In the absence of Mr. Jones, Mr. Bevan read the following paper:

TURBIDITY TEMPERATURE OF OILS AND FATS WITH GLACIAL ACETIC ACID.

By E. W. T. Jones.

This test, due to Valenta, is described by him in J. C. S., xlvi., p. 1078, where he also gives results on certain oils.

I have been investigating this test, and although the hopes I had entertained of its usefulness, as an independent and totally distinct test for differentiating between those butters which, although genuine, are low in the usual butter characteristics according to chemical testing, and actual mixtures approximating such butters, have not been realized, I have ascertained a few facts concerning the test which I think are worth recording.

Valenta indicates the requisite strength of the acid by specific gravity, which he gives as 1056·2. This, according to the most reliable table I can find (Oudeman's), may mean 44 per cent. HĀ, or 99·7 per cent. HĀ. Of course the former strength is not "glacial," but I shall show that specific gravity is altogether inadequate to determine the fitness of the acid for oil-testing; indeed, it will need no further demonstration when I mention that 4 c.c. of water, added to 2,300 c.c. (a Winchester quart) of acid, lowered the turbidity temperature 5° C. This means that a difference of less than 0·2 per cent. in the HĀ effects this divergence, and it follows that a very small dilution of the strongest acid may make it absolutely useless for the test at all. The turbidity temperature, say, with a known sample of butter-fat, is the most delicate test I know of for adjusting the requisite strength of this strong acetic acid for the purpose in view.

An acid which by titration contained 98 per cent. (97·99) of HĀ gave with a butter-fat a temp. of 48° C.; the addition of 2 per cent. of water made it over 100° C.—quite unfit for use; 1 per cent. made it 79° C., whilst 0·2 per cent. made it 55° C. This shows the importance, if this test is to be used to give at all comparable results, of adopting a scheme to secure exactly the right strength of acid, and the following is the course I have followed.

I have carefully filtered off some fat from a normal butter into a bottle, and this I employ to set every fresh batch of acid I use. I procure the best and strongest glacial acetic acid, and suppose I find it gives a temp. of 50° C. with my standard butter-fat, I carefully add water until the temp. with it is 60° C.; thus I know that whatever tests I make with this acid are strictly comparable with any previous tests I have made.

It is most important, too, that the relative proportions of the acid and fat or oil are pretty strictly adhered to, and absolutely necessary that the set proportion of the *fat* or *oil* to the acid is not exceeded; any error in measurement should lean to the full measurement of the acid, which does not make the difference that the converse proportion does. I make special pipettes, a narrow one delivering 3 grammes of water at 15·5°C. for the acid, and wider ones, with wider orifices, delivering

3 grammes of water at 15·5° C. for the fat. I measure all oils and fats at about 50° C.

The turbidity temperature of butter-fat varies from 40° to 70° C.—the general run being from 52° to 65° C. The following analyses show the temp. in conjunction with other estimations.

Turbidity temperature.	54° C.	56° C.	55° C.	60° C.	55° C.	56° C.	57° C.	41° C.	45° C.	59° C.	48° C.
Koettstorfer's deg.	226·8	224·0	226·2	220·0	223·4	226·2	225·1	224·5	225·7	217·8	221·2
Soluble acids ...	5·14	4·79	5·19	4·19	5·02	5·30	5·20	4·97	5·05	4·12	4·98
Insoluble acids ...	88·92	89·30	89·04	90·28	89·08	88·78	89·11	88·74	88·56	90·18	88·73
Reichert-Wollny ...	27·2	25·6	28·1	22·5	26·7	28 2	28·1	26·7	27·2	22·2	25·4
Equal to volatile acid, as butyric ...	4·79	4·50	4·95	3·96	4·69	4·97	4·95	4·69	4·79	3·91	4·47

Another sample had a temp. of 71° C., and gave a Reichert figure 23·9.

Margarine gives temp. 95° to 106° C., generally from 100° to 102° C.

A mixture of 4 parts of butter-fat, having temp. of 40° C., and 1 part margarine, having temp. of 95° C. gave a temp. of 52° C., against 51 calculated.

Another mixture of 27 parts butter-fat, of temp. 52° C., and 73 parts margarine, of temp. 105° C., gave a temp. of 92° C., against 90·7° C. calculated.

