

state of active fermentation. It was thought that the samples were of light gravity, but moisture determinations showed 21.1 per cent., the normal quantity for 41° Bé. syrup. This fermentation was found to exist not alone in the 41° syrup but in samples of 42° Bé. containing 20.19 per cent. moisture.

Cultures of the various liquors in the refinery showed that the ferment was introduced into the goods at some point after the 39° Bé. vacuum pan.

To prevent the finished goods from fermenting the following experiments were made with well-known antiseptic materials.

1.46 pounds of 40° Bé. sodium bisulphite added to each barrel of fifty-two gallons. No effect.

One-half ounce boracic acid and one-quarter ounce benzoic acid to each barrel of fifty-two gallons. No effect.

1.46 pounds of 40° Bé. sodium bisulphite, one-half ounce boracic acid, and one-quarter ounce benzoic acid to each barrel of fifty-two gallons. No effect.

TOPEKA, KANSAS, October, 1894.

ON THE TECHNICAL ANALYSIS OF ASPHALTUM.

BY LAURA A. LINTON.

Received September 21, 1894.

IN the year 1837, J. B. Boussingault published his celebrated memoir on the "Composition of Bitumens." In the researches upon which this memoir was based he had discovered that certain bitumens yielded to one class of solvents a portion of their content and to another class of solvents another portion of their constituent hydrocarbons. He called the first portion "Petrolene" and the second portion, "Asphaltene."¹

In 1827² Le Bel and Muntz went over the same ground and in 1883 Le Bel again went over it, adding a few facts in relation to other bitumens than those previously examined but leaving the two substances, petrolene and asphaltene, practically where he found them.³

In 1837 the conclusions based on chemical research were far less exact than at the present time and Boussingault concluded that the substances, petrolene and asphaltene, were simple sub-

¹ *Annales de Chimie et de Physique*, 64, 141.

² *Bull. Soc. Chim.*, 17, 156. ³ *ibid.*, 50, 359.

stances and also that they were identical from whatever sources they were derived. In this conclusion Le Bel in a measure appears to coincide.

It, however, requires no argument to prove, to any one at all familiar with the subject, that petrolene is nothing but a name that covers a great variety of substances, radically unlike, that exist in different forms of bitumen and are only related, in this instance, as being held in solution by a certain limited number of menstrua and which include the whole list of paraffines and iso-paraffines, the olefines, the benzenes and additive benzenes with many other less abundant and well-known substances.

Ethyl ether and so-called petroleum naphtha, which latter is an indefinite mixture of fluid paraffines and iso-paraffines of high specific gravity, are the solvents used; but no determination has been made as to the influence of proportion in the mixtures of the substances dissolved, or as to the relative solvent powers of the two menstrua upon the different constituents of these mixtures. In fact petrolene is nothing but a name which at present covers a vast expanse of the unknown.

It can be safely said that probability favors the assumption that asphaltene is a little more definite; but no certainty attaches to the identity of asphaltene from different sources or of asphaltene dissolved by different menstrua.

Therefore, in a general way, it may be said that asphaltene is that portion of the different forms of bitumen that is soluble in carbon disulphide, chloroform, benzene and a few other less well-known liquids and is not soluble in the menstrua that dissolve petrolene.

As the bitumens examined by the French chemists, above mentioned, have never assumed commercial importance, the questions relating to petrolene and asphaltene have remained matters of scientific interest only. However, since asphalt paving has become a business involving the expenditure of large sums of money these problems are beginning to assume a wide importance outside the laboratory of the chemist and to demand from technologists very serious consideration. Within recent years large numbers of so-called analyses have been reported, which represent various attempts to determine and set forth the rela-

tive value of many samples and kinds of asphaltum, that may or may not be suitable for the many uses to which asphaltum is applied, but more particularly with reference to street paving. Prominent among the chemists who have been more or less extensively engaged in these analyses of asphalts are Mr. Clifford Richardson, Dr. Henry Leffmann, Dr. Samuel P. Sadtler, and Dr. De Smedt.

A perusal of the numerous published reports of Mr. Richardson reveals the fact that in his tests the solvents used for the extraction of petroleum and asphaltene, were petroleum ether and carbon disulphide, while Drs. Leffmann and Sadtler, in their investigations and tests of asphalts, used alcohol—presumably ethyl-alcohol—carbon disulphide, and ether as shown by the report submitted to the Citizens' Municipal Association and the Trades League of Philadelphia.

