegetable matter. The spores, which can develop at 22° F. (-5.5° C.), are either oval in form, 8 to 16 μ \times 4 to 5 μ , or roughly spherical, 3.5 to 5 μ in diam., budded off in chains from the former. On meat the fungus develops particularly upon the subcutaneous connective tissue, sometimes penetrating to a maximum depth of 4 mm. It produces no toxic substances during growth, whether upon meat or other substrata, and its presence alone does not render the meat unfit for human consumption. It may, however, be accompanied by putrefactive bacteria, and in that case the meat will be soft and have an unpleasant odour. White moulds (species of *Sporotrichium* and *Oospora*) can also develop on meat at temperatures below freezing-point during prolonged storage.

Germicidal Properties of Milk. (*J. Amer. Med. Assoc.*; *Amer. J. Pharm.*, 1921, **93**, 281-282.)—Fresh raw milk allowed to stand for a short time shows an apparent decrease in the number of bacteria present, but this is not noticed if the milk be heated. Recent investigation by W. H. Chambers has confirmed these observations, and shown that this action varies with milk drawn from different cows, and also depends upon the bacterial species present. When the total number only, and not the species, of bacteria present is considered, a decrease in number may be evident, or an unaffected species may increase rapidly and conceal the germicidal action upon another less numerous species present. Lactic acid organisms are apparently unaffected, whilst other bacteria are restrained, and in some cases decreased in numbers. The germicidal property is destroyed by heating milk for two minutes to 80° to 90° C.
T. J. W.

Estimation of Tryptophane in Blood-Serum and Milk. O. Fürth and E. Nobel. (*Biochem. Zeit.*, 1920, **109**, 103-123; *Chem. Abstracts*, 1921, **15**, 377.)—A freshly prepared solution containing 0.1 per cent. of tryptophane and 2 per cent. of sodium fluoride is employed. To 2 c.c. of the standard in a graduated cylinder 1 drop of 2.5 per cent. formaldehyde is added, followed by 15 c.c. of concentrated hydrochloric acid and 10 drops of 0.5 per cent. sodium nitrite, the total volume being diluted to 20 c.c. by the further addition of hydrochloric acid, and the solution well mixed. The solution to be estimated is similarly treated, 2 c.c. portions being used, and, after standing from five to ten minutes, the colour is compared with that of the standard in a colorimeter. Any precipitate formed due to the presence of excess of inorganic salts is removed by filtration. By the above method it was shown that globulin contains almost three times as much tryptophane as does albumin, the percentage contained in casein being 2.02, in cow's milk whey from 1.8 to 2.3, and in the proteins of human milk from 3.4 to 6.8.
T. J. W.

Estimation of Sugar in Blood. E. Ponder and L. Howie. (*Biochem. J.*, 1921, **15**, 171-174.)—The blood is obtained from the finger, drawn into a 0.2 c.c. pipette, and run into 1 c.c. of water, after which the pipette is filled twice with water and the washings added to the diluted blood. To the mixture 0.2 c.c. of Folin and Wu's sodium tungstate solution (*ANALYST*, 1920, **45**, 227) and 0.2 c.c. of $\frac{2}{3}$ N-sulphuric acid are added, the tube being allowed to stand for five minutes, with occasional shaking. The mixture is transferred to a micro-filter, and 0.4 c.c. of the filtrate is run into a narrow-necked tube of about 1.5 c.c. capacity. A similar tube receives 0.4 c.c. of 0.01 per cent. dextrose solution, and 0.4 c.c. of alkaline copper tartrate solution is added to each. The narrow necks of the tubes are sealed off in the blowpipe flame, and the tubes are immersed in a boiling water-bath for six minutes, cooled to 80° C., the necks cut off, and 0.4 c.c. of the phenol reagent (*J. Biol. Chem.*, 1919, **38**, 106) is added. After cooling, the contents of the tubes are each added to 3.8 c.c. of water, and the colour of the solutions matched in a colorimeter. The results obtained are in excellent agreement with those given by the original Folin and Wu method (1920), and the advantages claimed for the method are the small amount of blood required, the accuracy with which the volume of blood used is known,

the prevention of reoxidation during boiling, and the similarity in colour finally obtained between the standard and the blood solution. T. J. W.

Estimation of Sodium in Small Volumes of Serum. B. Kramer and F. F. Tisdall. (*J. Biol. Chem.*, 1921, **46**, 467-473.)—The reagent employed is prepared by adding 10 grms. of potassium pyroantimonate to 500 c.c. of boiling water, boiling the liquid for a few minutes, and, after cooling, adding 15 c.c. of 10 per cent. potassium hydroxide. The filtered solution is kept in a bottle treated with paraffin wax, and will remain in good condition for at least one month at the ordinary temperature. Eleven mgrms. of sodium are precipitated by 10 c.c. of the reagent. To 2 c.c. of serum in a platinum dish 10 c.c. of the potassium pyroantimonate solution are added, followed by 3 c.c. of 95 per cent. alcohol, which is run in slowly with continuous stirring. After standing forty-five minutes, the precipitate is transferred to a Gooch crucible packed with alternate layers of filter-paper and asbestos, and which has been previously used for several similar precipitations, the last portions of the precipitate being washed in with a few c.c. of 30 per cent. alcohol. After drying for one hour at 110° C., the crucible is cooled and weighed. Although calcium phosphate is precipitated from the serum by the alkaline reagent, the amount present is so small that the error introduced is negligible. Estimations may be made with a maximum error of ± 2.5 per cent. of the actual amount of sodium present, and the same results are obtained whether the original serum or its ash be used. T. J. W.

Estimation of Inorganic Phosphate in Urine by Alkalimetric Titration. C. H. Fiske. (*J. Biol. Chem.*, 1921, **46**, 285-295.)—A volume of urine containing from 2 to 7 mgrms. of inorganic phosphorus is diluted with water to about 10 c.c. and treated with 1 c.c. of magnesium citrate reagent and 2 c.c. of concentrated ammonium hydroxide, the tube being gently shaken for fifteen minutes. The mixture is filtered under reduced pressure through a Soxhlet filter-tube containing a thin pad of paper pulp, and the precipitate in the tube and on the filter is washed with 10 c.c. of 2.5 per cent. ammonia solution and four 5 c.c. portions of 95 per cent. neutral alcohol. The precipitate is dissolved in $\frac{N}{10}$ hydrochloric acid added in 1 c.c. portions, and the pulp filter added to the solution, being washed in with 2 c.c. of methyl red solution and 13 c.c. of water. The addition of $\frac{N}{10}$ hydrochloric acid is continued until the solution remains acid in reaction after thorough shaking, and the whole solution is titrated with $\frac{N}{10}$ sodium hydroxide until the colour is slightly more yellow than a standard consisting of sodium acetate solution containing a slight excess of acetic acid and methyl red. Each c.c. of $\frac{N}{10}$ hydrochloric acid neutralised by the precipitate is equivalent to 1.552 mgrms. of phosphorus in the sample. The magnesium citrate reagent is prepared by dissolving 4 grms. of magnesium oxide in 100 c.c. of hot water containing 80 grms. of citric acid, cooling the solution, adding 100 c.c. of concentrated ammonium hydroxide, and diluting the mixture to 300 c.c. The methyl red solution contains 0.004 per cent. of the indicator in 50 per cent. alcohol. Experiments made with solutions containing known amounts of potassium dihydrogen phosphate and

with urines in comparison with the von Lorenz method (*Zeitsch. anal. Chem.*, 1907, 46, 193) have shown that accurate results are obtainable.

T. J. W.

AGRICULTURAL ANALYSIS.

