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THE ESTIMATION OF MERCURY.

BY H. B. GORDON, PH.D.

IN studying the estimation of mercury in an organic mercury compound it was found that precipitation of the mercury by means of hydrogen sulphide was not applicable, as nitric acid would be used for decomposing the compound. The apparatus used in the estimation of mercury as the metal was not available. Moreover, the electrolytic precipitation of mercury in a platinum dish is liable to be injurious to the platinum, particularly if chlorides are present. It therefore seemed advisable to employ some other method than those usually described in the standard works on quantitative analysis.

A number of investigators have precipitated the mercury from solution by means of some other metal. For this purpose C. Reichard (*Pharm. Zentr.*, **51**, 443) used aluminium, and found that copper, silver, and cadmium interfered. M. Francois (*Compt. Rend.*, 1918, **166**, 950-952) precipitated the mercury with pure zinc, dissolved the zinc in sulphuric acid, and weighed the mercury. He apparently regarded this method as sufficiently accurate. The zinc used must be pure, and an estimation appears to have required about three days for its completion. Obviously, copper or silver would interfere, but these were not present in the case to which the method was applied. Various investigators have precipitated the metal by means of copper, and have then converted the metal to iodide (M. Perlstein and J. Abelin, *Münch. Wochschr.*, **62**, 1181-1183; Menière, *Bull. médical*, June 29, 1910), or have volatilised the metal on to a weighed gold plate (K. M. Vogel and O. I. Lee, *J. Am. Med. Assoc.*, **62**, 532-534).

The author thought it should be possible to estimate mercury by precipitating it upon an element higher in the electromotive series, weighing the metal and mercury, volatilising the mercury, and reweighing the metal. The loss in weight should represent the mercury, unless some of the other metal was also volatilised. For the precipitating metal, copper was chosen, because partly it is not readily volatile and partly because it is lower than hydrogen in the electromotive series, and so can be used in acid solution and will not precipitate zinc, cadmium, etc., if they should be present.

In a quantitative method the completeness of the reaction is an essential consequence. The discharging potential of mercury and that of copper from normal solutions of their ions upon the respective metals differ, as given in the literature, by about 0·42 volt. It follows, then, that if a piece of copper is placed in a solution containing mercury ions, the mercury will be displaced until the copper ion concentration exceeds that of mercury ion to such a degree that, if the ratio of these two concentrations be substituted in Nernst's formula $e = \dfrac{RT}{nF}\log_e \dfrac{c'}{c''}$, the value of the electromotive force, e, should be about 0·42 volt. The copper strip on which mercury has deposited should show a less tendency to displace mercury ions than should pure copper, hence a large surface·of copper is advantageous to decrease this effect. In practice this effect was practically eliminated by putting a second piece of copper into the solution after the mercury had been nearly precipitated. Since the mercury is, in any case, diluted with copper when deposited on that metal, the electromotive force between the metallic mercury and the solution is not the same as if the metal were pure mercury, and the tendency for the ionic mercury to precipitate should be greater than if the metallic mercury were pure. The dilution of metallic mercury and copper by each other thus has two effects which tend to neutralise each other.

Substituting numerical values in the above equation, and bearing in mind that for the copper ion, whose discharging potential is to be decreased by increasing its concentration, the value of n, the valence, is 2, we find that at 25° C. $\dfrac{e'}{c''} =$ 1·7(10)14, or, in order that copper and mercury ions should be in equilibrium with metallic copper and mercury, the concentrations of copper ions should be 1·7(10)14 times that of the mercury ions—in other words, the precipitation is complete. To test this conclusion in practice, about 0·3 grm. of crystalline copper sulphate was dissolved in 100 c.c. of water, to which was added 0·1 mgrm. of mercuric chloride. A small piece of bright copper was placed in this solution and allowed to stand for about nineteen hours. The copper was then removed from the solution, and a dark stain, indicating mercury, was visible on its surface. It was washed with water, alcohol, and ether, and after standing for some time in a desiccator, was weighed. It was then heated in a current of dry hydrogen until the dark stain disappeared, and was cooled in hydrogen. When again weighed, it was found to have decreased in weight by about 0·1 mgrm. To be sure that the colour and loss in weight were not due to the formation of copper oxide and its subsequent reduction by hydrogen, the experiment was repeated, obtaining the same results as in the first experiment; but in the second trial the mercury was condensed in a constricted part of the tube in which the copper was heated, and, later, iodine vapour was drawn through the tube. A faint reddish tinge at the constriction of the tube showed the presence of mercury iodide. Narrow strips of bright copper were placed in cther samples of copper sulphate solution in which no mercury salt had been placed. These showed no tendency to acquire a dark stain such as the copper piece showed in the presence of mercury. In another experiment about 5 grms. of crystalline copper sulphate were dissolved in water, 200 c.c. of concentrated hydrochloric acid were added, and made up with water to 2,000 c.c. To this solution was added mercuric chloride

equivalent to 0·1 grm. of mercury; a small piece of copper was suspended in the solution by a fine thread. The next day the copper showed evidence of a mercury deposit, but it was allowed to stand in all about thirty-six hours; it was then removed and treated as in the previous experiments. Again a loss in weight of 0·1 mgrm. was observed, and the dark stain disappeared during the heating. The test with iodine vapour was negative in this case, but the stain could not have been due to oxide, as it would not form in the acid solution. From these experiments it is apparent that the darkening of copper by mercury gives an extremely sensitive test for that metal if the absence of other metals that could deposit on copper is assured.

The reaction may be hastened by having a large surface of copper, a small volume of solution, and by stirring. A volume of 60 to 70 c.c. was placed in a Nessler tube, and the copper, in the form of a coil of wire gauze, was hung in the solution from a platinum wire by a hook on the end of a glass rod. This rod was rapidly raised and lowered by attaching the rod to an eccentric rotated by a small water-motor. The solution was thus stirred, and the copper brought frequently into contact with all parts of it.

Preliminary experiments showed that, if the solution is neutral, some of the mercury is precipitated as a grey powder. 2N hydrochloric acid seemed to prevent this precipitation, as did a smaller concentration of nitric acid. Nitric acid, however, even when dilute, slowly attacks the copper. 2N acetic acid did not entirely prevent this precipitation, though it would doubtless do so if the mercury solution were sufficiently dilute as indicated (see Estimation No. 4, Table 1).

In rather concentrated solutions there is a tendency for some of the mercury to be deposited in the form of a very fine powder which floats on the surface of the solution. In some of the preliminary experiments, in which this phenomenon was shown to a marked degree, this floating mercury was recovered and weighed in a Gooch crucible. In these cases it weighed about 0·1 mgrm. In the experiments recorded in the table following, the loss due to this cause was not so large—in most cases this floating mercury was not observed at all—and no effort was made to collect it.

TABLE 1.

Time No. 1.	Time No. 2.	Conditions.	Mercury found.
20 min.	50 min.	2N with HCl	4·8 mg.
20 ,,	140 ,,	2N ,,	4·6 ,,
20 ,,	20 ,,	2N ,,	4·8 ,,
30 ,,	30 ,,	$\frac{N}{2}NH_4NO_3$ + acetic acid	4·8 ,,
18 ,,	30 ,,	$\frac{5N}{8}NH_4NO_3 + \frac{N}{4}$ nitric acid	4·6 ,,

In the preliminary experiments an effort was made to estimate considerable quantities of mercury—e.g., 0·2 grm.—but for this purpose rather large copper coils seemed necessary, and these were too heavy for the small water-motor to move them with a steady motion. The platinum wire available for hanging the coil from the

glass rod was of small diameter, and sometimes broke when large coils were used. Accordingly, coils weighing from 4 to 7 grms. were used, and only small amounts of mercury were estimated.

Table 1 gives the results of five consecutive estimations of mercury in a solution of mercuric chloride. A volume of 50 c.c. was used, the weight of mercury, as determined by the sulphide method, being 4·8 mgrms.

The first and second columns record the time the first and second coils were left in the solution.

The procedure was as follows : The measured volume of standard mercuric chloride solution was placed in a Nessler tube, to this was added the other solution to give the desired acidity or salt concentration, the Nessler tube was placed under the stirring apparatus, a copper coil was hung, by a platinum wire attached to it, from a hook at the end of the glass rod of the stirrer, and the rod was released, so that the coil was immersed in the solution. The water was then turned into the motor at such a rate that it gave the glass rod a fairly rapid motion. After a sufficient time had elapsed, the coil was replaced by a second one, and was washed by immersing several times in water, twice in alcohol, once in ether, and once in ether dried over metallic sodium. Upon removal from each liquid the coil was drained on filter-paper. After draining from ether, it was put in a desiccator under diminished pressure. When the second coil had remained in the solution for a sufficient time it was removed, washed in the same manner as the first coil, and also dried *in vacuo*. After sufficient time had elapsed for the ether to have evaporated from the coils they were weighed. After their weight had become constant they were placed in a hard glass tube, and a current of dry hydrogen passed through. When the air had been expelled, the coils were heated by the flame from a Bunsen burner with a wing tip, and kept at a dull red heat for about a minute, after which the flame was removed, and they were allowed to cool in a slow stream of hydrogen. They were then withdrawn from the glass tube and weighed. The loss of weight of the second coil was much less than that of the first coil. In only one case given in the above table was it as great as 0·7 mgrm., and in one case it was only 0·2 mgrm. This was to be expected, since the mercury was so completely removed by the first coil that the second coil was scarcely coloured by it. If the glass tube showed any copper on its walls as a result of heating the coils in it, this copper was estimated, and its weight subtracted from the total loss in weight of the coils due to heating. The result was the mercury found, given in the last column of the above table. In some cases no copper was seen on the glass tube. In other cases it was estimated by dissolving in nitric acid, washing into a suitable vessel, and making a colorimetric comparison with a known copper solution. In some cases the colours were matched in ammoniacal solution ; in others the solution was acidified with acetic acid (after making alkaline with ammonia) and potassium ferrocyanide added, and the colours matched. In some of the later estimations, when the copper did not exceed 0·2 mgrm., it was estimated by its appearance on the tube. One tenth of a mgrm. makes a considerable stain on the glass tube. In the presence of a nitrate, especially of free nitric acid, as in determination No. 5, the coil on which the mercury was deposited had a smoother, better-looking surface than when these were absent,

and there was also less tendency for copper to deposit on the glass tube when the mercury was volatilised.