Neither of these gentlemen describe any process or method employed in obtaining the results stated. It is hardly consistent with the nature of the reports that they should. Nor has Mr. Richardson, in an article published in the *Journal of Analytical and Applied Chemistry*, in the numbers for December, 1892, and January, 1893, given any detailed description of the process he employed in order to obtain the numerous results of analysis that he there uses.

But little satisfaction can be derived from consulting Allen's encyclopedic work so exhaustive upon every subject relating to technical organic analysis.¹

We find therein the following statements and notes concerning the solvents and methods used in the analysis of asphalts: "For the determination of the *total bituminous matters* in asphalt rock and mixtures containing it, C. T. Kingzett extracts the air-dried sample with freshly distilled Russian oil of turpentine, evaporates (*Analyst* 8, 4) the resultant solution and weighs the residue. The matter insoluble in turpentine is washed with ether, the *calcium* and *magnesium* carbonates dissolved in hydrochloric acid and the washed insoluble *siliceous matter* weighed."

"H. P. Cooper prefers carbon disulphide for dissolving out the bituminous matters from asphaltic mixtures."

¹ Commercial Organic Analysis, by Alfred H. Allen, London, 1886, 2, 375, 376, 377.

Allen adds in a note, "The carbon disulphide employed for dissolving the bituminous matter must not contain free sulphur. It may be replaced by chloroform or benzene (coal tar naphtha). If the residue left after extraction be dark colored, foreign organic matters of valueless nature are present. Their proportion may be determined by igniting the weighed residue left after dissolving out the asphaltum, recarbonating it with ammonium carbonate, again gently heating it and reweighing. The loss of weight is the amount of *non-bituminous* organic matter present. In the case of samples leaving a white residue after exhaustion with carbon disulphide, the bituminous matter may be simply and accurately ascertained from the loss on ignition, taking care to recarbonate the lime before weighing."

In another note, page 377, he says: "Five grams of the finely divided sample were digested for one hour with fifty cc. of petroleum spirit (sp. gr. 0.7) and the mixture frequently agitated. The liquid is then boiled for a short time, decanted and the residue boiled with another quantity of twenty-five cc. of petroleum spirit. This treatment is repeated eight or ten times until the exhaustion is complete.

"E. Davies (*Pharm. Jour.*, [3], 14, 394), reports that none of the organic matter in Val de Travers asphalt is insoluble in petroleum spirit."

Now, when we take into consideration the fact that turpentine, carbon disulphide, ether, chloroform, and benzene have been used indiscriminately by chemists in the extraction of asphaltene, the question very naturally arises are the results that have been and that are being obtained by these different methods of analysis strictly comparable—that is, are they convertible terms? Will the same asphalt treated with different solvents show in each case the same percentage composition? If not, then it is evident that asphalt taken from different localities and subjected to dissimilar methods of analysis cannot yield results of any value so far as purposes of comparison are concerned. Then again, if turpentine, carbon disulphide, and chloroform give a different proportion of asphaltene in the same asphalt it is just as evident that asphaltene, instead of being a definite

chemical substance, is a mixture, which mixture would doubtless vary in different asphalts.

It was for the purpose of determining whether petroleum ether (paraffines), California naphtha, and ethyl ether are interchangeable solvents of petrolene and whether turpentine, carbon disulphide and chloroform are interchangeable solvents of asphaltene that the research, the results of which are here given, was undertaken. That a series of such tests, faithfully carried out, should lead to the establishment of a method of analysis applicable to all asphalts and, at the same time, reveal something regarding the real nature of petrolene and asphaltene was inevitable.

The specimens analyzed were furnished me by Prof. S. F. Peckham, Chemist of the Union Oil Company of California, and were as follows:

1. *Crude Trinidad Asphaltum*.—From the Warren-Scharf Asphalt Company, of New York City. This specimen contained little or no water, as, for several months, it had been broken in small pieces, and so had lost the water which this asphaltum generally contains.

2. *Cuban Asphalt*.—A commercial sample obtained in New York City.

3. *Kuban Residuum*.—An artificial asphalt obtained from the distillation of Kuban petroleum from the western extremity of the Caucasus Mountains, Russia.