Estimation of Citrate-Soluble Phosphoric Acid in Superphosphates. Official Method of the German Agricultural Experiment Station. (*Chem. Zeit.*, 1921, 45, 487.)—The citrate solution is prepared by dissolving 173 grms. of crystallised citric acid in water, adding 536.9 c.c. of ammonia (sp. gr. 0.96), and diluting the solution to 1 litre. Each 2.5 c.c. of this solution must contain 0.1050 gm. of nitrogen. A weighed quantity of 2.5 grms. of the superphosphate is ground in a basin with 25 c.c. of water, the solution decanted through a filter into a 250 c.c. flask, and the insoluble portion treated twice in a similar way. The insoluble portion is then rinsed on to the filter and washed until the filtrate measures about 200 c.c.; if the filtrate is turbid, a drop of nitric acid is added and the solution then diluted to 250 c.c. The filter and insoluble portion are transferred to a flask, 100 c.c. of the citrate solution are added, and the mixture is shaken until the filter-paper is disintegrated; after standing for fifteen hours at the ordinary temperature, the mixture is heated for one hour at 40° C., cooled, diluted to 250 c.c., and filtered. Fifty c.c. of this solution and 50 c.c. of the aqueous extract obtained previously are mixed, and the phosphoric acid estimated by the molybdate method or the citrate method. The reagent used in the citrate method contains magnesium chloride 55.0 grms., ammonium chloride 70.0 grms., citric acid 61.6 grms., and ammonia (sp. gr. 0.91) 625 c.c. per litre; 25 c.c. of this reagent are required for the precipitation, and the ammonium magnesium phosphate is collected after eighteen hours.

W. P. S.

Rapid Combustion Method for the Estimation of Organic Matter and Organic Carbon in Soil. J. W. Read. (*J. Ind. Eng. Chem.*, 1921, 13, 305-307.)—One gm. of soil is digested for five minutes with 6 portions of dilute hydrochloric and hydrofluoric acid solution, the supernatant liquid being poured through a perforated platinum combustion boat containing a pad of asbestos. The residue is completely transferred to the boat and dried at 100° C. for sixteen hours, cooled in a phosphorus pentoxide desiccator, and weighed. It is then transferred to a silica combustion tube containing contiguous columns of cerium oxide asbestos and pumice, copper oxide, cerium oxide asbestos, and a roll of fine copper gauze filled with lead peroxide. The air-purifying train is filled with calcium chloride, soda-lime, and phosphorus pentoxide, whilst the absorption apparatus contains sulphuric acid pumice, phosphorus pentoxide, soda-lime, calcium chloride, and palladious chloride solution. The combustion is carried out in a rapid current of air and occupies no more than twenty minutes, the total time, including the initial and final weighings, not exceeding forty minutes. By determinations upon pure sucrose it was shown that the results obtained were of a high order of accuracy.

T. J. W.

ORGANIC ANALYSIS.

Estimation of the Organic Carbon in Bituminous Limestones. E. Sernagiotto. (*Giorn. Chim. Ind. Appl.*, 1921, 3, 153-154.)—The following modification of the Corleis method for determining the total carbon in steel gives good results when applied to the estimation of the organic carbon in bituminous limestones. The Corleis flask, coated externally with asbestos and furnished with an internal condenser, is connected on one side with a tower charged with lump potash and on the other, in succession, with a sulphuric acid drying tube, a short, hard glass tube containing cupric oxide and lead chromate, a phosphoric anhydride tube, a soda lime tube, and a phosphoric anhydride tube. A weighed quantity of the material containing about 0.1 grm. of organic carbon is introduced into the flask by means of a long, wide-necked funnel, which is rinsed down with 30 c.c. of syrupy phosphoric acid, and then with water from a wash-bottle; the flask is then closed by a rubber stopper traversed by two glass tubes. The carbon dioxide liberated is eliminated by warming the flask and repeatedly evacuating it with a water-pump, and is replaced each time by air which has passed through the potash tower. The condenser is then fitted, the sulphuric acid seal in the neck of the flask re-established, and connection made with the absorption apparatus, the copper oxide tube being heated to redness. Meanwhile pure chromic acid is dissolved in an equal weight of water, and 35 c.c. of the solution thus obtained boiled for half an hour with 200 c.c. of pure concentrated sulphuric acid (sp. gr. 1.84). When cooled, the liquid is introduced into the Corleis flask and heated gently to boiling, which is maintained for about four hours, the subsequent operations being as in the estimation of carbon in cast-iron.

T. H. P.

Separation and Detection of Lactic Acid as Sodium Ferric Lactate. K. A. Hoffman. (*Ber.*, 1920, 53, 2224-2226; *Chem. Abstracts*, 1921, 15, 813.)—The solution under examination is treated with ferric chloride in slight excess, and the mixture rendered alkaline with sodium carbonate. The solution is then acidified with acetic acid, concentrated on a water-bath, and allowed to stand several hours, when a pale green precipitate of sodium ferric lactate will be formed, even when only small amounts of lactic acid are present. The precipitate is practically insoluble in water, is unaffected by 15 per cent. acetic acid, but is attacked slowly by dilute ammonia solution. It is readily decomposed by stronger alkalis and acids.

T. J. W.

Detection of Oxalic, Tartaric, and Formic Acids in Presence of Each Other. F. Kraüss and H. Tampke. (*Chem. Zeit.*, 1921, 45, 521.)—The detection of oxalic acid by the violet coloration produced with resorcinol and concentrated sulphuric acid (Brauer, ANALYST, 1920, 45, 338; Chernoff, ANALYST, 1920, 45, 422) is affected by the presence of nitrites and nitrates and of iron salts; the former should first be reduced with nascent hydrogen, and the latter rendered inactive by boiling with sulphurous acid. Tartaric acid gives a deep red coloration with a 1 per cent. solution of resorcinol in sulphuric acid; even if iodides, nitrites,

and nitrates be present, a red ring may be obtained by carefully heating the mixture at the zone of contact of the reagents. Similarly, an orange-coloured ring is formed with formic acid. For the detection of oxalic, tartaric, and formic acid in a possible mixture of these, carbonates, sulphur, iodine, bromine, and other oxidising agents must first be removed, and 0.2 gm. of pure resorcinol is then added to a solution of the substance in 5 c.c. of dilute sulphuric acid, after which 10 c.c. of concentrated sulphuric acid are introduced. If all three acids be present, formic acid will be indicated by an orange ring which gradually expands. A narrower blue ring below this will denote oxalic acid, whilst careful heating of the sulphuric acid will give rise to the formation of a deep red ring, due to tartaric acid. W. J. W.

Analysis of Partly Hydrolysed Fats. W. Fahrion. (*Chem. Umschau Fette Oele*, 1921, **28**, 68-69.)—The errors which may occur in the calculation of the results of analysis of mixtures of neutral fat and free fatty acids such as are produced by fat-splitting or in so-called "acid oil" (*i.e.*, the mixture resulting from the acidification of soap stock obtained by the removal from oils of free fatty acids by means of alkali) are discussed in detail. If the free fatty acid content of the mixture be calculated from the ratio of the acid value to the saponification value, an error is introduced, because the equivalent weight of fatty acid is less than that of its glyceride by the equivalent weight of the glyceryl radicle, whilst another source of error is the small difference between the neutralisation and saponification values of free fatty acids; in many cases the errors compensate one another, and the results are sufficiently accurate for technical purposes. The following method is suggested: The acid value is determined in the usual way, alcoholic alkali is next added, and the saponification value is then determined; finally, the liquid is rendered alkaline, diluted to an alcoholic content of 50 to 20 per cent., and unsaponifiable matter (x) is estimated by extraction with petroleum spirit or ether. The percentage of free fatty acid (x) is then calculated from $x = (100 - y) \times \text{acid value} / \text{saponification value}$, and the neutral fat from $100 - (x + y)$. R. G. P.

INORGANIC ANALYSIS.