To attain constant weight in the vacuum desiccator, a coil had usually to be left in it several hours, though sometimes practically constant weight was reached in an hour. A means for drying the coils more quickly would evidently be advantageous. This was attempted by placing the coil, after draining off the ether, in an oven heated to 90° to 95° C., removing it after one minute, and cooling it in a desiccator without evacuation. In this case 4·9 mgrms. of mercury was found in 50 c.c. of the standard mercuric chloride solution. The second coil appeared to acquire a film of oxide which may account for the slightly high result. This modification of the procedure would apparently be useful when the time required for an estimation is of more importance than extreme accuracy. Under such conditions it should be possible to complete an estimation of mercury in a solution in about one and a half hours.

An attempt was made to avoid the use of the hydrogen during the volatilisation of the mercury. In this case the coils carrying the mercury were heated in the hard glass tube as usual, except that the tube was filled with air instead of hydrogen. The copper oxide formed was then reduced by placing the coil in alcohol vapour. To transfer the coil from the glass tube to the alcohol vapour without permitting it to cool, and without breaking off any of the copper oxide, requires great care. A tendency was also noted for thin flakes of copper, formed by reduction of the oxide, to shake loose from the coil. This method of reduction is therefore not to be recommended.

The usefulness of a method of analysis depends largely upon the number of conditions which interfere with its accuracy. For this reason, the effect of the presence of various substances was briefly studied. As indicated above, while the presence of nitric acid interferes with the estimation of mercury as sulphide it is rather helpful than otherwise in this method. Obviously those metals standing above copper in the electromotive series will not interfere with this method, so no attempt was made to study their effects, but such elements as arsenic, antimony, bismuth, and silver, which are displaced from solution by copper, would interfere with the estimation of mercury by this method if they were present in the solution and if they were volatilised to an appreciable extent with the mercury. To test the applicability of the method in the presence of these elements, pieces of copper gauze were placed in solutions containing the chlorides of arsenic and antimony. After some hours these were removed from the solution, were washed and dried, weighed, heated in hydrogen, and again weighed. The coil containing the arsenic lost 2·4 mgrms., and that containing antimony lost 5·3 mgrms. This was but a small part of the arsenic and antimony present. Similarly, a copper coil which ha stood for some hours in a solution containing about 10 mgrms. of bismuth, in the form of chloride, lost, upon heating, about 1 mgrm. of bismuth. Two estimations were also made with conditions as in No. 5, Table 1, except that about 10 mgrms. of arsenic in the form of chloride was added to the solution. In one of these cases the mercury (and arsenic) evaporated from the coils was 7·4 mgrms. In the other case it was 5·2 mgrms. Evidently but little arsenic was volatilised in the latter case.

The effect of silver upon the results obtained by this method was also tested. A dilute solution of mercuric nitrate was standardised by this method. The conditions as to time and concentration of reagents were essentially the same as in estimation No. 5, Table 1. Three results showed 6·2, 5·9, and 6·1 mgrms. of mercury in 25 c.c. of the solution. With conditions the same as in these estimations except that about 10 mgrms. of silver nitrate were dissolved in the solution, the copper coils lost, when heated, 6·6 mgrms. As no copper was deposited on the glass tube, the vaporisation of several tenths of a mgrm. of silver was indicated.

These results indicate that the estimation of mercury by this method, in a solution containing arsenic, antimony, bismuth, or silver, would not be satisfactory. It seems not improbable, however, that by heating the copper coils in a glass tube placed in a larger glass tube, whereby the heating would be more gradual, and the temperature under better control than by the method of heating used in the present investigation, it might be possible to volatilise the mercury without driving off a weighable amount of these elements. This method of heating would probably also eliminate all loss of copper, since the copper stain was usually on a part of the glass tube which had become unduly hot. ·

SUMMARY.

The estimation of mercury in dilute solutions has been carried out by displacing the mercury from its compound by means of copper in the form of gauze, heating the copper in hydrogen, and noting the loss in weight due to the volatilisation of mercury.

The detection of 0·1 mgrm. of mercury in two litres of solution has been found possible by this means.

The presence of nitrates does not interfere with this method, but is rather beneficial.

The presence of arsenic, antimony, bismuth, and silver interfere with the method, but it seems probable that, with careful heating, the method might be used in their presence.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Estimation of Amino-Acids in Wine. E. Garino-Canina. (*Annali Chim. Applic.*, 1919, **12**, 112-118.)—The formation of amino-acids in wine is due to the action of enzymes in yeasts or bacteria upon the proteins in the grape must or wine, or to the auto-digestion of the protoplasm of the *Saccharomycetes*. Acids of the type of leucine, tyrosine, aspartic acid, etc., may then undergo further enzymic decomposition, being converted into amyl alcohol, succinic acid, etc.; while at the same time the basic nitrogen group is liberated, and there is an increase in the amount of ammonia in the wine. Sörensen's method of estimating amino-acids by titration with formaldehyde (ANALYST, 1908, **33**, 364) gives good results in the case of wines when used in the following manner: the wine (500 c.c.) is nearly neutralised with barium hydroxide, and colouring matters are removed by treating it with 50 c.c. of a 20 per cent. suspension of animal charcoal. It is then evaporated to half its volume and filtered, the filtrate and washings (about 400 c.c.) treated with 2 grms. of barium chloride and a slight excess of saturated alcoholic barium hydroxide solution, and the ammonia distilled, by means of a current of air, into standard sulphuric acid and titrated. The liquid is then rendered neutral to azolitmin paper, 10 c.c. of 30 to 40 per cent. formaldehyde solution (recently neutralised towards phenolphthaleïn) added, and the acidity titrated, as in Sörensen's method. The amount of nitrogen in the form of amino-acids ranged in twenty-six samples of wine of different origin from a trace to 91·0 m. mgrms. per litre; whilst a sample of grape juice contained 112·0 m. mgrms., and a sample of sterilised must 98·0 m. mgrms. The total nitrogen in the wines varied from 28·0 to 453·0 m. mgrms., 30 to 40 per cent. of which was in the form of proteins, about 22 per cent. as amino-acids, 2 per cent. as amides, and up to 2 per cent. as ammonia. It is pointed out that the keeping properties of wine probably depend to a large extent upon the form in which the nitrogenous constituents are present, and that, as has been shown in the case of beer, the presence of complex nitrogenous compounds may be a direct cause of turbidity. C. A. M.

Determination of Moisture in Malt. T. J. Ward. (*J. Inst. Brew.*, 1919, **25**, 335-352.)—The author describes results of work extending over a considerable period, during which time over 10,000 malt moisture determinations were made. The malt was, in all cases, ground in a coffee-mill, and dried in a jacketed oven containing boiling water. A large number of conditions upon which correct results depend are summarised, among the more important being the following: Both ventilators of the oven must be open; no leak, however small, must allow access of steam to the interior of the oven; the vessels containing the malt should be flat-bottomed, provided with well-fitting lids, and must not contain an amount of malt exceeding 0·5 cm. in height; products of combustion from the heating burner must be pre-

vented from gaining access to the interior of the oven, and all dishes containing malt must be placed on the floor of the oven but not within 5 cm. directly behind the lower ventilator; a period of at least three hours must be used for drying, and no material other than malt should be placed in the oven during this time; the door of the oven must not be opened during the drying period. Among the factors found to have no influence upon the result are the following : The internal capacity of the oven within the limits of $3\frac{1}{2}$ and 33 litres; lifting the lid of the dish between cooling and weighing; coarse or fine grinding of the malt; the relative proportions of husk and endosperm weighed into the dish; the relative humidity of the atmosphere, provided this does not exceed 95 per cent., and the period during which the malts are dried in the oven within the limits of three and eighteen hours.   H. F. E. H.

Fruit of the South American Noli Palm as a Source of Oil. (*Bull. Imp. Inst.*, 1919, **17**, 186.)—The Noli palm (*Elæis melanococca Gaertn.*) is similar in character to *E. guineensis*, the West African oil palm, but is smaller in size; it is common in Columbia, from which place was derived the consignment analysed. The fruits were dry, of orange-yellow or greyish colour, from 0·8 to 1 inch in length, and from 0·5 to 0·8 inch in diameter; average weight of a single fruit, 2·5 grms. The shells of the nuts were very hard, and about 0·1 inch in thickness. The kernels were similar to the West African palm kernels from *E. guineensis*, but smaller in size; average weight of a single kernel was 0·5 grm. The fruits consisted of pericarp 16 per cent., shell 62 per cent., and kernel 22 per cent.

Pericarp.—The pericarp of the sound fruits contained 8·1 per cent. of moisture and 29 per cent. of oil, equivalent to 31·5 per cent. of oil from the dry pericarp. The yield of oil from the entire fruits is therefore only 4·6 per cent. The oil itself is an orange-yellow liquid containing a fairly high proportion of stearine. It is much more liquid and paler in colour than commercial palm oil from West Africa, but is similar in taste and smell.