4. *Egyptian Asphalt*.—An Assyrian asphalt taken from the Dead Sea and imported into Egypt. This specimen was obtained in New York City.

5. *Asphaltic Rock*.—From Val de Travers, Switzerland. This asphalt was a sample of natural rock obtained at the office of Wm. H. Delano, representative of the French Company in New York City.

6. *Seyssel Asphaltic Rock*.—From the well-known locality in eastern France, obtained from the same source as No. 5.

7. *Turrellite*.—From a deposit lately discovered in Uvalde County, Texas, consisting of a mass of sea-shells cemented together by bitumen into a solid rock mass. It occurs in a rock formation said to be of Jurassic age, in which formation the Val de Travers rock also occurs. This specimen was obtained from

the office of the Litho-carbon Company of New York City.

8. *Kentucky Asphaltic Rock*.—Obtained from Marshall Morris, Esq., Louisville, Ky.

9. *An Asphaltic Mineral*.—Resembling Gilsonite; reported as coming from Utah.

10. *California Maltha*.—Taken from a well at Summerland, on the coast, near Santa Barbara.

11. *Asphaltum*.—From mines recently opened near Asphalto, Kern County, California, in the eastern foot hills of the Coast Range Mountains, about thirty miles west of Bakersfield.

12. *Asphaltic Sandstone*.—From San Luis Obispo, California.

13. *Asphaltum*.—Picked up on the beach at San Buena Ventura, California, washed in from the Santa Barbara channel.

14. *Asphaltum*.—From the Ojai ranch, Ventura County, California.

15. *Grahamite*.—A so-called asphaltum taken from a vein in Ritchie County, West Virginia.

16. A portion of a compressed brick made from the asphaltic rock taken from the Seyssel mines. Exhibited at the Columbian Exposition.

17. *Hard Artificial Asphalt*.—An asphaltic residue obtained from the distillation of petroleum obtained near Santa Paula, California. It is known in the refinery of the Union Oil Company, of California, as grade "B."

18. *Soft Artificial Asphalt*.—From the refinery of the Union Oil Company, of California, at Santa Paula. Grade "D."

19. *Asphaltic Pavement*.—Obtained from Franklin Avenue, Buffalo, N. Y. It was laid in 1878, of Trinidad asphalt, wax tailings, and very fine sand. It is remarkable as having been laid for fifteen years with almost no need of repairs.

20. *Asphaltic Pavement*.—From Governor's Island, New York Harbor, laid within the Fort at an unknown date, but so old that it has begun to break up from natural causes. Obtained from J. A. W. Pine, of New York City.

21. *Dubb's Artificial Asphalt*.—A so-called asphaltum obtained in operating the Dubb's patent process for the manufacture of asphaltum by adding sulphur to hot Lima-tar and thereby burn-

ing out the hydrogen. This is an asphalt only in name. The specimen was obtained from J. A. W. Pine, of New York City.

22. *Roofing Pitch*.—Obtained from the Mica-asphalt Company, of New York City.

23. *Pitch*.—Obtained as a residuum in the distillation of Scotch blast-furnace tar. This specimen was obtained from the same source as Nos. 20 and 21.

In making tests to determine the best method to be used in the analysis of asphalts the well-known Trinidad and Cuban asphalts were used and all analyses were made in duplicate. In the case of asphalts rich in bituminous matter about a half gram of the material, finely powdered, was used but in the case of asphalts in which the mineral matter constituted a large proportion the quantity was increased to several grams.

The sample was weighed in an Erlenmeyer flask and digested over night in about fifty cc. of petroleum ether; in the morning the clear solution, containing the dissolved petrolene, was passed through a balanced filter and a fresh portion of petroleum ether added to the contents of the flask. The second digestion was continued for two or three hours when the solution, as before, was filtered off and the process repeated until the whole of the petrolene had been removed. The contents of the flask were then thrown upon the filter and thoroughly washed with petroleum ether. Cold turpentine was then poured upon the filter in successive portions until the filtrate passed through colorless when the assumption was made that all the asphaltene and consequently all the bituminous matter had been removed.

The remaining organic matter, not bituminous, was determined by difference, that is, the residue on the filter, after digestion in turpentine, was washed with ethyl alcohol, dried, and weighed in order to determine the percentage of asphaltene after which the residue was burned in a platinum crucible, the difference in weight representing the organic matter not bituminous.