Colorimetric Method for the Estimation of Hydrogen-Ion Concentration in Small Volumes of Liquid. L. D. Felton. (*J. Biol. Chem.*, 1921, **46**, 299-305.)—Drops of the liquid under examination are placed upon a glazed porcelain tile, and 1 drop of indicator solution is allowed to fall vertically upon it, complete mixture being attained by means of a small glass rod. After noting the colour produced, drops of various buffer solutions judged to give the same colour are placed close to the original drop, and the colours compared after the addition of a drop of indicator solution to each. The indicators are prepared by mixing equal volumes of 0.02 or 0.04 per cent. solutions of the dyes in 25 per cent. alcohol, and the following mixtures were employed: Thymol blue and bromphenol blue, giving a range of P_H from 1.2 to 4.6; methyl red and bromthymol blue, 4.6 to 7.6; methyl red and bromcresol purple, 4.6 to 7.0; and methyl red and thymol blue, 4.6 to 9.0. Tests made by the method show that an accuracy of at least 0.1 P_H could be obtained. T. J. W.

Reduction of Arsenic Halogen Compounds. O. Ruff. (*Chem. Zeit.*, 1921, 45, 522-523.)—If arsenic trichloride be heated with aluminium chloride and yellow phosphorus to 150° C., a red compound, containing arsenic, aluminium, chlorine, and phosphorus, is formed, from which the phosphorus can readily be separated. If the phosphorus be replaced by metallic aluminium, a similar compound having the formula $Al.As_3.Cl_3$ is produced, from which the aluminium chloride may be removed by means of solvents. In each case finely divided arsenic is simultaneously obtained.

W. J. W.

Colorimetric Estimation of Bismuth in High-Grade Ores. G. Spurge. (*Chem. Age*, 1921, 4, 584.)—The colorimetric method, based on the yellow colour produced by the addition of potassium iodide to a dilute solution of bismuth, and originally devised for the estimation of traces of bismuth, has been found suitable for the direct estimation of bismuth in high-grade ores. The ore is finely pulverised in an agate mortar, and 0.05 gm. in the case of ores containing over 3 per cent. of bismuth, or 0.50 gm. for those under 3 per cent., is dissolved by boiling with 25 c.c. of nitric acid and 75 c.c. of water for ten minutes, and, after cooling, the solution is made up to 500 c.c. and filtered. The filtrate is then run from a burette into a Nessler tube containing 10 c.c. of 10 per cent. potassium iodide solution and 3 drops of sulphurous acid until the colour matches that obtained under similar conditions in another tube containing 1 c.c. of standard bismuth solution, the liquid in both tubes being diluted to 50 c.c. before the final matching of colour. The standard solution is made by dissolving 0.025 gm. of pure bismuth as described above, and diluting the solution to 500 c.c. (1 c.c. = 0.00005 gm. bismuth). An estimation can be made in about fifteen minutes, and accurate results are easily obtained with ores containing up to about 20 per cent. of bismuth, though considerable practice is necessary for high-grade ores. The following are typical results, showing how the method compares with the oxychloride method: (1) 45.36; (2) 31.92; (3) 43.80; (4) 13.10; (5) 14.00; (6) 16.60; colorimetric method: (1) 45.5; (2) 31.8; (3) 43.5; (4) 12.8; (5) 13.8; (6) 16.3 per cent. Copper in large quantities may give a precipitate, which can be filtered off; this is generally unnecessary, as the solution is too dilute and the titration too rapid for the separation of any copper iodide. Lead, if present in quantity, might interfere with the estimation, but could, if necessary, be removed as sulphate.

R. G. P.

Electrolytic Estimation of Gold and its Separation from Copper, Palladium, and Platinum. W. D. Treadwell. (*Helv. Chim. Acta*, 1921, 4, 364-374.)—Gold may be deposited electrolytically from a faintly acid chloride solution to which 1 to 2 c.c. of strong hydrochloric acid and 1 to 2 grms. of ammonium acetate have been added; a platinum wire gauze cathode and platinum spiral are used. The operation is begun in the cold with 1 to 1.3 volts and 0.1 to 0.15 amp.; the temperature is gradually raised to 50° to 60° C. Deposition is complete in twenty minutes if nitrogen or carbon dioxide be bubbled through the electrolyte; the current density drops to 0.001 amp. when all the gold is precipitated. This procedure provides a quick and accurate separation from copper. For the separation from

palladium the chloride solution, prepared as above, is electrolysed with 0.4 to 0.5 volt at 50° to 55° C. After deposition of the gold, the electrolysis is continued for palladium with a fresh platinum cathode and a pressure of 1.2 volts. Gold is separated from platinum in a chloride bath by substituting sodium acetate for the ammonium salt, using a platinum dish and a rotating platinum disc anode, and electrolysing at 0.7 volt pressure while warming to 50° to 60° C. For the subsequent determination of platinum, the solution is transferred to a clean platinum dish and electrolysed with a current of 1.5 volts. Gold may be separated in this manner from palladium and platinum.

W. R. S.

Volumetric Estimation of Zinc. I. M. Kolthoff and J. C. van Dijk. (*Pharm. Weekblad*, 1921, 58, 538-553.)—In a direct acidimetric estimation, the best results (accurate to 1 per cent.) were obtained by adding 25 c.c. of $\frac{N}{10}$ zinc sulphate to 30 c.c. of $\frac{N}{10}$ sodium hydroxide, boiling for three minutes, and titrating with $\frac{N}{10}$ hydrochloric acid, with phenolphthalein as indicator. The indirect estimation of zinc, by precipitation with hydrogen sulphide and titration of the free acid in presence of an iron salt, gives fairly accurate results if the titration be carried out with sodium borate with brisk agitation. If an indicator be substituted for the ferrous salt, only iodo eosin is suitable. The estimation of zinc as mercury zinc thiocyanate gives the best results, provided chlorides be absent. With concentrations above $\frac{N}{100}$, the solution may be filtered immediately after adding the reagent, the excess being titrated with mercuric nitrate. If the zinc solution be weaker than $\frac{N}{100}$, the filtrate must be allowed to stand for one day, and the reagent, which must have a concentration of at least 0.006 N to render the solubility of the double salt negligible, is then titrated back by Volhard's method. The presence of sulphuric or nitric acid is not detrimental if the solution be filtered immediately.

W. J. W.

Estimation of Zinc by the Ferrocyanide Method. E. Olivier. (*J. Soc. Chem. Ind.*, 1921, 40, 107-108r.)—The zinc in Australian concentrates is generally estimated volumetrically by titration either with potassium ferrocyanide, or with ammoniacal sodium sulphide. The author points out that the solution finally titrated in the usual ferrocyanide method may contain cadmium and manganese, both of which are precipitated by ferrocyanide, and therefore returned as zinc; the cadmium content is generally too low (0.1 per cent.) to influence results, but manganese may be present to the extent of 1 per cent. or more. Manganese can be eliminated by adding a few c.c. of hydrogen peroxide to the mixed ammonia and ammonium chloride solution used to treat the residue obtained by the decomposition of the ore or concentrate with nitric acid and chlorate. The ferrocyanide method has the disadvantage that the solution has to be titrated hot, whilst the blue colour of the spot test is not always very distinct in presence of coloured ferrocyanides. In the author's opinion the sulphide method is preferable, especially as the zinc is precipitated as a colourless sulphide, which affords indication of its freedom from metallic sulphides other than cadmium.