The comparative analyses are as follows :

	Pericarp Oil from Noli Palm Fruits.	Commercial West African Palm Oil (*E. guineensis*).
Sp. gr. at 100/15° C.	0·8636	0·8586
Solidifying-point of fatty acids	33·6° C.	36° to 46° C.
Acid value*	29·7	—
Saponification value*	199	196 to 205·
Iodine value per cent.	83·5	53 to 57
Unsaponifiable matter per cent.	0·7	—
Volatile acids, soluble	0·7	0·86 to 1·87
,, ,, insoluble	0·5	—

* Mgrms. potash per grm. of oil.

Kernels.—The kernels contained 7·2 per cent. of moisture and 45·4 per cent. of oil—a solid fat of pale cream colour of pleasant taste and smell and slightly harder than ordinary coconut oil.

Comparative analytical values were as follows :

	Noli Kernel Oil.	Palm Kernel Oil.
Sp. gr. 100/15° C.	0·8651	0·8731
Solidifying-point of fatty acids	26·9° C.	20° to 25° C.
Acid value	0·6	—
Saponification value	234	243 to 255
Iodine value per cent.	27·7	10·3 to 17·5
Unsaponifiable matter per cent.	0·8	—
Volatile acids, soluble	1·4	5 to 6·8
,, ,, insoluble	3	10 to 12

H. F. E. H.

Indian Turpentine and Rosin. (*Bull. Imp. Inst.,* 1919, **17**, 159-177.)—Further samples of turpentine oil and rosin obtained by the distillation of the gum-oleo-resin of *Boswellia serrata* (nat. ord. *Burseraceæ*) have been analysed and described (ANALYST, 1916, **41**, 8). The average yield of gum-resin varies from 5 to 7·5 oz. per tree, and its average composition is as follows : Moisture, 10 to 11 per cent. ; turpentine oil, 8 to 9 per cent. ; rosin, 55 to 57 per cent. ; gum, 20 to 23 per cent. ; insoluble matter, 4 to 5 per cent.

1. *Turpentine Oil.*—Two samples prepared from the gum resin analysed as follows :

	1.	2.
Sp. gr. 15/15° C.	0·8446	0·8523
Optical rotation ... ... ··· ...	+31° 24'	+25° 57'
Acid value	nil	nil
Ester value before acetylation	2·6	3·0
Ester value after acetylation	36·4	54·3
Fractional Distillation :		
Fraction boiling at 153° to 160° C. ...	89 per cent.	56 per cent.
Fraction boiling at 160° to 170° C. ...	} 11 ,, ,, *{	24 ,, ,,
Fraction boiling at 170° to 180° C. ...		20 ,, ,,

The *Boswellia* turpentine oil readily dissolves resins such as colophony, dammar, sandarac, and soft copal, and practical trials with varnishes made with the oil showed that it could be successfully employed in place of ordinary turpentine oil.

* All between 160° and 180° C.

2. *Rosin.*—Five samples of *Boswellia* rosin were examined with the following results :

	1.	2.	3.	4.	5.
Moisture, per cent.	0·7	0·9	0·7	0·8	1·1
Ash, per cent. ...	0·5	0·4	0·03	0·3	0·2
Softens at ° C. ...	72	56	68	71	65
Melts at ° C. ...	—	—	—	78	73
Acid value ... ·...	51·5	25	55·1	52·4	50·8
Saponification value	92·0	66·0	90·2	87·8	75·6
Iodine value present	70·0	96·0	—	64·6	76·2
Sp. gr. ... ... {	1·082 at 20/20° C.	1·050 at 20/20° C.	—	1·077 at 18/18° C.	1·059 at 18/18° C.

All the samples were completely soluble in alcohol, ether, chloroform, benzene, and turpentine oil with the exception of No. 2, which was only partly soluble in alcohol. Varnish-making trials gave satisfactory results.

3. *Gum.*—Three samples were analysed as follows :

	1.	2.	3.
Ash	3·5	4·1	10·6
Resin (matter soluble in 95 per cent. alcohol) ..	27·6	24·0	19·3
Soluble gum (matter soluble in water)	50·1	56·3	44·8
Insoluble gum and dirt (exclusive of ash) ...	18·8	15·6	25·3
Matter soluble in ether (dry and free from alcohol) ...	24·4	20·1	13·2

Experiments made on the technical scale showed that the gum was much inferior to ordinary gum for use as a sizing material, and that it was unsuitable as a material for finishing textiles. It is probable that *Boswellia serrata* gum-resin, hitherto used chiefly as a substitute for *B. carteri* and *B. frereana* in the preparation of incense, has a future before it of considerable commercial importance.   H. F. E. H.

Sesbania : A Feeding-Stuff from South Africa. (*Bull. Imp. Inst.*, 1919, **17**, 184.)—Sesbania seeds (nat. ord. *Leguminoseæ*) are small and hard with a shiny dark greenish-brown coat. They measure about 0·1 inch in length and possess a fairly strong pea-like flavour and a slight aromatic odour. Analysis showed them to have the composition (per cent.): Moisture 9·6, crude proteins 32·9, consisting of true proteins 24·2, other nitrogenous substances 8·7, oil 6·2, carbohydrates by difference 39, fibre 10·9, ash 1·4. Hydrocyanic acid is absent. No previous experience of their feeding value in this country is available, but, provided that feeding experiments show no unsuspected disadvantage in actual use, it may be anticipated that they will be capable of replacing peas, lentils, or millet.   H. F. E. H.

ORGANIC ANALYSIS.

Analytical Method for the Separation of Acetylene, Ethylene, and Benzene. W. D. Treadwell and F. A. Tauber. (*Helv. Chim. Acta*, 1919, **2**, 601-607.)—A method for the successive absorption of acetylene, ethylene, and benzene vapour when these are mixed with carbon dioxide, oxygen, etc., is as follows: Carbon dioxide is removed by means of sodium hydroxide; the acetylene is then absorbed in alkaline mercuric cyanide solution (20 grms. of mercuric cyanide dissolved in 100 c.c. of $\frac{N}{2}$ sodium hydroxide solution) by shaking the gas mixture for two minutes with 5 c.c. of this solution. Ethylene is next absorbed by shaking the residual gas with 10 c.c. of acid mercuric nitrate solution (20 grms. of mercuric nitrate dissolved in 100 c.c. of $\frac{N}{2}$ nitric acid and the solution saturated with sodium nitrate, the latter preventing the absorption of benzene vapour). The benzene vapour is finally absorbed in fuming sulphuric acid in the usual way. Oxygen and carbon monoxide do not interfere with the above absorptions. Propylene is not absorbed by alkaline mercuric cyanide solution, but dissolves in acid mercuric nitrate solution and also in 25 per cent. sulphuric acid containing 10 per cent. of mercuric sulphate.

W. P. S.

Estimation of Cyanogen Compounds in Concentrated Ammonia Liquor. II. Estimation of Thiocarbonate. P. E. Spielmann and H. Wood. (*J. Soc. Chem. Ind.*, 1919, **38**, 369-370T.)—A method described previously (ANALYST, 1919, **44**, 143) for the estimation of cyanogen compounds in ammonia liquor, based on the depth of colour after their conversion into ferric thiocyanate, has now been extended to include the estimation of thiocarbonate. The present method depends on the fact that digestion for forty-five minutes at 70° to 75° C. will convert thiocarbonate completely into thiocyanate without affecting the cyanide, and, further, that polysulphide at 30° to 35° C. will convert cyanide into thiocyanate in thirty minutes without attacking the thiocarbonate. The various estimations are made as follows, separate quantities of 25 c.c. of the liquor being used for each: *Thiocyanate as such.*—The method described previously (*loc. cit.*) is used. During the addition of the sulphuric acid the liquid should be kept cold by means of pieces of ice. *Cyanide and Thiocyanate.*—The liquid is digested at 30° C. for thirty minutes with an excess (2 c.c.) of ammonium polysulphide. *Thiocarbonate and Thiocyanate.*—The liquid is diluted with 15 c.c. of water, 10 c.c. of concentrated ammonia are added, and the mixture is digested at 75° C. for forty-five minutes. *Ferrocyanide.*—This is estimated from the amount of "blue" obtained in the estimations of the thiocarbonate and thiocyanate. On acidifying the mixtures after digestion, precipitated sulphur may obscure the red coloration of the ferric thiocyanate. In such cases an excess of iron alum is added, the mixture heated at 40° C., and filtered. If after polysulphide treatment large quantities of slimy sulphur are precipitated and much hydrogen sulphide is evolved, it is preferable to remove most of the sulphur by a preliminary treatment with lead carbonate. Provided that the estimations are carried out in conical flasks fitted with loose stoppers there is no need to exclude air from the reacting substances, the vapours and evolved gases affording sufficient protection from the atmosphere.

W. P. S.

Detection and Estimation of Cyanides and Thiocyanates in Complex Mixtures. L. Chelle. (*Comptes rend.*, 1919, **169**, 973-975.)—Fifty c.c. of the solution, containing a very small quantity of cyanide, are acidified with 5 c.c. of 50 per cent. sulphuric acid, and a current of air is passed through the mixture for three hours at the rate of 25 litres per hour; the hydrocyanic acid is collected by passing the air through an absorption vessel containing 1 c.c. of potassium hydroxide solution. The cyanide in the latter solution is then detected and estimated by the ferrocyanide or ammoniacal silver iodide methods. If the test solution also contains thiocyanate, the solution remaining after the removal of the hydrocyanic acid is treated with an excess of potassium chromate. This converts the thiocyanate into hydrocyanic acid, which is removed, collected, and estimated as before. The method is applicable to the estimation of amounts of cyanide as small as 0·01 mgrm. In the presence of bromides, hydrochloric acid must be used in place of sulphuric acid; iodides, if present, must be separated previously.   W. P. S.

