

and  $\text{AlCu}_3$  are solid solutions of one compound in the other, and those between 92.5 and 100 per cent. copper are solid solutions of  $\text{AlCu}_3$  in copper. We have only commenced work upon the micro-structure of these alloys. We hope ultimately to explain all the points in this curve which, as yet, are not understood. The long line of horizontal points below the eutectic line is as yet unexplained. As a basis for further study, we shall consider that all the alloys of aluminum and copper belong to three groups as shown by our curve: (1) From 0 to 48.4 per cent. copper, the alloys consist of aluminum and  $\text{Al}_2\text{Cu}_3$ ; (2) from 48.4 to 87.6 per cent. copper the alloys consist of the compounds  $\text{Al}_3\text{Cu}_2$  and  $\text{AlCu}_3$ ; alloys within this range contain neither free aluminum nor free copper; (3) from 87.6 to 100 per cent. copper, the alloys consist of  $\text{AlCu}_3$  and pure copper. These three pairs of constituents mixed or dissolved in various proportions probably compose all the possible alloys. The other compounds mentioned by LeChatelier seem to give no indications of their existence so far as pyrometric evidence is concerned.

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## ON THE TEMPERATURE REACTION OF OILS WITH SULPHURIC ACID—MAUMENÉ'S TEST.<sup>1</sup>

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MAUMENÉ in 1852<sup>2</sup> showed that the rise of temperature on mixing with strong sulphuric acid is considerably greater with drying than with non-drying oils and that the difference may be of practical value in testing olive oil for the presence of poppy or other seed oils with which it may be adulterated. This method has generally been known as the Maumené test. As originally described and generally carried out, it consists in adding to 50 grams of the oil in a beaker, 10 cc. of strong sulphuric acid (according to Maumené, 66° Bé.), stirring with a thermometer, and observing the rise in temperature. Obviously it is essential that the test be always carried out under similar

<sup>1</sup> Read at the meeting of the New York Section of the American Chemical Society, June 7, 1901.

<sup>2</sup> *Compt. rend.*, **35**, 572.

conditions and that the oil and acid have the same initial temperature, and it is desirable that the beaker in which the test is made be so surrounded as to minimize the loss of heat by radiation.

Various workers<sup>1</sup> have altered the quantities used by Maumené or employed more elaborate forms of apparatus for carrying out the test but none of these modifications seem to have come into very general use, perhaps because the extreme simplicity of the original method counts so strongly in its favor.

In general those oils which absorb more iodine will yield more heat on treatment with sulphuric acid, and since the iodine absorption can be quite accurately measured by the Hübl method there has been a tendency to regard the Maumené test as being of secondary importance in the examination of ordinary oils and of use mainly as a rough substitute for the Hübl method or as a preliminary "sorting test." Lewkowitsch does not include it among the "quantitative reactions." In many cases it is doubtless true that the information to be obtained by the Maumené test is given more accurately by the Hübl method, but the former possesses the great practical advantages of being much simpler and more rapid, of requiring no standard solutions or special reagents and only such apparatus as is always at hand. Hence if it could be made as accurate as the Hübl method it might often replace the latter with considerable saving of time and trouble. Moreover there are cases in which these methods do not give parallel results, and in which after the halogen absorption has been determined additional information may still be obtained from the Maumené test.

The errors affecting the Maumené test we believe to arise mainly from three sources:

(1) The secondary reactions which occur when the heat generated is considerable; (2) the uncertainties involved in diluting the sample with some other oil to prevent too violent a reaction; (3) variations in the intensity of the reaction caused either by differences in the strength of acid used or in the conditions affecting the radiation of heat.

The chief object of the work here described is to throw some

<sup>1</sup> Wiley: Bulletin 13, Division of Chemistry, U. S. Department of Agriculture, p. 443; and "Principles and Practice of Agricultural Analysis," Vol. III, p. 357. Jean: *J. Pharm. Chim.*, [5], 20, 337, (1889). Blasdale: *J. Am. Chem. Soc.*, 17, 935 (1895). Richmond: *Analyst*, 20, 58 (1895).

light upon these sources of error, and to ascertain if they can be minimized without sacrificing the simplicity of the original method.