R. G. P.

Approximate Estimation of Iron and Manganese. L. J. Curtman and N. H. Hecht. (*Chem. News*, 1921, 122, 254-255.)—A precipitate containing

aluminium and chromium hydroxides, and nickel, cobalt, iron, manganese and zinc sulphides, is treated with hydrochloric acid, the insoluble nickel and cobalt sulphides are separated by filtration, the filtrate is then evaporated to a small volume, and diluted to 50 c.c. Twenty-five c.c. of this solution are boiled with the addition of sodium hydroxide and sodium peroxide; the precipitate is collected, dissolved in hydrochloric acid, the solution treated with potassium thiocyanate solution, and then titrated with standardised stannous chloride solution until the pink coloration matches that obtained by adding thiocyanate to 0.05 mgrm. of iron in 50 c.c. of dilute hydrochloric acid. It is not convenient to continue the titration to a colourless end-point owing to the slowness of the final reaction. Another portion of 25 c.c. of the solution is treated as described, the precipitate produced by the peroxide treatment is washed free from chlorides, dissolved in nitric acid, the solution diluted to a definite volume, and an aliquot portion treated with sodium bismuthate; the permanganate produced is titrated with hydrogen peroxide solution.

W. P. S.

Detection and Estimation of Cobalt. S. A. Braley and F. B. Hobart. (*J. Amer. Chem. Soc.*, 1921, **43**, 482-484.)—In the absence of elements which give coloured solutions or precipitates with sodium acetate or dimethylglyoxime (with the exception of nickel), the brown colour of cobalt dimethylglyoxime is proportional to the concentration, and affords a basis for the colorimetric estimation of this metal. The solution containing cobalt and nickel, prepared as for the estimation of nickel, is slightly acidified, 10 per cent. sodium acetate solution is added, the mixture boiled and treated with an excess of dimethylglyoxime. Nickel is separated by filtration, the filtrate cooled, and the coloration compared with that of a standard containing a known amount of cobalt.

W. P. S.

Sodium Salicylate as Reagent for Detecting Aluminium and Manganese. C. van Zijp. (*Pharm. Weekblad*, 1921, **58**, 694-698.)—When solutions of sodium salicylate and aluminium nitrate are caused to react, a microscopic examination reveals the formation of colourless needles which tend to coalesce into spherical groups. With excess of aluminium solution, a granular mass is first formed and development of crystals is retarded, whilst excess of salicylate dissolves the reaction product. Addition of caesium chloride assists the reaction, and detection of the crystals is further facilitated by exposing the drop of the mixed solutions to the action of ammonia vapour, by which any precipitated hydroxide is dissolved. The method is suitable for detecting aluminium, iron, and chromium, either alone or in presence of each other; the solutions must be of such concentration as to prevent formation of crystals before treatment with ammonia, and, if any hydroxides are precipitated, the dried residue must be carefully treated with a drop of water, which is then separated and again allowed to evaporate. Iron salts give a violet coloration, changing to yellow after treatment with ammonia, but no hydroxide is precipitated. On the other hand, ammonia precipitates chromium hydroxide from chromium salts, and from mixtures of iron and chromium salts hydroxides of both metals are formed. Crystals are only produced when aluminium salts are

present. If the aluminium solution contains iron as well, the crystals show a brown coloration, but no hydroxides are precipitated; in presence of chromium, on evaporation of the drop there is considerable formation of hydroxides, but the crystals obtained after treatment with water are colourless. The presence of both iron and chromium in the aluminium solution is indicated by separation of mixed hydroxides with a yellow colour, and by the brown colour of the crystals. Manganese solutions, when mixed with sodium salicylate, do not crystallise, but when the mixture is exposed to the action of ammonia, light green, pointed crystals are formed. If zinc be present in the manganese solution, a slight excess of sodium salicylate must be employed, and the mixed solutions are then treated with ammonia vapour until any hydroxides formed redissolve; such solution will not occur if too little salicylate was used in the first case.

W. J. W.

Estimation of Phosphorus in Phosphor-Bronze. G. Greenwood. (*Chem. News*, 1921, 122, 225-226.)—A mixture of 1 grm. of the alloy and 0.5 grm. of iron wire or mild steel borings is dissolved in 15 c.c. of *aqua regia*, the solution boiled for a few minutes, cooled, and nearly neutralised with ammonia. Potassium permanganate is then added in quantity sufficient to produce a distinct precipitate when the mixture is boiled for two minutes, the precipitate is dissolved by the addition of a few drops of hydrochloric acid, the solution is cooled, diluted, and treated with 25 cc. of ammonia (sp. gr. 0.880). The precipitated basic ferric phosphate is dissolved by the addition, drop by drop, of concentrated nitric acid, an excess of 3 c.c. of nitric acid is added, the mixture boiled, and the phosphoric acid precipitated by the addition of molybdic acid reagent. After twenty minutes, the yellow precipitate is collected, washed with 2 per cent. nitric acid, then with 2 per cent. potassium nitrate solution, dissolved in a known excess of standard sodium hydroxide solution, and this excess titrated with standard nitric acid, using phenolphthalein as indicator. The solutions should be standardised against a steel of known phosphorus content; an allowance is made for the small amount of phosphorus in the added iron wire or mild steel.

W. P. S.

Electrometric Titration of Hypochlorous Acid. W. D. Treadwell. (*Helv. Chim. Acta*, 1921, 4, 396-405.)—The end-point of the titration of hypochlorite with arsenious acid (Penot, 1851) may be determined accurately by electrometric means. As comparison electrode, use is made of a glass tube about 8 cm. long, with its end drawn out to a capillary and bent upwards, the tip of the capillary being closed in the ordinary way with a plug of filter-paper or a drop of gelatin containing potassium sulphate. The tube is filled with potassium sulphate solution to which has been added either a little hypochlorite solution already titrated, or a drop of about 0.01 *N*-iodine solution containing iodide. Two smooth platinum wires serve as electrodes, one dipping into the hypochlorite solution, and the other fairly deeply into the comparison electrode. The two electrodes are connected either through a high-resistance millivoltmeter, or through a galvanometer with suitable resistance. The end-point of the titration is indicated by a sudden fall of the galvanometer deflection

to zero. Titration of an alkaline hypochlorite with arsenious acid must be carried out immediately after the neutralisation of the solution; if the titration is effected in dilute solution at the ordinary temperature and within a few minutes of neutralisation, the losses due to premature formation of chlorate remain immeasurably small. In the case of solutions containing alkali carbonate or hydroxide this titration should not be applied, the end-point then losing in sharpness.

As regards titration of hypochlorite with potassium iodide, the optimum acidity for the end-point of the titration may be calculated from the equilibrium, $\text{IO}_3' + 5\text{I}' + 6\text{H} \rightleftharpoons 3\text{H}_2\text{O} + 3\text{I}_2$, which has been thoroughly investigated. At 25°C . the relation

$$\frac{(\text{H}\cdot)^6 \cdot (\text{IO}_3') \cdot (\text{I}')^5}{(\text{I}_2)^3} = 2.8 \times 10^{-46} \text{ holds. During the titration } (\text{H}\cdot) \text{ is virtually constant,}$$

and at the end of the titration (IO_3') may be regarded as constant, and it has been shown that in iodide of starch the ratio $(\text{I}_2) : (\text{I}')$ has the value 2. From these considerations it follows that the optimum acidity of the end-point is represented by $(\text{H}\cdot) = 10^{-7}$, which is that of the neutral point. The great sensitiveness of the end-point to acid constitutes the essential weakness of this method, and Pontius (1904), to whom the method is due, employed a too highly alkaline solution $[(\text{H}\cdot) = 10^{-9}]$, resulting in a retardation of the end-point. If the available chlorine amounts to about 0.1 equivalent per litre, a solution alkaline with bicarbonate yields satisfactory results, but with 0.01 *N*-hypochlorite the results are uncertain. If, with a highly dilute solution, the final stage of the titration be not carried out very slowly, the blue coloration of the starch appears far too late. Here, too, the end-point may be determined electrometrically, but in any case the method is less exact and less sensitive than titration with arsenious acid.