Identification of Dyes. E. F. Hitch and I. E. Knapp. (*J. Ind. and Eng. Chem.*, 1919, **11**, 1076-1079.)—An account of the well-known methods of identifying and separating unknown dyestuffs, including colour reactions with acids, etc., dyeing tests, microscopic and spectroscopic examination, and adsorption and solubility methods.   J. F. B.

Estimation of the Strength of Dyestuffs. W. H. Watkins. (*J. Ind. and Eng. Chem.*, 1919, **11**, 1079-1080.)—The author calls attention to the precautions necessary in making comparative dye tests in the examination of dyestuffs, particularly as between buyer and seller.   J. F. B.

Change of Refractive Indices of Fixed Oils with Temperature. C. H. Wright. (*J. Soc. Chem. Ind.*, 1919, **38**, 392-394т.)—The change of the refractive indices of fixed oils with change of temperature varies with the change in density, and the modulus of expansion, k, may be used likewise for calculating the refractive index at any temperature, t', from observations made at another temperature, t. The value of k is practically a constant for all the fixed oils which have been examined, and may be taken as 0·00076. The correction factor for the refractive index is given by the expression

$$n^1 = (n - 1) \times \frac{1 - 0·00076\,t'}{1 - 0·00076\,t} + 1.$$

There is no generally agreed temperature which may be taken as a standard for the refractive indices of the fixed oils, and the author proposes a temperature of 40° C. as a standard temperature suitable both for oils and fats. Substituting 40° C. for t' in the above expression, the value of the refractive index of any fixed oil determined at any other temperature is calculated by the factor :

$$\frac{0·9696}{1 - 0·00076\,t}$$

The error involved in using this method of correction is less the nearer the temperature of observation be to the standard temperature of 40° C., and it is better to

make the observations at any steady temperature near 40° C. than to maintain the instrument exactly at 40° C. The correction factor can then be used for recording the results at the standard temperature.　　　　　　　　　　J. F. B.

Characterisation of Fuel Oils, particularly Petroleum Spirit, by the Picric Acid Value. J. Tausz and E. Schnabel. (*Chem. Zeit.*, 1919, **43**, 726.)— The solubility of picric acid in the different types of hydrocarbons shows very wide divergencies, and may form the basis of a method for the approximate estimation of benzene in petroleum spirit. Picric acid is practically insoluble in *n*-hexane, but is soluble in benzene to the extent of about 10 per cent. About 50 grms. of the fuel to be examined are treated with excess of solid picric acid in a 200 c.c. stoppered bottle. About 3 grms. of the acid are initially added, and if this quantity proves to be insufficient a further quantity is added, so as to leave yellow crystals undissolved. The liquid is thoroughly shaken for ten minutes and then filtered. About 20 grms. of the filtrate are weighed out into a stoppered bottle, treated with 30 c.c. of water, and titrated with $\frac{N}{10}$ sodium hydroxide in the presence of phenolphthaleïn. The pink colour must persist after prolonged shaking. The picric acid value is expressed in terms of c.c. of $\frac{N}{1}$ alkali required per 100 grms. of the saturated solution. The picric acid value of light petroleum spirit (petrol) ranges between 0·05 and 0·3 ; the heavier fractions, which are used for lacquers, etc. ("white spirit"), show higher values —*e.g.*, 0·9 and 1·25 ; whereas crude 90 per cent. benzene has a picric acid value of 38·6, and commercial toluene, 43·0. In the case of mixtures the picric acid value is not a linear function of the percentage of benzene, but the delicacy of the method increases with the proportion of aromatic hydrocarbon present. The method is not very sensitive in the presence of less than 20 per cent. of benzene, but this circumstance is not of much importance, since genuine petroleum spirits contain a certain quantity of aromatic hydrocarbons, and the addition of further quantities of benzene to a natural product must always increase the picric acid value.　　　　J. F. B.

Determination of the Saponification Value of Dark Resins. H. Salvaterra. (*Chem. Zeit.*, 1919, **43**, 765-766.)—From 1 to 4 grms. of dark resins are saponified by boiling for thirty minutes beneath a reflux condenser with 50 c.c. of approximately $\frac{N}{2}$ alcoholic potassium hydroxide solution. The resulting soap solution is treated with 32 c.c. of approximately $\frac{N}{2}$ barium chloride solution and 300 c.c. of recently boiled neutral water, thoroughly shaken, and heated for three-quarters to one hour on the water-bath. It is then cooled, made up to definite volume (500 or 600 c.c.), and filtered, and 100 c.c. of the filtrate are titrated with $\frac{N}{2}$ hydrochloric acid, using phenolphthaleïn as indicator. In some cases the barium soap agglomerates and adheres to the bottom of the flask, rendering filtration before the titration unnecessary. At the same time a blank determination is made under the same conditions, in order to eliminate the error due to the unequal action of the atmospheric carbon dioxide upon the barium hydroxide, formed by interaction of the excess of the barium chloride and the potassium hydroxide.　　　　C. A. M.

Estimation of Paraffins and Unsaturated Compounds in Commercial Toluols. H. G. Evans.

(*J. Soc. Chem. Ind.*, 1919, **38**, 402-405T.)—For the estimation of the paraffins in toluene the sulphonation method, carefully standardised, is the most convenient. About 50 c.c. of toluene are measured accurately to within 0·5 c.c. by pouring slowly upon the surface of 150 c.c. of 98 per cent. sulphuric acid contained in a 250 c.c. stoppered and graduated cylinder. The cylinder is shaken gently until fairly warm (not more than 45° C.), the pressure being released occasionally. After standing for about five minutes it is shaken vigorously for three or four minutes to complete the sulphonation. The contents are then transferred to the measuring vessel, consisting of a 350 c.c. separating funnel, the neck of which is fitted with a graduated tube reading to 0·01 c.c., and the stem of which is connected with a mercury reservoir. The last drops are rinsed in with 50 c.c. of sulphuric acid, the liquid is allowed to cool and finally the layer of paraffins is forced up into the graduated tube and measured. A correction must be applied for the solubility of the paraffins in the acid ; this correction amounts to 0·60 per cent. on the volume of the toluene, to be added to the volume of the paraffins when this is below 5 per cent. ; it is slightly higher, 0·62 to 0·63 per cent., for the range 5 to 10 per cent. of paraffins. An alternative method for the estimation of paraffins is based on the accurate determination of the sp. gr. at 15·5°/15·5° C. The sp. gr. of pure toluene at this temperature is 0·87193 and that of the paraffins separated by sulphonation is 0·73539, but, since the paraffins are always accompanied by a proportion of unsaturated compounds having a lower sp. gr. than pure toluene, the calculation of the percentage of paraffins must be made by using a corrected sp. gr. = 0·7208. In commercial toluenes the presence of 1 per cent. of paraffins by volume is associated with a lowering of the sp. gr. amounting to 0·00151, whereas in a synthetic mixture of pure toluene and separated paraffins the lowering is only 0·00136. Using the corrected figure, the results found by the specific gravity method are in good agreement with those by the sulphonation method, but a high degree of accuracy is necessary in the determination of the sp. gr., which must be correct to within 4 units in the fourth place of decimals. The method for the estimation of the unsaturated compounds in toluene consists in titrating with $\frac{N}{10}$ bromide-bromate solution in the presence of sulphuric acid : 10 c.c. of the sample are treated in a small stoppered bottle with 20 c.c. of dilute sulphuric acid (1 : 5) and the bromide-bromate solution, containing 9·9167 grms. of potassium bromide and 2·7833 grms. of potassium bromate per litre, is run in until the colour of the bromine persists in the toluene layer after five minutes' shaking. If the colour persists after standing for a further ten minutes the titration is considered to be finished. On an average, commercial toluene requires 9·58 c.c. of $\frac{N}{10}$ bromine solution, which corresponds to 0·2068 per cent. of unsaturated compounds as calculated from the sp. gr. In practical work, the estimation of the unsaturated compounds by bromide-bromate solution, and of the paraffins by sulphonation, gives a sufficiently accurate and rapid valuation of the sample.   J. F. B.

Criteria of the Degree of Purity of Commercial Toluene. J. S. Lumsden.