The contents of the crucible were now purely inorganic and, in the case of most asphalts, the residuum was sand more or less colored with iron.

The analysis of Trinidad asphalt under this treatment gave so low a percentage of asphaltene and so large a proportion of

organic matter not bitumen, that it was clearly evident that *cold* turpentine had not dissolved, and could not dissolve all of the asphaltene.

A second set of experiments was then tried in which cold turpentine and carbon disulphide were used as solvents of asphaltene. The results obtained for samples 1 and 2 were as follows :

Sample.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1.....	32.54	20.3435	12.368	34.6775	99.929
" 2.....	25.049	54.53	2.441	17.9215	99.9415

The experiment was now made of somewhat varying the method of treatment for the following reasons: First, because of the difficulty of dissolving out the asphaltene while on the filter by simply allowing the solvent to run through it, and secondly, because, in consequence of the high specific gravity of petroleum ether, a considerable portion of sand or other mineral matter, mixed with asphaltene, always adhered to the flask, thus necessitating a separate determination of this portion. The method now employed for the removal of petrolene and asphaltene was the decantation method, and the solvents used for asphaltene were hot turpentine and chloroform.

The samples were digested over night in petroleum ether; in the morning the solution containing the petrolene was, as far as practicable, removed from the flask and the remainder was evaporated over a steam-bath; after weighing, the residuum containing the asphaltene was digested in hot turpentine over the steam-bath, and finally, the whole contents of the flask were poured upon a balanced filter and treated as in the first experiments.

The percentage composition of Nos. 1, 2, and 17, as determined by the decantation method, was as shown in the following table :

Sample.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1.....	31.51	22.9865	11.4195	34.073	99.989
" 2.....	25.055	52.245	5.758	16.918	99.962
" 17.....	64.571	21.2545	13.706	0.3613	99.8928

In carrying out this method a great many determinations were lost, due to the fact that, in evaporation to dryness over the steam-bath, the contents of the flask were in part bumped out. In consequence, this method was soon abandoned as impractical.

ble, and finally, funnels with stop-cocks were employed, in which the contents of the filter could be digested. Boiling hot instead of cold turpentine was used, and, when necessary, the digestion was continued over night, and all the after washings were made with hot turpentine. Numerous trials showed that carbon disulphide dissolves little more than hot turpentine. The last trace of asphaltene, insoluble in either turpentine or carbon disulphide, was removed by chloroform.

In order to determine the relative solvent power of hot turpentine, carbon disulphide, and chloroform, the following method of qualitative analysis was applied to the twenty-three samples enumerated above. From a half gram to one gram of the material was digested over night in a four-ounce Erlenmeyer flask with about fifty cc. of petroleum ether. Next morning the contents of the flask were poured upon a filter, and the undissolved residue washed with petroleum ether until the filtrate was no longer colored. Boiling spirits of turpentine was then poured upon the filter until it passed through colorless, when carbon disulphide was used in the same manner, followed lastly by chloroform. The action of the successive solvents is shown in the following table :

Sample No.	Hot turpentine.	Carbon disulphide.	Chloroform.
1.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 2.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a perceptible amount.
" 3.	Dissolves nearly all.	Dissolves a trace.	Dissolves a trace.
" 4.	" " "	" the slightest trace.	" the slightest trace.
" 5.	" " "	Dissolves a trace.	Dissolves a perceptible amount.
" 6.	" " "	" "	Dissolves a perceptible amount.
" 7.	" " "	" the slightest trace.	Dissolves the slightest trace.
" 8.	" " "	Dissolves the slightest trace.	Dissolves a trace.
" 9.	" nothing.	Dissolves nothing.	" "
" 10.	" nearly all.	" a trace.	" a perceptible amount.
" 11.	" " "	" "	Dissolves a perceptible amount.

Sample.	Hot turpentine.	Carbon disulphide.	Chloroform.
No. 12.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 13.	" " "	" "	Dissolves a perceptible amount.
" 14.	" " "	" "	Dissolves a perceptible amount.
" 15.	" a large amount.	" a considerable amount.	Dissolves a considerable amount.
" 16.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 17.	" a large amount.	" a considerable amount.	Dissolves a considerable amount.
" 18.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
" 19.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 20.	" " "	" "	Dissolves a perceptible amount.
" 21.	" " "	" "	Dissolves a trace.
" 22.	" a large amount.	" a considerable amount.	" "
" 23.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.