T. H. P.

Separation and Detection of Arsenate and Arsenite. G. W. Sears.

(*J. Amer. Chem. Soc.*, 1921, **43**, 466-470.)—The method depends on the solubility of silver arsenate and on the insolubility of silver arsenite in dilute sodium hydroxide solution; the concentration of the latter should not exceed 1.5 *N*. A nitric acid solution containing an arsenite and arsenate and an excess of silver nitrate is treated with sodium hydroxide solution until the dark silver oxide precipitate just fails to redissolve; the precipitate is collected, washed, rinsed into a graduated cylinder with 20 c.c. of water, 3 c.c. of 6 *N* sodium hydroxide solution are added, and the mixture is diluted to 25 c.c. The amount of sodium hydroxide required depends on the quantity of arsenate present; 3 c.c. of 6 *N* sodium hydroxide solution in 25 c.c. of total liquid will dissolve more than 0.45 gm. of arsenate, whilst 5 c.c. of the alkali solution in the same volume of liquid has no apparent solvent action on the arsenite. The contents of the cylinder are mixed, filtered, and the insoluble portion washed until free from alkali. *Detection of Arsenite*: The insoluble portion is dissolved in a small quantity of dilute hydrochloric acid and the solution tested with hydrogen sulphide; if the sulphide precipitate has a dark colour, heavy metals are present, and must be separated by the usual methods. *Detection of Arsenate*: The filtrate is acidified with acetic acid, uranyl acetate is added in slight excess, the precipitated uranyl hydrogen arsenate is collected, dissolved in hydrochloric acid,

and the arsenic precipitated with hydrogen sulphide. The method is capable of detecting 1 mgrm. of either ion in the presence of 450 mgrms. of the other.

W. P. S.

PHYSICAL METHODS, APPARATUS, ETC.

New Technique for Microscopical Preparations of Vegetable and Animal Tissues. Larbaud. (*Comptes rend.*, 1921, 172, 1317-1319.)—The ordinary method of preparing fresh tissues to be imbedded in paraffin wax consists in treating them successively in baths of aqueous alcohol of increasing concentration, followed by two mixtures of alcohol and xylene (or toluene) and then by pure xylene. This procedure is disadvantageous, owing to the presence of impurities in the reagents, to the presence of traces of water in so-called absolute alcohol, to the contraction of the protoplasm and the hardening of the tissues, and to the costliness of the solvents employed. A mixture of normal butyl alcohol with 95 per cent. (by volume) ethyl alcohol is preferable. For the first four baths, 100 c.c. of this mixture is mixed with 225 c.c., 62.5 c.c., 21.87 c.c., and 2.63 c.c. of water respectively. The treatment is completed by means of two baths of the butyl alcohol, to the second of which paraffin wax is added little by little; the subsequent operations are as usual. Specimens thus treated become neither hard nor brittle, whilst the protoplasm undergoes no contraction.

T. H. P.

Spectrum Analysis by Means of Roentgen Rays. M. Siegbahn, A. E. Lindh, and N. StenSSon. (*Zeit. Physik.*, 1912, 4, 61-67; *J. Chem. Soc.*, 1921, 120, ii. 344.)—A vacuum spectrograph enables the X-ray spectrum to be employed for spectrum analysis of mixtures in the usual course of analysis. The instrument has an opening angle of about 40° and a fixed crystal of calcspar or gypsum, making it possible to obtain with two exposures of about two hours each photographs of the lines of all elements from uranium to sodium.

R. G. P.

Check Valve for Water Vacuum Pumps. E. A. Andelin. (*Chem. Zeit.*, 1921, 56, 448.)—The check valve described by Pinoff (*Chem. Zeit.*, 1920, 671) is not absolutely reliable, as it does not always function instantaneously. An improved device comprises a rubber bung, 10 to 12 mm. diam., with a central perforation of 5 mm. diam., through about two-thirds of its length. A transverse cut is made in the bung so as to separate the unbored portion and form a flap valve, and the whole is fitted on a glass tube. By means of another rubber bung the device is fixed in a second tube of 20 mm. diam., which is drawn out at its lower end. The apparatus should always be used in a vertical position.

W. J. W.

Slide Rule for Calculation of "Wet" and "Dry" Weights of Damp Material. R. Scott. (*J. Soc. Chem. Ind.*, 1921, 40, 96r.)—A slide rule which will show the amount of "wet" material required to give a specific amount of "dry" material, and *vice versa*, may be constructed by dividing the frame scale in the usual logarithmic manner, and the slide scale proportionally to $\log 100/(100 - \text{moisture per cent.})$. It is convenient to make the distance from 10 to 100 on the frame

1,000 mm. long, and to extend the frame beyond 100 to a length equal to that of the slide scale. If then the zero mark on the slide scale be placed opposite the division of the frame corresponding to the "dry" weight, the wet weight is read off opposite the division on the slide scale corresponding to the moisture content. For calculating dry weight the procedure is reversed. The results should be accurate to within 0·5 per cent.

H. E. C.



DANGEROUS DRUGS ACT.

REVISED REGULATIONS.

IN pursuance of Section 3 of the Dangerous Drugs Act, 1920, the Home Secretary has made the following Regulations, the full text of which is published in the *London Gazette* of May 24, 1921. These Regulations come into force on September 1, 1921.

Opium : (1) to (3) No person shall supply, procure, or be in possession of raw opium, unless licensed by the Secretary of State, or authorised by these Regulations. (4) Records in specified form shall be kept of all dealings in raw opium.

General Authorisations.—(5) Any duly qualified medical practitioner, or any person lawfully keeping open shop for the retailing of poisons in accordance with the provisions of the Pharmacy Act, 1868, as amended by the Poisons and Pharmacy Act, 1908, or any person employed or engaged in dispensing medicines at any public hospital or other public institution being a person duly registered under the Pharmacy Act, 1868, as amended by the Poisons and Pharmacy Act, 1908, or any registered veterinary surgeon or any person in charge of a laboratory for purposes of research or instruction attached to any University, University College, public hospital, or other institution approved by the Secretary of State for the purpose, or any person appointed by a local authority with the approval of the Minister of Health as an analyst for the purposes of the Sale of Food and Drugs Acts, 1875 to 1907, is hereby authorised so far as is necessary for the practice of his profession or employment in such capacity to be in possession of and supply raw opium, but subject always to the provisions of the foregoing Regulation. (6) Licences will be withdrawn for offences against the Act. (7) No raw opium is to be delivered to messengers unless written authority from a licensed person is produced. (8) "Possession" means at the order or disposition of a person.

Morphine, Cocaine, Ecgonine, and Diamorphine : *Application.*—(1) The drugs to which these Regulations apply are morphine, cocaine, ecgonine, and diamorphine (commonly known as heroin), and their respective salts, and medicinal opium, and any preparation, admixture, extract, or other substance containing not less than one-fifth per cent. of morphine or one-tenth per cent. of cocaine, ecgonine, or diamorphine. For the purpose of the foregoing provision, the percentage in the case of morphine shall be calculated as in respect of anhydrous morphine. (2) Prohibits the manufacture of these drugs, except by licensed persons on licensed premises. (3) and (4) Prohibit the sale, distribution, or possession of the drugs, except by licensed persons or those authorised by the Regulations. (5) and (6) Give the conditions for the prescription and dispensing of the drugs by authorised persons. (7) Prohibits possession except by licensed or authorised persons. (8) Requires packages to be marked with the amount of drug contained in them, except in the case of authorised prescriptions. (9) Records must be kept in specified form.