(*J. Chem. Soc.*, 1919, **115** and **116**, 1366-1372.)—Commercial toluene contains varying amounts of a liquid which cannot be nitrated and has distilled along with the toluene

during rectification. This liquid has not been isolated, but is probably of the nature of a paraffin mixture (B. Pt. 108-112. Density 0·743). The presence of 1 per cent. of such a liquid lowers the density of pure toluene (density 0·8712) by 0·0013, and a close approximation to the purity of a sample may be based upon a graph involving these data. *Estimation of Toluene by Nitration.*—Two methods may be adopted: (a) nitrating with a weighed excess of potassium nitrate, and determining the weight of nitric acid remaining: the amount of acid used is thus found which gives the weight of toluene nitrated; or (b) isolating and weighing the dinitro compound. The first of these works well, but with the second the whole of the dinitro compound cannot be recovered, as a small but definite trace remains in solution; this can, however, be allowed for. Examples of both methods, and the quantities used and obtained, are appended, together with working details. *Estimation of Toluene by Miscibility with Acetic Acid.*—Orton (*J. Chem. Soc.*, 1919, **115** and **116**, 1055) has shown that when acetic acid of 88 to 90 per cent. purity is mixed with toluene in certain proportions two layers are formed, and, on raising the temperature, a point of complete miscibility is reached which is definite for the same strength of acid and so sharply defined that it can be read to $\frac{1}{10}$ degree. The method is accurate, but it is very difficult to prepare and keep strong acetic acid at a definite strength without absorption of moisture from the air, and the author has devised a modification which consists in the changing of an absolute to a comparative method which may be carried out in any commercial laboratory. A quantity of concentrated acetic acid of unknown strength is taken, and, with equal volumes of this, the temperatures of miscibility with equal volumes of pure toluene, toluene with 5 per cent. of paraffins, and the sample of toluene to be tested, are found. Then, since the percentage of paraffins is proportional to the increase in the temperature of miscibility, the comparison of the rise of temperature of miscibility of the sample with that of the 5 per cent. paraffin mixture gives the paraffin content of the sample. As the miscibility point is approached, the two layers disappear, the liquid becomes opalescent, and then suddenly transparent. This is the point at which the temperature is noted. The same procedure is adopted with the 95 per cent. toluene and with the sample under examination. It is not necessary that the strength of the acid should be known, so long as it remains constant during the time that the three portions are withdrawn. When the same samples of toluene were tested by the different methods, the following results were obtained:

From sp. gr. curve	...	...	...	92·3 per cent.
From nitrometer estimation after nitration	...			92·9 ,, ,,
By weighing dinitro compound	...		...	92·6 ,, ,,
By temperature of miscibility with acetic acid				92·5 ,, ,,

The author concludes that the sp. gr. of commercial toluene gives a fair indication of the amount of impurity present; the estimation of the temperature of miscibility with acetic acid is quickly done, and, although a comparative method, if skilfully carried out it is trustworthy; the nitration and estimation of the excess of nitric acid by the nitrometer are believed to be the most accurate test and to indicate the total nitration which has taken place, while the weighing of the solid after nitration gives the actual practical yield of nitro compound. By none of the methods, under ordinary conditions of working, can an accuracy closer than 0·5 per cent. be expected.

H. F. E. H.

INORGANIC ANALYSIS.

Rapid Estimation of Carbon Monoxide in Air. A. R. Lamb and A. T. Larson. (*J. Amer. Chem. Soc.*, 1919, **41**, 1908-1921.)—Two rapid methods of estimating carbon monoxide in air are described. In the first method the mixture of gases is passed over a red-hot platinum wire, in contact with which the carbon monoxide is partially burned, and then through heated copper oxide to complete the combustion. After removal of the carbon monoxide, the gaseous mixture is conducted over a second platinum wire exactly similar in every respect to the first wire and heated by the same electric current. The first wire will be the hotter, owing to the combustion which occurs upon it, and this difference of temperature will cause a change in the relative resistance, which is indicated upon a suitable galvanometer. To insure uniformity of temperature in the surroundings the apparatus is enclosed in a regulated water thermostat, and the current of gas is conducted through long copper spirals, also within the thermostat, before reaching the platinum wires. It was found necessary to prevent eddies in the gas current, and this was effected by passing the gas through layers of cotton gauze before reaching the platinum wires. The second method is based upon the catalytic combustion of the gas at 275° to 300° C., in contact with platinum. The rise of temperature is measured by means of a thermo-couple and galvanometer, the deflections of the latter corresponding with definite concentrations of carbon monoxide. The apparatus consists of a vertical steel tube about 90 cm. long and 7·5 cm. in diameter, closed at one end, and covered, except for the uppermost 25 cm., with layers of asbestos paper. Diphenylamine is heated in this to produce a vapour-bath, the zone of condensation being kept within about 30 cm. from the top of the tube. The gaseous mixture is brought to the temperature of the vapour-bath by means of a 4 mm. pyrex glass tube extending to about 5 cm. from the bottom of the vapour-jacket, whence it winds backwards as a close coil about 15 cm. long and 6 cm. in diameter. Attached to this coil is a pyrex glass tube 15 mm. in diameter extending about 30 cm. above the top of the steel tube, and into this is fitted a tube containing the catalyst and thermo element. The catalyst is prepared from fine platinum wire or gauze. In the case of the former the wire is wound into a 2 mm. spiral and then compressed. The wire is cleaned with acid, then coated with platinum black electrolytically, washed, and electrolysed first in dilute sodium hydroxide solution and then in dilute sulphuric acid. The apparatus is calibrated by passing through it air containing known quantities of carbon monoxide at a constant speed and noting the deflections of the galvanometer. The introduction of halogens has a permanent toxic action upon the catalyst. Sulphur dioxide is also injurious, but its effect may be removed by raising the temperature to 350° C. and passing a current of air through the catalyst. It is shown that the method gives results accurate within 0·0038 per cent. on the total air mixture in the case of a mixture containing about 1 per cent. of carbon monoxide.

          C. A. M.

Rapid Tests of Cement. A Cavazzi. (*Annali Chim. Applic.*, 1919, **12**, 59-73.)—Samples of cement alone and in admixture with 2 and 3 parts of sand

were exposed to the action of hot (100° C.) and cold soft and sea water for periods up to 140 days, and the usual compression and tensile tests then applied. The comparative results indicated that at first cement hardens much more rapidly in hot water, but that after the seventh day there is not so much difference between the hardening in hot and in cold water. The results obtained with twenty-five different slow-setting cements and four quick-setting cements in comparative tests after exposure of 7, 28, and 90 days in cold water, and 2, 4, and 6 days in hot water respectively, varied according to which periods were chosen for the comparison, but the general conclusion from the whole series of experiments is that the more rapid heat test yields results quite in accordance with practice. C. A. M.
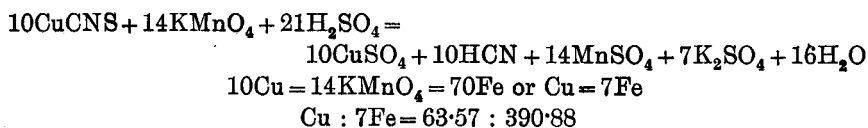
Moisture in Blast Furnace Coke. **W. H. George.** (*J. Soc. Chem. Ind.*, 1919, **38**, 394-396т.)—The best method of sampling when the wagon is unloaded through a side door is to wait until the wagon is one-third to one-half empty, and take the sample from the vertical sections thus exposed. The coke at the top is generally either wetter or drier than the rest owing to its exposure to the weather, and there is a tendency for the breeze (the wettest portion of the coke) to collect at the bottom during transit. Tests have shown that the small coke may contain two to eight times as much moisture as the large ; further, the outer layer of a lump may contain ten times as much water as the interior. These points have to be borne in mind when selecting the samples, which should be taken at regular intervals apart ; lumps should be broken through the middle. For routine work a sample weighing about 14 lb. consisting of about twenty pieces is sufficient. Owing to the extreme differences between the large coke and the small coke closer concordance than 1 per cent. is hardly to be expected. Crushing of the sample must be undertaken without delay, and the size of the sample must be reduced by quartering. Sieves should not be employed, as the loss of moisture during treatment is very rapid. The actual estimation of moisture in the prepared sample is a relatively simple matter, requiring none of the precautions which are necessary in the case of coal, and any temperature between 105° and 200° C. may be used. The distillation method is also applicable. The amount of water that can be absorbed by coke after immersion varies with its porosity and is given as 30·49 per cent. for hard coke, 39·26 per cent. for soft coke, and 51 per cent. for very soft coke. The effect of 1 inch of rain falling on a wagon designed to carry 12 tons of coke is to raise the moisture content of the coke by 2·4 per cent. J. F. B.

Permanganate Method for Copper. **L. F. Clark.** (*J. Ind. and Eng. Chem.*, 1919, **11**, 1138-1139.)—The following modification of this method is recommended. The copper is precipitated as cuprous thiocyanate from acid solution in the usual manner. The filter-paper containing the cuprous thiocyanate is placed in the beaker in which the precipitation was made, 25 c.c. of hot 4 per cent. sodium hydroxide solution are added, and the mixture stirred until the paper is shredded and the precipitate decomposed. About 25 c.c. of cold 15 per cent. sulphuric acid containing 1 per cent. of ferric sulphate are next added. The result is a mixture of ferric thiocyanate, ferrous sulphate, cupric sulphate, and a large proportion of

cuprous thiocyanate re-forms when the mixture is acidified. The mixture is titrated with permanganate until the ferric thiocyanate colour gives way and the mixture becomes 'whiter. Concentrated hydrochloric acid (5 c.c.) is now added to aid the solution of the residual cuprous thiocyanate. Finally, the solution is titrated to a stable permanganate pink. The equation for the reaction may be written :

$$10CuCNS + 14KMnO_4 + 21H_2SO_4 =$$
$$10CuSO_4 + 10HCN + 14MnSO_4 + 7K_2SO_4 + 16H_2O$$
$$10Cu = 14KMnO_4 = 70Fe \text{ or } Cu = 7Fe$$
$$Cu : 7Fe = 63{\cdot}57 : 390{\cdot}88$$

whence $Cu = 0{\cdot}1626$ Fe (Fe value of the permanganate). This is the theoretical factor, and the actual factor under the conditions followed by the author is $0{\cdot}1646$, a closer agreement with the theoretical than is found in older modifications of the permanganate method. G. C. J.

Electrolytic Estimation of Copper in Pyrites and Pyrites Cinders.