The following are the turbidity temperatures of other oils and fats I have tried with this same acetic acid:

Rape oil	101° C.
Sesame oil	77°
Linseed oil (i.)	53°
Linseed oil (ii.)	57°
Lard oil	96°
Cottonseed oil	76°
Olive oil	89°
Arachis oil (i.)	61°
Arachis oil (ii.)	88°

If any member desires to adopt the same strength of acid as used in my experiments, I shall be happy to communicate with him for the purpose.

Discussion.

Mr. Allen thought the society were very much indebted to the authors of the paper on the acetic acid test, for the observations they had brought forward, and for their improved method of operating. He did not quite know why the authors adopted the weight of 2·75 grammes of oil instead of taking a measure of 3 c.c. It was adding a complication to the test, which he thought was not capable of giving results other than what might be called of a preliminary kind. He had met with acetic acid which it was necessary to freeze in order to render it strong enough to use for the test; but he had never realized that it was necessary to employ such very strong acid as the authors preferred. In stating as he did in 1866 in "Commercial

Organic Analysis" that the strength of the acetic acid employed was not of great importance, he had in mind the comparative results yielded by different oils, rather than the absolute turbidity temperatures. There was no doubt that the weaker the acid was the higher became the turbidity-point with all butters; but, then, the margarine point rose also. As Mr. Jones had stated, it was necessary to have a standard sample of butter with which to compare others. When the Valenta test for oils was first published, he suggested its possible application to butter, and it had since been used in his laboratory on several thousands of samples. As a preliminary or sorting test, he had found it exceedingly useful. The authors' experience showed that genuine butters gave turbidity temperatures varying as much as 10° C., so that the quantitative results could not be very precise; but the same objection applied to every test for butter, and as this was based on an entirely different principle from most others, it was distinctly of value; and he was glad to see that it had assumed an improved form. He was also interested to see that the olive oils gave such approximately constant results. He observed that figures for three specimens of cod oil and three specimens of cod-liver oil were given in the table. He would like to know whether Mr. Chattaway knew the history of these cod oils. When it came to the point, "cod oil" meant, or should mean, cod-*liver* oil. Hence, it was clear that, if the oil really came from the cod, there was no necessity to insert the word "liver," and therefore the cause of the difference in the results obtained was not apparent. The influence of the volume of acetic acid used had been investigated by Mr. G. H. Hurst (*Jour. Soc. Chem. Ind.*, vi. 22), who had also tried the plan of surrounding the tube with a beaker of water.

Mr. H. Droop Richmond wished to know how the strength of the acetic acid was determined. Titration was not a very accurate method when the acid was nearly 100 per cent. The indicator to be used had to be considered; and it was also possible to over-estimate, according to the carbon dioxide present in the solutions of the acid. It was further possible to under-estimate, according to the amount of carbon dioxide in the standard solution against which the alkaline solution was standardized, and these two errors would not necessarily compensate each other. He believed that the density would be the best means of estimating the strength, but it was not actually known what the density of 100 per cent. acetic acid was. Some tables had been published, but they did not agree very well. By far the best table was that of Oudemans, but it only extended to four places of decimals, and one could not be certain whether it was accurate to the fourth place. He had made some experiments which seemed to him to indicate that water was soluble in butter-fat to the extent of nearly a quarter of a per cent. He did not agree with Mr. Allen in thinking that Valenta's test was only of value as a preliminary one. He believed that it was almost as good a test as the density, and, in combination with others, promised to be valuable. As for the Reichert-Wollny, he thought it should not be too implicitly relied upon, as many methods which were looked upon as preliminary showed actually less variation in genuine samples. With regard to cheese, there were two rather interesting determinations, showing that the butter of sheep's milk differed from that of the cow, though Besana had not found any marked difference (Nos. 26 and 28 in the Reichert-Wollny figures). Sample No. 27, Parmesan cheese, was prepared from

skimmed milk. He thought that, as a general rule, all samples were distinctly suspicious in which the fat fell below the casein, estimated, as the authors of the paper had estimated it, by determining the nitrogen and multiplying by the factor, 6·38. Had Mr. Chattaway determined the amount of sodium chloride in the ash?

Mr. R. Bodmer found that the great trouble of the test was that no acetic acid of the requisite strength was readily obtainable.