General Authorisations.—(10) Any person lawfully keeping open shop for the retailing of poisons in accordance with the provisions of the Pharmacy Act, 1868, as

amended by the Poisons and Pharmacy Act, 1908, is hereby authorised—(a) To manufacture at the shop in the ordinary course of his retail business any preparation, admixture, or extract of any of the drugs; (b) to carry on at the shop the business of retailing, dispensing, or compounding the drugs, but subject always to the provisions of these Regulations. (11) to (14) are the same as (5) to (8) in the Opium Regulations. (15) Gives the Regulations affecting the captains of ships not carrying a medical practitioner. (16) Hospitals or other public institutions may be exempted from the operation of the Regulations.

Preparations Exempted from the Regulations.—(17) These Regulations shall not apply in respect of the preparations named in Schedule II. to these Regulations, nor to any of the drugs when denatured in a manner approved by the Secretary of State. The Secretary of State may from time to time by order add any other preparation to the Schedule, or remove any preparation from the Schedule.

SCHEDULE II.

Cereoli Iodoformi et Morphinae, B.P.C.	Pil. Hydrarg. c. Cret. et Opii, B.P.C.
Emp. Opii, B.P., 1898.	Pulv. Cretae Aromat. c. Opio, B.P.
Lin. Opii, B.P.	„ Ipecac. Co., B.P. (Dover's Powder).
„ Opii Ammon., B.P.C.	„ Kino Co., B.P.
Pasta Arsenicalis, B.P.C.	Suppos. Plumbi Co., B.P.
Pil. Hydrarg. c. Opio, B.P.C.	Tablettæ Plumbi c. Opio, B.P.C.
„ Ipecac. c. Scilla, B.P.	Ung. Gallæ c. Opio, B.P. (Gall and Opium Ointment).
„ Plumbi c. Opio, B.P.	„ Gallæ Co., B.P.C.
„ Digitalis et Opii Co., B.P.C.	

FOOD CONTROL.

STATUTORY RULES AND ORDERS.

No. 350, 1921.

THE MILK (ENGLAND AND WALES) ORDER, 1921, DATED MARCH 22, 1921, MADE BY THE FOOD CONTROLLER UNDER THE MINISTRY OF FOOD (CONTINUANCE) ACT, 1920 (10 AND 11 GEO. 5, c. 47).

1. EXCEPT under and in accordance with a licence granted by or under the authority of the Minister of Health, a person shall not—(a) Sell or expose for sale any milk as “Grade A (certified)” or “Grade A” milk; or (b) describe or refer to any milk under these names in any advertisement, circular, or notice in connection with the sale of milk; or (c) sell or offer or expose for sale as milk, or under any description of which the word “milk” forms part, any liquid in the making of which dried milk or condensed milk has been used.

2. A licence may be granted under this Order for such period and subject to such terms and conditions as the Minister of Health may think fit.

3. No colouring matter or water shall be added to milk or cream intended for sale, and no milk or cream to which any colouring matter or water has been added shall knowingly be sold or offered or exposed for sale.

4. (a) Every local authority is hereby authorised to execute and enforce the provisions of this Order within their area, and to institute proceedings for any offence against this order. (b) For the purposes of this clause “local authority” means any local authority authorised to appoint an analyst for the purposes of the Sale of Food and Drugs Acts, 1875 to 1907.

5. For the purposes of this Order, “milk” shall include any milk which has

been submitted to one or more of the following processes—viz., sterilisation, pasteurisation, homogenisation, or any other like process, but shall not include condensed, separated, skimmed, or butter milk.

6. The Milk Order, 1920, is hereby revoked, so far as it applies to England and Wales, as on March 24, 1921, but without prejudice to any licences granted thereunder and in force at the date of this Order.

7. (a) This Order may be cited as the Milk (England and Wales) Order, 1921, and shall come into force on March 24, 1921. (b) This Order applies only to England and Wales. (c) The Interpretation Act, 1889, applies to the interpretation of this Order as it applies to the interpretation of an Act of Parliament.

No. 379, 1921.

THE LOCAL AUTHORITIES (MILK) ORDER, 1921, DATED MARCH 24, 1921, MADE BY
THE MINISTER OF HEALTH.

THE MINISTER OF HEALTH by arrangement with the Food Controller orders as follows :

1. (i.) Every local authority authorised to appoint an analyst for the purposes of the Sale of Food and Drugs Acts, 1875 to 1907, shall have all such powers and duties as may be necessary for the execution within their area of the functions assigned to them by the Milk (England and Wales) Order, 1921.

(ii.) Every local authority as aforesaid, and any officers of the local authority duly authorised in that behalf, may at all reasonable times enter and inspect any premises in which milk sold or offered for sale in accordance with a licence given under the Milk (England and Wales) Order, 1921, is produced or prepared for sale.

2. Any expenses incurred by a local authority as aforesaid in the execution of this Order shall be defrayed in the same manner as expenses of the local authority are defrayed for the purposes of the Sale of Food and Drugs Acts, 1875 to 1907.

3. This Order may be cited as the Local Authorities (Milk) Order, 1921.

No. 406, 1921.

THE MILK (SCOTLAND) ORDER, MARCH 31, 1921, MADE BY THE FOOD CONTROLLER
UNDER THE MINISTRY OF FOOD (CONTINUANCE) ACT, 1920.



REVIEWS.

THE ELECTRONIC CONCEPTION OF VALENCE AND THE CONSTITUTION OF BENZENE.

By H. S. FRY. Monographs on Inorganic and Physical Chemistry; edited by Alexander Findlay. Pp. xviii+300. London: Longmans, Green and Co. 1921. Price 16s. net.

The subject of valency and valence is one in which English chemical literature is sadly deficient, so that the present volume is a most useful and welcome addition; the more so as most of the theories of valence have been expounded and discussed in foreign journals. We have now presented to us in a most lucid manner by Professor Fry a detailed account of the electronic theory of valence, which, even in the Annual Reports of the Chemical Society, has not received much notice in this country. Professor Cohen, in his "Organic Chemistry" (vol. i. p. 161), remarks that "the theory is so mobile, so adaptable, and so ingeniously applied as to explain most of the facts of substitution as well as many of the reactions of organic compounds." One cannot read this fascinating volume without being impressed with the truth of this statement; the manner in which the hitherto most baffling problems in organic reactions are explained in the light of a single fundamental conception of the chemical bond as a unit Faraday tube connecting charged atoms is quite remarkable. The theory put forward, only as a formulative hypothesis, is developed so as to account rationally for not only the problems of substitution in the benzene nucleus, but the whole range of organic chemistry, including such diverse branches as velocity of substitution, absorption spectra, physical properties, molecular volumes, and fluorescence. Even the complexities of the structure of the metal-ammines are smoothed out by the skilful treatment of the author, and discussed with mathematical exactness without the introduction of speculative assumptions or vague statements. The fact that the electronic theory can be successfully applied over such a wide range of experimental results places it above any other theory of valence extant; it certainly maintains its inventor's modest claim that it should function as a formulative hypothesis in the interpretation and correlation of chemical and physico-chemical phenomena.

The book, in its presentation and detail, maintains well the excellent standard of Professor Findlay's series of monographs. The style is lucid and exact, the development of the subject is quite fascinating, and there is an almost complete freedom from typographical errors. The table of contents is very full, but a subject

index at the end would be a useful adjunct for reference purposes, and the table of references to other literature might be a little extended, as there are a few places (*e.g.*, pp. 18 and 144) where quotations are made and the reference is not given.

Probably the advocates of alternative theories of valence will find points in the arguments which may be debated and controverted, but the book is undoubtedly a most valuable contribution to modern chemical theory, and one on which the author, editor, and publishers may well be complimented. H. E. Cox.

THERMODYNAMICS AND CHEMISTRY. By F. H. MACDOUGALL, M.A., Ph.D. John Wiley and Sons. Pp. v+391. London: Chapman and Hall, Ltd. Price 30s. net.