In all cases we have used the proportions originally suggested, 50 grams of oil and 10 cc. of acid. To reduce the radiation of heat the beaker in which the test was made was either packed with asbestos in a larger beaker, or one of the smaller of a nest of beakers was used, the rest of the nest with the straw packing intact serving quite as well as the asbestos. The acid was added from a pipette of which the tip was drawn down so that the delivery of the 10 cc. occupied about fifty seconds. The mixture was thoroughly stirred with the thermometer until the maximum temperature was reached.

All of our results are stated as "specific temperature reaction" according to the suggestion of Thomson and Ballantyne;<sup>1</sup> that is, instead of giving simply the observed rise in temperature (which is largely affected by the strength of the acid and other conditions) this rise is multiplied by 100 and divided by the rise observed when 50 grams of water are treated with 10 cc. of the same acid under the same conditions.

In order to have a satisfactory basis for this calculation it is, of course, necessary that the 50 grams of water used shall completely cover the bulb of the thermometer. This limits the size of the beaker which can be used, and hence also the amount of frothing which may take place without loss of the determination. A deep narrow beaker or large test-tube has sometimes been used, but if the reaction is allowed to become so violent as to cause much frothing and evolution of volatile products, it is evident that heat will be lost. It thus becomes important in testing any but the non-drying oils that some means be taken to regulate the reaction.

This is accomplished by mixing the sample with a known proportion of some comparatively inactive oil. Maumene<sup>2</sup>, Bishop,<sup>3</sup> Ellis,<sup>4</sup> Jenkins,<sup>5</sup> and Gill<sup>6</sup> have used mineral oil for this purpose. Thomson and Ballantyne<sup>7</sup> used olive oil and Allen<sup>8</sup> suggests the use of olive or lard oil as a diluent.

<sup>1</sup> *J. Soc. Chem. Ind.*, **10**, 233 (1891).

<sup>2</sup> Original publication by Imperial Academy, Rheims abs. by Ellis: *J. Soc. Chem. Ind.*, **5**, 361 (1886).

<sup>3</sup> *J. Pharm. Chim.*, [5], **20**, 302 (1889).

<sup>4</sup> *J. Soc. Chem. Ind.*, **5**, 150, 361 (1886).

<sup>5</sup> *Ibid.*, **16**, 194 (1897).

<sup>6</sup> "Handbook of Oil Analysis," p. 47, (1900).

<sup>7</sup> *J. Soc. Chem. Ind.*, **10**, 234, (1891).

<sup>8</sup> "Commercial Organic Analysis," Vol. II, Part I, (3rd Edition) p. 79.

# INFLUENCE OF DILUENTS.

Mineral oil being cheaper and giving less heat with sulphuric acid than lard or olive oil, is the diluent most often used. Generally the sample and diluent are mixed in equal proportions, and the rise shown by 50 grams of the mixture is taken to be the mean between the rise given by 50 grams of diluent (which has been previously determined), and that which would be given by 50 grams of the sample.

This method assumes that the specific heat of the diluent is the same as that of the sample. As the different hydrocarbons which may occur in petroleum differ considerably in this respect, and some of them have specific heats much lower than those of the fatty oils, this assumption can hardly be regarded as free from error. The oils used in our own experiments, however, differed so little in their specific heats<sup>1</sup> that any discrepancy which may have arisen from this cause seemed negligible as compared with the other and greater uncertainties which the method involved; for it was found that whenever the reaction was moderated by the addition of mineral oil the result calculated from the mixture was much higher than that obtained by treating the same oil directly with the same acid.

Thus using an acid which gave with water a rise of 43°, we obtained the results shown in Table I in which the first column gives the values obtained by treating 50 grams of the sample directly with the acid, and the second column those calculated from the rise shown by a mixture of 25 grams of sample, and 25 grams of mineral oil. To facilitate the stirring of the mixture a thin oil (sp. gr. 0.817) was selected. This mineral oil alone gave with the acid a rise of 4°.

TABLE I.—EFFECT OF DILUTION WITH PETROLEUM UPON TEMPERATURE REACTION.

Oil tested.	Specific temperature reaction.	
	Direct treatment of oil with acid.	Oil diluted with petroleum as described above.
Lard oil.....	101	126
Olive oil.....	103	138
Almond oil.....	114	154
Sesame oil.....	158	200
Cottonseed oil.....	167	200
Peanut oil.....	176	194

<sup>1</sup> Approximate determinations of the specific heats of some of the samples gave the following values: olive oil, 0.493; lard oil, 0.50; raw linseed oil, 0.474; menhaden oil, 0.474; the mineral oil used as diluent, 0.50. We hope to extend these determinations later.