The Chairman (Mr. Hehner) said that the figures did not show how nearly margarine could be determined in commercial samples, but how accurately two substances, separately known, could be re-estimated after having been mixed. He had experimented a good deal with the Valenta test, and once thought highly of it; but on fuller experience he had been disappointed, as was the case with all other methods of fat-analysis. Figures obtained from the examination of a limited number of samples always broke down on wider experience. Further, a slight alteration in the strength of the acid made a considerable difference in the figures. Even when using acetic acid from the same stock-bottle, the latter having been opened frequently, the acid changed in its action when the bottle was getting empty. The state of freshness of the butter also required consideration. In the acetic turbidity table given by the authors there were shown the results of 24 samples of butter-fat, and in a second table the Valenta figures of 26 samples of cheese-fat. The fresh butter-fats gave figures which varied only by 10° C.; but in the fats obtained from those cheeses which according to the Reichert number were almost certainly genuine and free from margarine, and carefully excluding cheeses which appeared to be "filled," the variation was from 19° to 45° C. Even excluding the Roquefort cheese, the variation was yet so great as to allow of the introduction of a large percentage of margarine, that percentage being not less than that covered by the variations in the figures obtained by other processes. That was the conclusion which was forced upon him by his practice in the laboratory, and which he was confirmed in, subject to any explanation which the writers of the paper now under discussion might offer. A very interesting point was raised which had been frequently before his mind; that was, What was the real significance of the Valenta test? Mr. Richmond justly endeavoured to attain the highest possible accuracy in everything. If the significance of the figures was not known, it seemed to him this high degree of accuracy was largely wasted. He had made inquiry into this matter, and found that the fat which crystallized from the acetic acid consisted of the saturated fatty compounds, whilst the unsaturated remained in solution. It seemed to him that these small mixtures up to about 15 or 20 per cent. were as undetectable by the Valenta as by any other process.

Mr. Cassal would like to know whether, in the authors' experience, the Valenta test was one which could be relied upon for the quantitative analysis of samples of butter, as the other processes now used could be relied upon. At first sight the authors' table appeared to be remarkable, and it looked as if they had arrived, by the use of the Valenta test, at a process whereby the amount of margarine that was actually present in an adulterated butter could be determined with an extraordinary degree of accuracy. But he understood that this table was merely intended

to represent the powers of the Valenta test when applied to mixtures of a particular butter and a particular margarine separately giving certain results with the Valenta test. There was, however, nothing to show that upon taking any mixed sample the Valenta test applied to it would enable one to detect the percentage of the adulterant with anything like such accuracy. Great caution should be exercised in drawing conclusions from a test founded upon conditions as yet not fully determined, and in regard to which but little in the way of satisfactory scientific explanation had as yet been given.

Mr. Chattaway, in reply, said that the reason why 2·57 grammes of fat were taken was with a view to as nearly as possible approximate the weight of 3 c.c. at a temperature of 40° C. He did not approve of Mr. Allen denoting the method as a mere sorting test. It was, in the opinion of the authors, quite as useful and valuable, if not more so, than the Reichert-Wollny. He could have wished not to have occasion to speak so strongly in favour of the Valenta test, seeing that it is not as yet fully understood; but the authors had every reason to regard the test as decidedly more valuable than the Reichert determination. The butters mentioned were taken from some examined during the past few weeks, and although not truly representing the *possible* variations of butter, they were fairly representative of the butters of commerce. The same remarks applied also to the margarines, the figures of which are recorded. So far as the table to which Mr. Cassal and Mr. Allen had called attention was concerned, the authors wished particularly that it should not be misunderstood. A butter and margarine were taken, mixtures made, and then, starting with the initial figures of the butter and margarine, the calculations were made. The cod oil was a crude specimen used for leather dressing. The authors had been able to buy the acid quite strong enough; indeed, they had had to dilute it down to the proper strength. Referring to Mr. Richmond's observations, the strength of the acid was determined as usual by baryta and phenolphthalein, and, in the opinion of the authors, this was quite satisfactory. Mr. Chattaway thought that the attempt to place the test in a higher position than it had usually held had been severely—too severely—dealt with by Mr. Hehner. It seemed that Mr. Hehner did not so much really disapprove of the test, as that he did not think *any* test was at the present moment perfect enough to deal with certain cases. Touching again the question of sensitiveness of the test, the authors were in a position to prove that, taking hundreds of figures and determinations into consideration, the Valenta test was capable of just twice the accuracy of the Reichert-Wollny. The explanation of the solution at certain temperatures of some fats and not others was dependent, in the speaker's belief, on the intermixibility question. Butyric acid, for example, existing in butter in combination with glycerin was readily soluble in acetic acid at a certain temperature, and this mixture then had the power of taking into solution the glycerin compounds of the higher fatty acids. The authors did not wish to place too much stress upon the Valenta figures obtained in the case of fat from cheese, owing to the imperfect knowledge of the changes which take place in the maturing of cheese.