E. Mengler. (*Chem. Zeit.*, 1919, 43, 729.)—The following method avoids the use of hydrogen sulphide to separate copper from iron. The pyrites (5 grms.) is treated with 50 c.c. of dilute (1 : 1) nitric acid, which is subsequently evaporated until fumes of sulphuric acid arise. The residue is redissolved in 50 c.c. of fuming hydrochloric acid, 2 grm. sodium hypophosphite dissolved in a little water are added, and the solution evaporated to dryness at 110-120° C., whereby all arsenic is reduced and got rid of. Cinders are dissolved in hydrochloric acid direct and evaporated as described. To convert the chlorides to sulphates, the residue is heated with sulphuric acid containing a little nitric acid, and heating continued until dense fumes arise. The nitric acid ensures the solution of copper sulphide which may be present as a consequence of secondary reactions during the preceding operations. The residue is taken up in hot water, the solution filtered off from the lead sulphate and insoluble matter, 1 gr. citric acid and 2 grms. ammonium nitrate are added, the solution is diluted to 200 c.c., and the copper deposited electrolytically, using a platinum cathode of 200 sq. cms. surface and a current of 0·3 to 0·4 ampère (2·8 volts). Not all the lead present is deposited on the anode ; some comes down with the copper on the cathode, and the deposit must be redissolved in hot nitric acid and the solution re-electrolysed after cooling and addition of sulphuric acid. Pyrites free from arsenic and lead can be dissolved direct in 50 c.c. dilute (1 : 1) nitric acid and 20 c.c. dilute (1 : 2) sulphuric acid, evaporated to fuming, diluted, filtered, and electrolysed once after addition of citric acid and ammonium nitrate. The double precipitation in the process outlined above makes the process a slow one, but a number of estimations can be conducted simultaneously and the electrolysis can proceed overnight. The avoidance of the use of hydrogen sulphide is a point in favour of the method, which has been in use in the Duisburg copper works for twenty-five years. G. C. J.

Bibliography of the Use of "Cupferron" as a Quantitative Reagent.

S. A. Braley. (*J. Ind. and Eng. Chem.*, 1919, 11, 1144-1145.)—The author thinks

that " cupferron," the ammonium salt of nitrosophenylhydroxylamine (Baudisch : ANALYST, 1910, **35**, 78 ; 1911, 520), has not been given due consideration as a quantitative reagent. Reference is made to the works of Bellucci and Grassi (ANALYST, 1913, **38**, 390), Hanus and Soukup (*ibid.*, 1910, **35**, 453), R. Fresenius (*ibid.*, 1911, **36**, 175), Thornton (*ibid.*, 1914, **39**, 332, 565), Biltz and Hödke (*ibid*, 1910, **35**, 327); and to that of James Brown (*J. Amer. Chem. Soc.*, 1917, **39**, 2359), who used the reagent to separate iron, titanium, and zirconium from manganese and aluminium ; of Turner (*Am. J. Sci.*, 1916, [iv], **41**, 339) and Rodeja (*Anal. Soc. Espan. Fis. Quim.*, 1914, **12**, 379), who used it to separate vanadate from arsenate and phosphate ; of Wissenson (*Zeitsch. augen. Chem.*, 1911, **23**, 969), who used it to estimate iron in ferrocyanide ; and of Schroeder (*Zeitsch. anorg. Chem.*, 1911, **72**, 94), who gives some additional data for the separation of iron from cobalt and nickel.   G. C. J.

Electrometric Titration. W. D. Treadwell and L. Weiss. (*Helv. Chim. Acta*, 1919, **2**, 680-697.)—The electrometric titration of silver (with sodium chloride), hydrogen sulphide (with silver), mercurous salts (with sodium chloride), cuprous salts (with thiocyanate), zinc (with ferrocyanide), ferrous salts (with dichromate), uranyl salts (with permanganate), vanadyl salts (with permanganate), and acidimetric estimations are trustworthy.   W. P. S.

Theory of Electrometric Titration. W. D. Treadwell. (*Helv. Chim. Acta*, 1919, **2**, 672-680.)—The author discusses the electrometric titration of silver, mainly from a mathematical point of view. The influence of the presence of other salts on the change in potential during the titration has been investigated.   W. P. S.

Indirect Method for the Electrolytic Estimation of the Halogens. J. H. Reedy. (*J. Amer. Chem. Soc.*, 1919, **41**, 1898-1902.)—Solutions of halogen salts may be electrolysed with silver anodes, with the formation of an adherent deposit of silver halide on the anode and without precipitation in the solution, provided that an anodic potential of 0·59 volt is not exceeded. The use of a 0·5 molar solution of sulphuric acid was found most suitable for maintaining the electrolytic conductivity of the solution of the halogen salt. The cathode used was of bright sheet platinum, whilst the anode was composed of a frame of heavy silver wire covered with fine silver gauze, the whole being coated electrolytically with silver, and subsequently heated in an electric oven to make the deposit firm and adherent. The deposit of silver halide upon this anode was weighed, and the electrode then made the cathode in a dilute solution of sodium hydroxide, which was electrolysed until hydrogen formed freely on the surface. The resulting deposit of silver was washed, and the electrode heated to about 500° C. in an electric furnace, and again weighed, the loss in weight on reduction representing the weight of the halogen. Even in the case of chlorine, where the potential required for complete deposition lies very close to the solution potential of silver, the latter does not begin to dissolve until the deposition of the halogen is practically complete. If the solution becomes opalescent it can be cleared again by lowering the potential below 0·59 volt.   G. A. M.

Electrolytic Separation of Lead from Chromium and the Analysis of Chrome Yellow and other similar Mineral Pigments. J. Milbauer and I. Setlik. (*J. prakt. Chem.*, 1919, **99**, 85; through *Chem. Zeit. Uebersicht*, 1919, **43**, 257.) —Lead may be easily separated from chromium in the form of lead peroxide by using a solution containing 0·2 grm. of lead, 0·1 grm. of chromium, 20 c.c. of nitric acid (sp. gr. 1·4), and 15 c.c. of perchloric acid (sp. gr. 1·12) in 150 c.c. The mixture of nitric and perchloric acids readily dissolves all samples of lead chromate, including orange and red, on heating. On electrolysis of this solution, lead peroxide separates quantitatively and the chromic acid is reduced at the cathode to the chromium state. With a rapid rotation of the cathode (800 revs. per minute) and a current of 3·5 ampères at 2·5 volts, the separation of the lead peroxide and the reduction of the chromic acid is completed in half an hour. J. F. B.

Application of Rotating Reductors in Estimation of Iron. W. Scott. (*J. Ind. and Eng. Chem.*, 1919, **11**, 1135-1137.)—Ferric sulphate is rapidly reduced by rapidly rotating reductors of zinc or aluminium, either with or without the aid of a current of electricity. Quantities of iron such as 70 mgrms. are reduced quantitatively in less than three minutes by the use of a zinc reductor of 45 sq. cm. surface making 800 revs. per minute. For the reduction of such small quantities, the use of a current presents no advantage. In the reduction of quantities like 700 mgrms., using a rotating zinc cylinder of 75 sq. cms., the time required may be reduced slightly by using a current of 6 ampères, but by working at a boiling temperature only four minutes are required even without the use of a current. Aluminium operates somewhat more rapidly than zinc, but there is greater difficulty in obtaining aluminium of the necessary degree of purity. G. C. J.

Detection of Molybdenum by Means of Xanthic Acid. J. Koppel. (*Chem. Zeit.*, 1919, **43**, 777-778.)—This reaction, first noted by Siewert in 1864 (*Zeitsch. ges. Naturw.*, 1864, **23**, 5), has recently been referred to by Malowan (*Zeitsch. anorg. Chem.*, 1919, **108**, 73) as having been entirely overlooked by compilers of textbooks. It is, however, to be found in Gmelin-Kraut's *Handbuch* (7 Aufl., Band III., Abt. 1, 907), from which the author became acquainted with it many years ago. He adds a few lumps of potassium xanthate to the cold solution of the molybdenum compound, which solution should be as nearly as possible neutral. Mineral acid is then added. A yellow opalescence, due to separated xanthic acid, first appears, but in presence of molybdenum this becomes gradually red, and finally deep blue. If very large quantities of molybdenum are present, black oily drops separate. Malowan says the reaction is only produced by freshly prepared solutions of potassium xanthate, and that the solid reagent is useless. The author agrees that solutions do not keep, but finds the solid quite satisfactory. Oxalates must be absent, as their presence enormously reduces the sensitiveness of the reaction which will detect 0·005 mgrm. molybdenum in solutions containing as little as 0·0007 per cent. The fact that the coloured compound is soluble in chloroform makes it possible to detect molybdenum in even lower concentrations. Copper, [cobalt, nickel, iron, uranium, and tungsten interfere. G. C. J.

Volumetric Estimation of Nickel. J. Holluta. (*Monatsh. Chem.*, 1919, **40**, 281-291; through *J. Soc. Chem. Ind.*, 1919, **38**, 965A.)—The process depends on the fact that when a nickel salt reacts with dimethylglyoxime, acid is liberated, which is estimated by titration with alkali in the presence of phenol-phthaleïn or methyl red. A standard $\frac{N}{50}$ solution is prepared by dissolving 4·64 grms. of dimethylglyoxime in the requisite quantity of 97 per cent. alcohol (300 to 400 c.c.); 20 c.c. of $\frac{N}{1}$ potassium hydroxide solution are added with constant shaking, the solution is diluted to 1,000 c.c. with CO_2-free distilled water and filtered after twenty-four hours from any slight precipitate of potassium carbonate (the alcohol used must be free from aldehyde and neutral in reaction). The alkali content of the solution is checked by titration with standard acid, using phenolphthaleïn or methyl red as indicator. The nickel solution under examination is diluted to the required extent, exactly neutralised with $\frac{N}{10}$ or $\frac{N}{50}$ potassium hydroxide solution, 2 to 5 c.c. of the standard dimethylglyoxime solution are added, and, after vigorous agitation, the mixture is gently warmed, whereby the precipitate is caused to collect, leaving a clear liquor; the standard solution is then gradually added with frequent agitation until the solution acquires a permanent pale pink coloration. In consequence of the bulky nature of the nickel precipitate the amount of the metal in the solution should not exceed 0·03 grm. The method is particularly advantageous in dealing with very small quantities of nickel, and titration can readily be effected with $\frac{N}{100}$ solutions if methyl red is used as indicator. The results are not affected by the presence of the alkali salts of strong acids.