A few experiments were made in which olive oil, chloroform or carbon tetrachloride was used as the diluent, allowance being made for the low specific heats of the latter solvents. Although the discrepancies were not so great as with the petroleum the results obtained were somewhat too high. Olive oil, besides being liable to change from exposure, gives of itself sufficient rise with sulphuric acid so that only a small proportion of drying oil can be tested with it and any errors are multiplied in the calculation. The same is true of lard oil which seems to be even more liable to variation. With chloroform or carbon tetrachloride the proportion of drying oil to diluent must be small on account of the low boiling-point of the latter. By the use of a sufficiently large and constant proportion of a suitable solvent such as carbon tetrachloride, with very accurate thermometric measurements, and special precautions to prevent loss of heat, the reaction might be put upon a true calorimetric basis.<sup>1</sup> Such a method, however, would probably be too complicated to take the place now occupied by the Maumené test, and it seemed to us that a simpler and more satisfactory method would be to use a somewhat diluted acid instead of diluting the oil.

#### INFLUENCE OF THE STRENGTH OF ACID USED.

Thomson and Ballantyne<sup>2</sup> found that when the results were calculated as "specific temperature reaction" as above described, there was no apparent difference between those obtained with acids of different strengths, the acids used in their experiments being between 95 and 99 per cent. Working with somewhat weaker acids (89 to 95 per cent) we find a distinct difference according to the strength of the acid, the more concentrated giving a higher result although in each case the rise is referred to that given by water with the same acid. It is evident that the extent of the rise will be determined not only by the strength of the acid but to some extent also by the method of manipulation and the precautions taken to avoid radiation of heat. It seems better, therefore, to state the rise of temperature which an acid gives on mixing with water rather than its percentage strength. The acids are thus designated in Table II below which shows the specific temperature reactions of a number of oils with acids of different strengths.

<sup>1</sup> This has been undertaken by Mitchell (*Analyst*, **26**, 169 (1901)), whose paper has appeared since the above was read.

<sup>2</sup> *Loc. cit.*

TABLE II.—EFFECT OF STRENGTH OF ACID ON SPECIFIC TEMPERATURE REACTION.

Sample.	Specific temperature reaction with acid which gave with water a rise of			
	33.3°.	37°.	40°.	43°.
Olive oil.....	90	96	100	103
Almond oil.....	95	100	108	114
Castor oil.....	84	88	89	94
Lard oil, I.....	81	89	92	95
Lard oil, II.....	88	95	99	101
Arachis (peanut).....	161	..	..	176
Rape oil.....	144	..	160	..
Cottonseed oil.....	152	..	..	167
Sesame oil.....	143	..	..	158
Sperm oil.....	102	106	..	111
Resin oil.....	72	..	..	72

It will be seen that with all of the fatty oils examined the specific temperature reaction became higher as the strength of the acid was increased from 89 to 95 per cent. The differences seem to be as great with the non-drying as with the semi-drying oils. The sample of resin oil showed no difference.

#### SPECIFIC TEMPERATURE REACTION WITH DILUTED ACID.

It is evident that the use of an acid of 89 to 90 per cent., giving with water a rise of 33° to 34°, will usually yield results somewhat lower than would be obtained with acid of 95 to 99 per cent. as used by Thomson and Ballantyne. It is believed, however, that the figures obtained with the weaker acid will be more uniform since the temperature rises more steadily and there is less frothing and evolution of sulphur dioxide than when the stronger acid is used. The secondary reactions and the errors arising from inaccuracy in reading a rapidly changing temperature are thus considerably reduced. The great advantage, however, is that the simple method heretofore used in testing the non-drying oils can, with the diluted acid, be applied to all oils alike and the results obtained with the drying and non-drying oils become comparable with each other. Table III shows the results obtained with 89 per cent. acid upon several samples of oils of which the specific gravities, Hübl figures, and acidity are also given.

TABLE III.—SPECIFIC TEMPERATURE REACTIONS OF OILS WITH SULPHURIC ACID.