The outstanding feature of Professor Macdougall's book may be said to be thoroughness. No pains are spared in the definition and explanation of every term used, and in the explanation as well as the rigid proof of the most elementary of the thermodynamical deductions. Throughout the book stress is laid upon the empirical nature of such doctrines as the First and Second Laws of Thermodynamics, and also the fundamental chemical laws, the Atomic Theory and Avogadro's Hypothesis. The First and Second Laws are treated at some length, and thence the questions of entropy and the thermodynamical scale of temperature, which are considered in detail.

The treatment of the Phase Rule is exhaustive both in proof and in illustration, and the various types of phase system are considered minutely. A point that might well be copied is the inclusion with each type of phase diagram of a list of examples of the various systems belonging to the type illustrated. The increasingly popular system of triangular co-ordinates is well illustrated in some examples of ternary systems. The excellent section on fractional distillation and on partially miscible liquids should be of particular value to the organic chemist.

The laws of osmotic pressure are deduced as applications of the Phase Rule—rather a departure from usual practice. Chapter XVI., which contains some ionisation equations, necessary but not strictly thermodynamical, comprises a useful section on Activity, and a summary of the equations expressing the behaviour of strong electrolytes. Electromotive Force is dealt with in a comprehensive and complete manner. In view of the increasing part played in chemical theory by surface tension and adsorption, Chapter XVIII. is of great interest.

The final chapter is a triumph of conciseness and thoroughness. Within thirty-three pages it embraces the Laws of Radiation, the Quantum Theory, Debye's Theory of Atomic Heat, and the Nernst Heat Theorem and some of its applications, and concludes with a set of tables of numerical values of the Einstein and Debye functions. We might well wish this chapter to be amplified and subdivided in order to give a greater number of examples of the application of these most important principles.

Altogether the book is a masterly treatment of thermodynamics and its bearing on chemistry, and should commend itself equally to the chemist and to the physicist.

H. R. AMBLER.

INTRODUCTION TO QUALITATIVE CHEMICAL ANALYSIS. By TH. W. FRESENIUS. Seventeenth Edition of the Original Work by C. R. FRESENIUS. Translated by C. A. MITCHELL, M.A., F.I.C. Pp. 954. London: J. and A. Churchill. 1921. Price 36s. net.

The appearance of a new English edition of Fresenius is an event of very much more than passing interest to the great body of professional chemists in all countries in which the English language is spoken.

Despite the fact that the production of Fresenius was planned as long ago as 1840, and that, nearly fifty years ago, nine English and fourteen German editions had already appeared, this work still remains the standard textbook of general analytical chemistry—a book which the young student may take as his safest guide, and to which, at the same time, the experienced practitioner may confidently turn for help and sound advice in cases of uncertainty and difficulty.

To attempt anything in the nature of detailed criticism of a work of this character would obviously be a task beyond the power of any one reviewer, and, even if it were possible, it would be a work of supererogation, for the best testimony to its value and its accuracy is to be found in the esteem in which it is still held by many thousands of chemists in all parts of the world, who during many years have, like their predecessors, tested it thoroughly, and have very rarely found it wanting.

One's first impulse, on the appearance of a new edition of a classic such as this, is to compare it with previous editions, for the purpose of seeing what new features have been introduced, and of ascertaining to what extent the work has kept pace with the progress made in the subject.

The edition on which the writer of this review was brought up was the ninth English, corresponding with the fourteenth German edition, published in 1876.

As a reply to those persons who have, on occasions, foolishly expressed the opinion that analytical chemistry represents a branch of the science in which little further progress can be expected, it may be pointed out that, although the volume under review deals with qualitative analysis alone, and is written in a condensed style, the number of pages has increased from 400 in 1876 to 950 in the present volume.

In the Preface to the 1876 edition, the following statement by the author, in reply to a letter of remonstrance from the late Sir Edward Frankland, is of interest: "I do not retain the old notation from prejudice, but from a most firm conviction that, for inorganic chemistry, it is the simplest and the best. This view is not peculiar to myself alone, but is shared with the highest authorities in Germany—Wohler and Bunsen; Professor Kopp also, one of the first representatives of theoretical chemistry, had advised me decidedly not to relinquish my notation."

In the present volume, not only the notation, but the whole presentation of the subject, are in accordance with the most recent chemical and chemico-physical theories, and in this respect the book may certainly be said to have kept abreast of the developments of the science.

Notwithstanding the very great improvement which has been made during recent years in the status of analytical chemistry, there is still a rather widespread

impression that it is a useful art or, at the best, an inferior branch of the science, and Professor Dittmar, in his admirable little work on "Qualitative Chemical Analysis," published in 1876, put the matter very clearly when he said :

"All we desire is, at the very outset, to make the student understand that analysis is not an art which can be learned independently of chemistry itself. It is possible to be a fair theoretical chemist without being able to execute an analysis, but most assuredly no one can be an analyst without being a scientific chemist."

If that was true—as it undoubtedly was—in Dittmar's time, it is more than ever true to-day, and this view has clearly been uppermost in the mind of the author of the work under review.

Full, clear, and, in the main, adequate descriptions are given of the fundamental conceptions of chemistry, as well as of the general principles underlying all the various procedures with which the analyst is concerned. At the same time, the author has avoided the danger of overloading the book with matter for which the student must in any case consult general systematic treatises.

So far as the reviewer can see, the work has been brought thoroughly up to date. Among other things, much new matter in relation to the reactions of the rarer elements has been added, and the many reactions in which organic substances are employed as reagents are accurately and adequately described.

The only serious criticism which the writer has to make is one which can be made of most German scientific works—namely, the failure of their authors to refer to original sources other than German. Had the author of this work avoided this national failing, one or two sections would certainly have gained in value.

On what principle the properties of the alkaloids are given in a lengthy appendix, to the exclusion of other poisonous organic compounds, is not very clear, especially as the information is to be found in all treatises on general toxicology.

The writer has observed only a few typographical errors, and the printing and paper are all that could be desired.

The translation is good, and the translator, Mr. C. A. Mitchell, is to be warmly congratulated on the successful manner in which he has accomplished a somewhat difficult task.

For the sake of old associations, if for no other reason, one is glad to see that the coloured frontispiece representing metallic spectra is retained. Without it Fresenius would scarcely be Fresenius.

A. CHASTON CHAPMAN.

APPLIED COLLOID CHEMISTRY—GENERAL THEORY. By WILDER D. BANCROFT, Ph.D.,
Professor of Physical Chemistry at Cornell University, U.S.A.. Pp. 345.
London: McGraw-Hill Book Co. Inc. Price 18s. net.

The importance of colloid chemistry for the solution of ubiquitous industrial problems is being more and more recognised. Propaganda work is being carried on by committees of experts on colloid chemistry in England and in the United States of America. Foremost amongst the American authorities is Professor Bancroft, and

his book, part of the general scheme of the American programme, is very welcome indeed.

His treatment of the subject differs from the usual textbook on colloid chemistry. In his Preface he says: "The earlier books on colloid chemistry presented the subject empirically, because no other method was then possible. While we do not know much about gelatinous precipitates and jellies, the theory of the rest of the subject is in fairly good shape, and consequently I have written this book deductively. While my point of view differs considerably from Freundlich's, it is a pleasure to acknowledge my debt to him for what he did in his admirable book."

Professor Bancroft makes out a good case for treating colloids from the standpoint of adsorption, a field in which we now possess more definite *quantitative* data than in other fields of colloid phenomena. He shows how adsorption must be taken into account in connection with surface tension effects, coalescence, precipitation, peptisation, the properties of colloidal solutions, emulsification, and fogs and smokes. The discussion is well presented, and is far from being a mere statement of facts. There is a welcome critical vein throughout, new problems for research are suggested, and obvious difficulties in the acceptance of certain deduced propositions are not shirked.