Of the twenty-three asphalts examined, there was not one that did not yield some asphaltene on treatment with chloroform; consequently, it is safe to infer that in the analysis of asphalts, unless final washing be made with chloroform, the per cent. of asphaltene will be too low. There was a marked difference observed in the different asphalts as to the manner in which their constituent asphaltene was dissolved on treatment with hot turpentine. In Nos. 4, 5, 6, and 7, and a few others, the asphaltene dissolved out in a few minutes, while in the case of others, notably No. 15, it was a matter of hours, and even of days, before every trace soluble in turpentine could be removed. No. 9 seems to be an asphaltic freak as it contains no petrolene whatever and is insoluble in both hot turpentine and carbon disulphide, while chloroform and amylic alcohol dissolve but the slightest trace.

It was a difficult matter to determine the relative quantity of asphaltene dissolved by the different menstrua, as the only guide used was the color of the filtrate. This suggests a most

interesting research—the fractional, quantitative determination of asphaltene.

From my experience in the analysis of asphalts, I would advise that a preliminary qualitative analysis be always made of each new variety of asphaltum before any quantitative determinations are attempted, care being taken to observe the behavior of different asphalts with the different solvents. This method of procedure is to be recommended, not only because it would prove an economy of time and reagents used, but also because, in this way, much would be learned concerning the nature of petroleum and asphaltene.

A trial was made with Cuban asphalt to determine the solvent power of petroleum ether (87° Beaumé) as compared with that of California naphtha (74° Beaumé) and ethyl ether with the following results:

Sample.	Solvent for petroleum.	Per cent. of petroleum.
No. 2.	Petroleum ether.....	25.8516
“ “	California naphtha.....	32.444
“ “	Ethyl ether.....	32.5455

The high percentage of petroleum when California naphtha or ethyl ether are used indicates that the asphaltene is, in part, dissolved, and consequently, that these menstrua can not be used as solvents of petroleum in the determination of asphalts.

In selecting a method for the quantitative analysis based upon the results of these experiments, it is assumed that, until a strictly scientific method is worked out, the present empirical determination of petroleum and asphaltene will continue in use. The three considerations of economy, speed, and convenience, will together control the selection. So long as the significance of the difference between the 25.8 per cent. dissolved by petroleum ether and the 32.5 per cent. dissolved by ethyl ether is an unknown element in the problem—that is, whether it be seven per cent. of petroleum or of asphaltene that is involved—it is better to use petroleum ether, because it is cheap and easily obtained of a uniform quality. So, too, it is better to use boiling hot turpentine followed by chloroform as solvents of asphaltene, and thus rid ourselves of carbon disulphide altogether.

With these considerations in view the following method of analysis is recommended:

Weigh two suitable portions in four-ounce Erlenmeyer flasks, add fifty cc. of petroleum ether, cover, and allow to stand over night. The following morning decant the liquid upon a balanced filter placed within a three-inch funnel provided with a stop-cock in the neck. Add another portion of petroleum ether to the flask, allowing two or three hours for digestion, and decant the liquid upon the same filter as before; this process is to be continued until the liquid ceases to be colored, then transfer the whole of the bitumen to the filter. Dry the flask in a steam-bath and weigh; any increase in weight of the flask should be subtracted from the amount determined as petrolene. Wash the filter and its contents with petroleum ether, place these with the filter counterpoise in a steam-bath, dry, and weigh; the loss in weight of the bitumen represents the petrolene.

Rinse the flask thoroughly with boiling turpentine and add the liquid to the filter in the closed funnel, pour upon the filter a sufficient quantity of boiling turpentine to wholly submerge it, cover and allow the digestion to continue for several hours or over night. Repeat the digesting and filtering with boiling turpentine until the filtrate becomes colorless. The filter should be much smaller than the funnel. Rinse the flask with chloroform and pour upon the filter, add sufficient chloroform to wholly submerge the filter and allow at least an hour for digestion; wash with chloroform until the filtrate passes through colorless, then dry and weigh; the loss in weight represents the asphaltene. The filter is now to be burned in a platinum crucible and, if the asphaltum be combined with limestone, the residue recarbonated with ammonium carbonate, dried in a steam-bath, and weighed, the loss in weight represents the organic matter not bitumen, or coke, in the case of artificial asphaltic residuum, produced by heat.