Method for the Analysis of Nitrous Gases and its Application to the Study of Towers for the Absorption of such Gases. A. Geake and F. J. Squire. (*J. Soc. Chem. Ind.*, 1919, **38**, 387-369T.)—The method described was devised for the analysis of gases in a system of absorption towers used in connection with a plant for the denitration of nitroglycerin spent acid; the gases consisted of a mixture of nitric oxide and peroxide, carbon monoxide and dioxide, oxygen and nitrogen. The sample of gas was collected in a bottle of such capacity that the sample contained about 0·3 grm. of nitrogen oxides; this bottle was fitted with a stopper through which passed a tapped tube. The portion of the tube inside the bottle was bent so as to reach nearly to the side of the bottle near the shoulder. The bottle was charged with 25 c.c. of $\frac{N}{2}$ permanganate solution and 1 c.c. of sulphuric acid, and the air was then exhausted as completely as possible. To take the sample of gas the external part of the tube (this had a diameter of 2 to 3 mm.) was inserted in the sampling hole while the bottle was held in an inclined position so that the permanganate solution covered the inner end of the tube, and the tap was opened for about one second, closed, and the bottle shaken thoroughly. The residual volume of gas, still under reduced pressure, was then measured by connecting the bottle with an Orsat apparatus. The portion of gas passing into the Orsat apparatus was used for the estimation of carbon dioxide (by sodium hydroxide) and oxygen (by phosphorus); the residue was taken to be pure nitrogen. Actually it contained carbon monoxide, but, as this is inactive, and has the same density as nitrogen, its presence was unimportant. Air was now admitted to the sample bottle,

and the excess of permanganate titrated with $\frac{N}{2}$ ferrous sulphate solution. The total combined nitrogen was estimated in this titrated solution by the ferrous sulphate method described by Bowman and Scott (ANALYST, 1915, **40**, 474). All the calculations were made in weights, the unit taken being 1 lb. per hour, and an explanation is given of the methods of making these calculations of the weights of the constituent gases passing through the plant.   W. P. S.

Estimation of Titanium in certain Italian Puzzuolanas.   **A. Cavazzi.** (*Annali Chim. Applic.*, 1919, **12**, 105-111.)—For the estimation of titanium in puzzuolanas the sample is finely powdered in an agate mortar, and 0·5 grm. moistened with 20 drops of dilute (1 : 1) sulphuric acid in a platinum crucible, mixed with 10 c.c. of hydrofluoric acid, and the liquid evaporated to dryness. The residue is heated with sulphuric acid to carbonise organic matter, then pulverised and fused with 4 grms. of potassium pyrosulphate at a temperature insufficient to liberate fumes of sulphuric acid, until the mass becomes of a grey tint. The temperature is then increased until the residue becomes yellowish-white, and is finally heated over a blow-pipe flame until the mass has become reddish-orange, but without excessive fumes appearing. The fused mass is dissolved in water and the solution, made up to 100 c.c., is stirred at intervals for thirty minutes and filtered. The titanium in the filtrate is estimated by adding 2 c.c. of 3 per cent. hydrogen peroxide and 2 c.c. of sulphuric acid and comparing the coloration with that given under the same conditions by standard solutions of titanium. A convenient method of preparing the standard solution is to use titanium sulphate, the amount of titanium oxide (TiO_2) in which may be rapidly estimated by heating the salt with successive quantities of ammonium carbonate until all sulphuric acid has been removed, and weighing the residue. The same method may also be used with any salt of titanium which is soluble in sulphuric acid and can be converted into pure TiO_2 by ignition. The amount of titanium estimated by this colorimetric method in four samples of Italian puzzuolanas ranged from 0·312 to 0·558 per cent.   C. A. M.

New Colorimetric Method for Estimation of Uranium.   **Von Müller.** (*Chem. Zeit.*, 1919, **43**, 739-740.)—The author finds that uranyl salts give intense colorations with aliphatic α-hydroxy and ketonic acids, with aromatic hydroxy-acids, and especially with polyhydric phenols. The colorations given by the polyhydric phenols are the most intense, but these substances are not suitable for quantitative colorimetric work because they and their compounds are so readily oxidised with consequent change in the intensity of the coloured compounds. Salicylic acid is free from this objection, and may be used for the colorimetric estimation of uranium. As little as 0·01 per cent. can be detected, and the most convenient concentration for colour comparisons is 0·05 per cent. uranium. The uranyl solution, which must be free from iron and from mineral acids and must not contain large quantities of free acetic acid, is mixed with an equal bulk of a 2 per cent. solution of sodium salicylate, and comparison is made with a standard solution in a Dubosc colorimeter.   G. C. J.
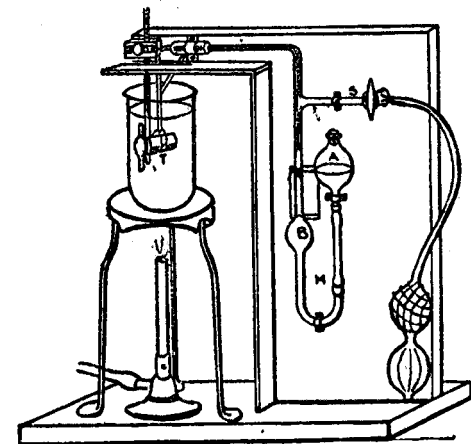
Analysis of Vanadium Compounds by Means of Carbon Tetrachloride.

P. Jannasch and H. E. Harwood. (*J. prakt. Chem.*, 1918, **97**, 93 ; through *Chem. Zeit. Übersicht,* 1919, **43**, 209.)—A general method for the separation of vanadium from other metals depends on the volatility of vanadium oxychloride when the vanadium salt or compound is heated in a current of carbon tetrachloride vapour. The carbon tetrachloride is added drop by drop to sulphuric acid heated at 120° to 140° C., and the vapour is led into the slightly heated tube containing the vanadium compound. A current of carbon dioxide is also passed through the tube, and, when all the vanadium has been volatilised, the residue is allowed to cool in a current of this gas. The vanadium oxychloride is collected in a receiver containing 200 c.c. of water and 50 c.c. of nitric acid. The contents of the receiver are then evaporated, the vanadic acid dissolved in dilute sulphuric acid, reduced with sulphurous acid, and the resulting bright blue vanadyl sulphate solution titrated with hot permanganate sc'   W. P. S.

APPARATUS, ETC.

Determination of the Softening-Point of Asphaltum and other Plastic Substances.

D. F. Twiss and E. A. Murphy. (*J. Soc. Chem. Ind.*, 1919, **38**, 405-406т.)—The apparatus illustrated in the figure has been designed to overcome certain objections attendant upon the Krämer-Sarnow method, which is regarded as the most satisfactory method hitherto proposed. The apparatus consists of a U-tube, *M*, one arm of which is connected by capillary tubing with a gun-metal tap, *T*. The central plug of this tap has a conical or tapered bore, $\frac{1}{4}$ in. in length and $\frac{1}{8}$ in. and $\frac{1}{16}$ in. in diameter at the respective ends. The bore is terminated at each end by a flat groove, to which its axis is perpendicular ; the capillary metal tube of the tap is connected with the glass capillary by means of a well-s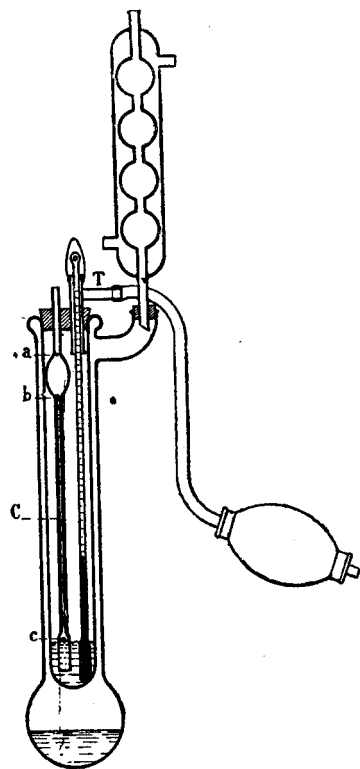ealed metal sleeve. To carry out the test the sample of bituminous material and the clean plug of tap *T* are warmed in a steam-oven for about ten minutes so that the material becomes somewhat plastic ; a piece of the softened material is then pressed into the wider end of the bore of the warm tap plug as speedily as possible with a small spatula until the bore is filled and a little protrudes from the other end. The tap plug is then allowed to cool and the excess of material is carefully removed so as to leave the exposed surfaces of material flush with the metal. The plug is refitted in the tap with the narrow end of the bore facing downward. Air is forced into the apparatus until the

U-tube containing mercury indicates an internal pressure equivalent to 1·5 in. of mercury. The medium in the bath is then warmed until the bitumen in the tap plug is so softened that it is forced completely through the narrow end of the bore, a point which is immediately indicated by the mercury in the U-tube. The construction of the tap in metal affords ready transmission of heat, and, since the indication of the softening-point takes place outside the bath, any discoloration of the latter is of no account. The results obtained with this apparatus are substantially higher than by the Krämer-Sarnow method, the differences ranging from 5° to 30° C. The apparatus is equally suitable for the examination of balata and gutta-percha. It is essential that the material to be examined be prepared free from air and moisture.

<div align="right">J. F. B.</div>

New Form of Viscometer. G. Baume and H. Vigneron.