The chapter on emulsions and foams is good and up to date. Colloid textbooks so far have only dealt with the subject of emulsions in most meagre fashion, so that students will thank the author for his summary in this field. New, also, are the discussions on colloids in relation to catalysis, colour, and fogs and smokes. The closing chapter deals with the thickness of surface films, and is a useful summary of the work done, though a discussion of the new views on the orientation of molecules in liquid surfaces and their relation to colloid phenomena would have been welcome. One notable omission from this excellent book is that of Donnan's theory of membrane equilibria, to which Loeb has recently announced his ardent support, as a result of his own extensive investigations, particularly on gelatin.

This book is well bound, and the paper and printing are also good. Several typographical errors are apparent, among them an error in the equation on p. 141, but they do not detract from the value of a refreshingly up-to-date and readable textbook on the general theory of colloid phenomena.

WILLIAM CLAYTON.

LUBRICATING AND ALLIED OILS. By ELLIOTT A. EVANS. Pp. 128. London: Chapman and Hall, Ltd. 1921. Price 9s. 6d. net.

In perusing this book, it is difficult to decide exactly what ground the author intended to cover. The title includes lubricating and allied oils, whatever that may mean; but in the Foreword by Sir Charles Wakefield lubricating oils alone are mentioned, and in the Preface the author says he wrote the book "after repeated requests from chemists, engineers, and others for a useful non-too-technical book on lubricating oils . . . with a view to assist chemists in compiling specifications and examining lubricating oils; also to give engineers an insight into the application and properties of such oils and the interpretation of their specifications." He curiously complains that existing treatises are "too technical, except for the specialist or person

who desires knowledge on a specific section of the subject." He admits that chemists require detailed information on the methods used in the laboratory, which he says some of the books do not provide. One is curious to find how this kind of information is to be given in a "non-too-technical" book, and one finds that when the author sets out to seriously describe or discuss a test or method he has either to be as technical as any other author or to slur over the subject.

Another point one notices is that, whilst the author says he has endeavoured to include only those tests which are commonly demanded, he has gone into quite a lot of technical detail regarding tests of quite minor importance, such as the determination of specific heat, with tables of the specific heats of a number of pure hydrocarbons, occupying seven pages of this small book. One also finds, as foreshadowed by the title, that the author has included a number of tests used in the examination of fuel oils and transformer oils, which do not concern lubricating oils. One finds in the book very little real guidance in the framing of specifications or in their interpretation, and in the chapter on the oils employed for various purposes three pages contain a list of proprietary grades of Wakefield's "Castrol" suitable for the various types of motor vehicles, which is, of course, pure advertisement. No reference whatever is made to the value of a little free fatty acid in improving the friction-reducing qualities of mineral oils. We are told, for instance, on p. 110 that "locomotive engineers in this country call for an oil containing anything from 5 to 75 per cent. of rape oil, according to their needs, in the mineral oil"; but the author does not advise whether this is good or bad practice, whether such variation in the proportion is necessary, and whether, in fact, the whole or the greater part of this rape oil might not be saved and a little fatty acid used instead. Few locomotive engineers now use anything like so large a proportion as 75 per cent. of rape oil in the lubricant.

In the first three chapters, occupying only seven and a half pages, the author gives a scrappy but interesting account of the history of petroleum, and very brief remarks on oil refining and on the fatty oils. "Ravine rape" at the foot of p. 9 presumably refers to the oil usually known as ravinon oil. In Chapter IV., on Physical Tests, the author shows how the presence of water in an oil may influence the flash-point, but "does not favour the drying of the oil before making a test, because he believes it detracts from the value of the test." Whether it does or not would seem to depend upon whether the operator wishes to ascertain the flash-point of the oil or has some other object in view. The author remarks that, "pending a better system of classification, lubricating oils are generally grouped according to their viscosity." Seeing that viscosity is one of the most important properties of a lubricant, one wonders what better system of classification the author has in his mind. As an example of loose phraseology, the author states on p. 30 that in the Engler, Redwood, and Saybolt viscometers "the greater portion of the energy of flow is lost in the rapid passage of the liquid through the tube." What is probably meant is that when thin liquids are being tested the greater part of the energy due to the head appears as energy of flow—*i.e.*, kinetic energy—instead of being converted into heat by the viscosity, as the author shows in the sentence following that from which the quotation is taken. It is time that the viscosity values of oils were expressed in absolute

measure or in units, such as the centipoise, which are independent of the instrument used in determining them, but the author seems to have no definite views on the subject, and to be quite content with the present system.

Those chemists who have to advise on lubricating and other oils will find useful information in this book, but it cannot, in the reviewer's opinion, be regarded as a very valuable addition to the literature of the subject. L. ARCHBUTT.

FAMOUS CHEMISTS: THE MEN AND THEIR WORK. By Sir WILLIAM A. TILDEN, F.R.S., D.Sc. London: George Routledge and Sons, Ltd. Price 12s. 6d. net.

Sir William Tilden, in his Preface, disclaims for his book the character of another history of chemistry, but thinks he is justified in offering to the public this volume of biographical essays dealing with well-known chemists, because other similar works have not been contributions to the history of chemistry. All chemists will be indebted to him for his book. It was a good idea to make use of the atomic theory as the string on which to thread his biographical beads, of which there are twenty-one divided into ten groups. The groups are appropriately named to mark the epochs in the history of the theory of chemistry.

The author anticipates criticism with regard to the names which he has felt himself compelled to reject. Those which he has selected for treatment will, one feels sure, commend themselves to all those who have regard to the fact that the available space in the book is only about three hundred pages. Sir William's own career would lead his readers to expect that any such book as this written by him would at least subserve a didactic purpose in the field of chemical theory. It does this most admirably, and, let it be gratefully added, most agreeably.

Robert Boyle is the subject of the first essay, which is a quite satisfactory account of "the father of chemistry," inasmuch as that, in addition to the compendious biographical matter, particulars are given as to the experiments establishing the "Law of Boyle"; and it is indicated what Boyle did in bringing the conception of an *element* out of the realms of philosophy and pseudo-philosophy into the realm of matter. The author has most significantly succeeded, without using any undue emphasis, in displaying the development of the conception of the element, considered from the atomic point of view, from the purely speculative stage, through the material stages, right down to the physical conception of ultra-chemistry of the present day.

After Boyle comes the second group of "The Phlogistians," comprising Black, Priestley, Cavendish, and Scheele. Scheele has been dealt with most sympathetically. Lavoisier is taken as the representative of the antiphlogistic revolution. The article on Davy is one of the longest and probably the best, and it would lead one to think that Davy is one of Sir William's favourites. As a presentation of the character of this great man it is, on the whole, rather too favourable. It is only on reading a subsequent essay on Berzelius that one learns, from the remarks of Berzelius on the character of Davy, that Sir William is aware that the impression produced by Davy on his contemporaries was not consonant with either his position in the world of science or with his undoubted abilities.

On the whole, the subjects of the book are treated so as to produce the feeling

that they are altogether in the hands of a warm admirer rather than in the hands of a historian. In the case of Cavendish there is only the barest reference to the "water" controversy. It is matter for commendation that the author has written so excellent an account of Berzelius and his work, and attempted to do justice to his memory as a great and widely influential teacher. Space forbids the dealing at length with features of the other essays which treat of Dalton, Gay-Lussac, Proust, Faraday, Avogadro, Cannizzaro, Liebig, Dumas, Frankland, Williamson, Mendeléeef, Crookes, and Ramsay.

The book contains nearly forty illustrations, and there is at least one portrait of each chemist mentioned. The printing and paper are good, and the proof-reading has been pretty well done; on p. 105 Dalton's birth year is given as 1706 instead of 1766, and there are less than half a dozen other "literal" errata. The volume is in every respect an admirable one for the chemist and for the general cultured reader.

W. KIRKBY.