No.	Description of oil.	Specific gravity. $\frac{15.5^\circ}{15.5^\circ}$	Hübl figure.	Free acid as oleic. Per cent.	Specific temperature reaction.
1.	Linseed (raw), 1900.....	0.934	182.4	4.30	300
2.	Linseed (raw), 1898.....	0.938	175.9	1.22	298
3.	Poppyseed, age unknown..	0.926	129.6	2.66	212
4.	Peanut (arachis), 1899 ....	0.917	105.9	0.16	161
5.	Maize, 1900.....	0.924	120.3	3.32	158
6.	Maize, 1898.....	0.926	120.7	2.56	168
7.	Rape, age unknown.....	0.920	108.6	0.68	155
8.	Rape, 1901.....	0.920	107.4	0.82	144
9.	Cottonseed I, 1900.....	0.920	102.5	0.20	147
10.	Cottonseed II, 1900.....	0.921	106.4	0.32	157
11.	Cottonseed III, 1900.....	0.923	105.5	0.08	152
12.	Cottonseed, old.....	0.926	103.0	0.44	197
13.	Cottonseed, very old .....	0.941	93.7	2.03	245
14.	Sesame, 1899.....	0.924	105.3	1.65	143
15.	Almond, 1898.....	0.919	98.1	5.13	95
16.	Olive, 1899.....	0.917	85.1	2.51	90
17.	Castor, 1898.....	0.964	86.9	2.18	84
18.	Menhaden, refined.....	0.935	....	0.36	309
19.	Menhaden, crude, 1899....	0.934	....	1.92	356
20.	Codliver, 1901 .....	0.926	149.6	....	280
21.	Codliver, 1900 .....	0.927	165.6	0.56	259
22.	Seal, 1901.....	0.926	140.6	....	255
23.	Lard oil, 1900.....	0.917	74.3	0.74	81
24.	Lard oil, 1899.....	0.919	72.5	1.25	88
25.	Lard oil, 1897.....	0.924	69.3	2.34	122
26.	Sperm oil, age unknown...	0.886	78.7	0.78	102
27.	Resin oil, age unknown...	0.989	76.9	14.40	72

The samples marked "1900" were obtained directly from the makers and were undoubtedly pure and reasonably fresh. The other samples were purchased from responsible dealers in the years indicated, and are believed to be pure. Numbers 12, 13, and 25 are examples of oils exhibiting some abnormality which is much more strikingly shown by the temperature reaction than by the other determinations. As each of these samples is some years old and has a high specific gravity it is probable that they had become somewhat oxidized by exposure. These three samples are omitted from the averages given below.

COMPARISON OF ABOVE RESULTS WITH THOSE OF THOMSON AND BALLANTYNE.

Table IV shows in parallel columns the averages of the deter-

minations of specific temperature reaction published by Thomson and Ballantyne,<sup>1</sup> who have done most toward putting the test upon a satisfactory basis, and those obtained by us as described above and shown in detail in Table III.

TABLE IV.—COMPARISON OF AVERAGE RESULTS—SPECIFIC TEMPERATURE REACTION.

Description of oil.	Thomson and Ballantyne.		Table III above.	
	No. of samples examined.	Average figure.	No of samples examined.	Average figure.
Linseed (raw) .....	4	315	2	299
Poppyseed .....	..	...	1	212
Maize .....	..	...	2	163
Cottonseed .....	3	167	3	152
Rape .....	5	133	2	150
Peanut (arachis) .....	2	121	1	161
Sesame .....	..	...	1	143
Almond .....	..	...	1	95
Olive .....	11	92	1	90
Castor .....	2	91	1	84
Menhaden .....	1	306	2	333
Codliver .....	3	254	2	270
Seal .....	4	222	1	255
Whale .....	1	157	..	...
Lard oil .....	..	...	2	85
Sperm oil .....	1	100	1	102
Arctic sperm .....	1	93	..	...
Rosin oil .....	..	...	1	72

With most of the vegetable oils the results obtained by us with the diluted acid are slightly lower than those reported by Thomson and Ballantyne, while with the few animal oils compared our results are a little the higher. In general the agreement between the two sets of results is sufficiently close to indicate that the adoption of the modification here used involves no radical departure from what has heretofore been considered the best practice.

## A NOTE ON THE DETERMINATION OF MOLYBDENUM IN STEEL.<sup>2</sup>

BY GEORGE AUCHY.

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UP to recently the analyst has not often been called upon to determine molybdenum in steel, but in the future this determination will be frequently made. To steel works chemists

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Read at the meeting of the Philadelphia Section of the American Chemical Society, January 16, 1902.