There is necessity for washing the flask with the different solvents, not only because the petroleum ether is too light to rinse out all of the mineral matter, but also because some of the asphaltene adheres to the flask. Generally the turpentine removes all of the mineral matter, as well as part of the asphaltene, but if it does not, then after the flask is rinsed with chloroform it must be again dried and weighed and the increase in weight added to

the weight of the mineral matter in the platinum crucible. If water be present the asphalt should be dried in a steam-bath to a constant weight before being digested in petroleum ether. It is possible that some natural asphalts might experience a trifling loss of volatile oils at the temperature of the steam-bath, but in most instances such loss would be too slight to be regarded. With care and patience this method has been found capable of yielding very closely concordant duplicate results at each step.

The following table exhibits the results of a number of quantitative analyses made according to this method.

Sample.	Water.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1.....	2.029	32.4455	22.1115	8.1215	35.2865	99.994
" 2.....	0.3911	25.4605	54.414	2.469	17.0305	99.7651
" 4.....	35.087	63.183	1.7285	99.9985
Not recarbonated.						
" 5.....	8.518	3.924	25.791	61.764	99.997
" 6.....	7.486	4.316	88.198	100.
" 7.....	8.786	3.267	87.947	100.
" 8.....	3.349	2.4215	94.228	99.9985
" 12.....	0.335	11.323	3.81	1.124	83.407	99.999
" 15.....	49.959	50.041	100.
" 17.....	64.571	21.2545	13.706	0.3613	99.8928
" 18.....	63.498	29.966	6.095	99.559
" 19.....	4.387	2.831	4.102	88.65	99.97
" 20.....	0.434	6.666	1.87	3.697	87.33	99.997
" 21.....	66.788	31.932	1.278	99.998

While this research is in no sense complete—it has in fact but opened up a wide field for further work—yet, sufficient evidence has been obtained to show that petrolene and asphaltene are not substances, but empirical terms that designate mixtures of substances soluble under certain conditions in different menstrea.

It is not unfair to assume that in these empirical mixtures, so long known under the names of petrolene and asphaltene, the lower members of all the different groups of hydrocarbons now known may be found. Again—just as some petroleum, which are varieties of bitumen, consist chiefly of paraffines—notably Pennsylvania petroleum—and some, like Russian petroleum, consist of the additive benzenes, while still others contain mixtures of the two is it not reasonable to presume that solid bitumens, like liquid bitumens, are equally variable in composition?

If this be the case, then it is equally fair to assume that any solvent taken will not dissolve substances of identical composition from different asphalts.

A review of the results here given suggests the query, have the methods heretofore employed for the technical analysis of asphaltum really been analytical at all? Would not a method and process suggested by the results of the qualitative analyses given in this paper and based on the successive application of different solvents and yielding results similar to those of fractional distillation really become analytical, especially if the separate portions dissolved by the different solvents were subjected to such treatment by oxidizing agents as would enable us by a comparison of the products of oxidation to determine to what groups of hydrocarbons the different substances dissolved respectively belong?

I take pleasure in hereby acknowledging my indebtedness to the courtesy of Hon. Thos. R. Bard, President of the Union Oil Co., of California, for the use of the laboratory of the company while engaged in this research.

MINNEAPOLIS, MINN., Sept. 16, 1894.

ACTION OF METALLIC MAGNESIUM UPON MANGANOUS SALTS.

BY JOS. G. HIBBS AND EDGAR F. SMITH.

Received June 18, 1894.

THE statements relating to the action of metallic magnesium upon solutions of manganous salts are contradictory; thus Manck (*Ueber d. Verh. d. Magnesium und Aluminium gegen Salzlösungen*, Goettingen, 1862) states that metallic manganese is readily precipitated by magnesium from neutral solutions of manganous nitrate or chloride. Phipson (*Jahresb.*, 1864, 192) corroborates this and remarks that the manganese separates as a regulus. The observations of Roussin (*Jahresb.*, 1866, 170), Comaille (*Comptes Rendus*, **63**, 556; *Jahresb.*, 1866, 171), and Kern (*Chem. News*, **33**, 236), on the other hand, seem to demonstrate that metallic manganese is not thrown out of manganous salts by metallic magnesium.

We have tried the action of the last metal on manganous salt solutions, both in the presence of alcohol and ether. In using