(*Ann. Chim. anal. appl.*, 1919, **1**, 379-383.)—The apparatus here shown affords a simple means of determining the viscosity of liquids either in terms of absolute viscosity or in conventional degrees (Barbey or Engler). The viscosimetric tube, C, of the capillary type, is immersed at one end in the oil, etc., under examination in the tube C, whilst its upper end passes through the rubber stopper of C. This tube is surrounded by an outer thermostatic jacket in which a liquid of constant boiling-point (ether, 33·5° C.; acetone, 56·5° C.; benzene, 80·3° C.; or water) is kept boiling, the upper branch of this tube being connected with a reflux condenser. After the thermostatic liquid has boiled for fifteen minutes, oil is forced up into the viscosimetric tube by compressing the bulb connected with T. The time in seconds occupied by the oil in falling between the points a and b is noted, and the absolute viscosity is calculated by means of the formula $\eta = K.d.t$, where K represents a constant of the apparatus, d the sp. gr. of the liquid, and t the time. Duplicate determinations should agree within a few tenths of a second. The relationship between the absolute viscosity and the Barbey and Engler degrees is found by means of the formulæ,

$$E = \frac{663}{F}, \quad E = \frac{\eta}{0·0732d},$$

where E and F represent the respective Engler and Barbey degrees, η the absolute viscosity, and d the sp. gr. of the liquid.

<div align="right">C. A. M.</div>

Clip for preventing Rubber Connections from slipping off Glass and Metal Tubing, and for attaching Pressure Pumps to Taps. C. A. Keane and G. Patchin. (*J. Soc. Chem. Ind.*, 1919, **38**, 391т.)—The clip is made in two halves hinged together and held in the closed position by means of a thumbscrew so that it encloses the rubber connection around the glass tube. For attaching a pump to a water tap a special form of hinged clip provided with a sleeve is employed. The tap and pump are first connected with rubber tubing, and the clip with the sleeve is fitted over the rubber attached to the pump. A second hinged clip without a sleeve is then clamped over the portion of the rubber attached to the tap. The second clip should slightly overlap the top of the sleeve of the first one. This form of attachment prevents the bulging of the rubber when the pump is in use. J. F. B.

New Method for the Physico-Chemical Analysis of Precipitates. Application to the Study of Calcium Phosphates. P. Jolibois. (*Comptes rend.*, 1919, **169**, 1161-1163.)—The reacting solutions are allowed to mix in the stem of a Y-tube, to which they are admitted separately through the two arms; the solutions mix in about 0·01 second. The author has studied the reactions taking place when calcium hydroxide solution (1 grm. of CaO per litre) is mixed with phosphoric acid solutions of varying strength, the precipitates formed after one second being separated and analysed. Dicalcium phosphate forms only in a solution containing at least 0·800 grm. of P_2O_5 per litre in the form of monocalcium phosphate, whilst tricalcium phosphate is stable only in a solution containing less than 0·1 grm. of P_2O_5 per litre as monocalcium phosphate. A well-crystallised phosphate having the formula $P_2O_5 2CaO, P_2O_5 3CaO, 10H_2O$ was obtained when the solution contained from 0·375 to 0·870 grm. of P_2O_5 per litre as monocalcium phosphate; if the P_2O_5 content of the solution was increased this compound changed gradually into dicalcium phosphate. W. P. S.

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REVIEWS.

An Introduction to Theoretical and Applied Colloid Chemistry. By Wolfgang
Ostwald: translated by Martin H. Fischer. Pp. xv + 232. New York:
John Wiley and Sons. London: Chapman and Hall. 1919. Price 11s. 6d. net.

The last twenty years have witnessed remarkably successful attempts to bridge
the gap existing between molecular solutions on the one hand and coarse mechanical
suspensions on the other. The author speaks of this gap as "the world of neglected
dimensions," and in his enthusiastic exposition refers to colloid chemistry as a separate
and independent science. "Since the birth," he says, "of the so-called classical
physical chemistry of the molecular solutions, some thirty years ago, no branch of
physics or chemistry has arisen which can be compared in importance, so far as
scientific and technical applications are concerned, with that of colloid chemistry."
Whether this contention is justified or not, the author has produced in the present
volume an authoritative summary of the physics and chemistry of dispersed systems
which is well worth perusal by chemists of all kinds.

The book is based on a series of lectures delivered in North America in the
winter of 1913-14, the lectures being designed mainly for audiences without any
specialised knowledge of colloid chemistry. The survey is therefore a general one,
but is at the same time very comprehensive, as may be seen from the main headings
of the five chapters: Fundamental Properties of the Colloid State; Colloids as
Examples of Dispersed Systems; Methods of Preparing Colloid Solutions; Classifi-
cation of the Colloids: The Physico-chemical Properties of the Colloids and their
Dependence on the Degree of Dispersion; The Changes in State of Colloids; Some
Scientific and Technical Applications of Colloid Chemistry.

So numerous are the points at which the author detects the trail of the colloid
that organic and analytical chemists, scientific and technical workers, will all find
interest and stimulus. In the region of analytical chemistry reference may be made,
for example, to the passing of precipitates through filters, to the Cassius purple test
for gold, to Donau's borax bead method of detecting minute traces of the noble
metals, and to Ley's test for distinguishing natural from artificial honey, as cases
where the principles of colloid chemistry are applicable.

The author discusses at some length, and rightly so, the exact meaning to be
attached to the term "colloid," and the relation of colloids to mechanical suspensions
on the one hand, and to molecular solutions on the other. Colloids, it must be
clearly borne in mind, are not a particular class of chemicals, for apparently every
substance may assume the colloidal state under suitable conditions. The colloidal
state is determined solely by the degree of dispersion, and colloids are accordingly
defined as dispersed systems in which the diameter of the dispersed particles in
typical cases lies between 0.1μ and 0.001μ. This clear definition suggests criticism of
the author's introduction of the term "isocolloid," by which he appears to indicate
certain substances capable of furnishing both the dispersion medium and the dispersion
phase, and which, therefore, seems to the reviewer to be incongruous with "colloid."

The relation of colloid chemistry to the older branches of the science is, in various directions, somewhat ill defined, and one prominent feature of the present volume is the challenging attitude adopted towards some of the generally accepted views held by physical chemists. The author tilts, for example, at the rôle assigned to osmotic pressure in connection with water movement in organisms, at the neglect of the capillary factor in the theory of freezing-point depression, and at the van't Hoff theory of solid solution and the phase rule as applied to alloys in which the degree of dispersion is particularly high. Such pleas for the reconsideration of current views rather add to the stimulating character of the volume, but it is unlikely that the author's contentions will be satisfactorily established unless colloid chemistry can be developed, much more than has been found possible hitherto, on the quantitative lines to which physical chemistry owes the strength of its present position.

JAMES C. PHILIP.

THE LIBRARY OF THE CHEMICAL SOCIETY. A RECORD OF A ·RECENT ATTEMPT AT CO-OPERATION. By F. W. Clifford. Reprinted from the Library Association Record, 1919, Caxton House, London.

In this reprint from the Library Association Record, Mr. Clifford gives an account of the inception of the scheme inaugurated two years ago for widening the scope of the Chemical Society's library by adding to it works of a technical character hitherto regarded as being outside the range of that Society's purview.

The outstanding feature of the scheme, however, is the extension of the valuable privilege of using the library to the members of other societies which in their corporate capacity have arranged to give it financial support. These are the Association of British Chemical Manufacturers, the Biochemical Society, the Faraday Society, the Institute of Chemistry, the Society of Chemical Industry, the Society of Dyers and Colourists, and the Society of Public Analysts. The members of these, whether Fellows of the Chemical Society or not, are allowed the full use of the library both for loan and reference, and the value of the privilege is increased by the fact that the hours of opening have been extended, being now from 10 a.m. to 9 p.m.; Saturdays, 10 to 5.

That stern taskmaster, the Great War, is responsible for bringing about this far-reaching change in the attitude of the oldest of the societies connected with chemical science, and, as a first step towards the removal of the arbitrary barriers which have hitherto separated the pure and the applied branches of the science, can only be to the good. It is greatly to be hoped that it will not stop here, but will eventually lead to a much closer association between some of the societies concerned.

One thing seems quite clear—namely, that with the extended use of the library and the addition to its shelves of books dealing with fresh classes of subjects, the premises at Burlington House will soon become as hopelessly inadequate, as they always were unsuitable, for their purpose.

A building consisting mainly of staircase with a library perched at the top, so small that many books have to be stored in the basement forty or more feet below, and unprovided with a lift, can hardly be considered a fitting home for the premier chemical society, or worthy of the science to which the country owes so

much. In recognition of its services during the war, surely the Government might find some edifice—even a *small* hotel might do—where all the societies concerned with the science could have a common meeting-place, with ample space for the library and a museum of old apparatus (why not modern, too?) and prints and pictures connected with the early days of the science. The apathy of the chemist towards the historical side of his subject is notorious, and the appliances of the earlier workers are in many cases either left to decay or find their way to America, where the great Universities seem to be more alive to interest of these relics of bygone days.

There is one other matter which has long been talked about which the broad-minded policy of the Chemical Society must surely have brought at last within the range of practical politics. It is a standing reproach to our commonsense that four or five different journals should at the same time be abstracting the same papers and printing them each in different type and on pages of a different size, when, with co-operation of the various institutions concerned, much of all this unnecessary labour and expense might be avoided. No doubt there are serious difficulties in the way—vested interests might have to suffer and long-established practices have to be given up—but the latest enterprise of the Chemical Society warrants the belief that even these obstacles might be overcome.   C. H. CRIBB.