

THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute of Petroleum was held at Manson House, 26, Portland Place, London, W.1, on Wednesday, June 12, 1946, Mr J. S. Jackson (Chairman of the Standardization Committee) presiding.

The following paper was read :

THE APPLICATION OF VARIANCE ANALYSIS TO SOME PROBLEMS OF PETROLEUM TECHNOLOGY.

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SUMMARY.

The importance of measuring variation in experimental data is emphasized and some methods of handling variable material and coping with variable conditions are described, in particular the statistical technique developed by R. A. Fisher and known as the analysis of variance. The fluctuation of octane ratings is typical of the variation met with in experimental work. After an indication of the underlying statistical ideas the arithmetical procedures involved in variance analysis are briefly outlined, using twenty rich mixture ratings by the British 3-C method as an example. These are first treated as two groups of ten results (grouped data), and then as ten pairs (paired data), to show how the appropriate form of analysis depends on the way in which the results have been obtained.

Efficient experimental designs based on statistical methods have been developed. The randomized block arrangement, illustrated by means of kerosine burning test results, secures the separation of major causes of heterogeneity so that their effects do not interfere with the comparisons the experiment is designed to make. The Latin square carries this a stage further, giving control of error in two directions simultaneously. This is illustrated by a test of the m.p.g. performance of seven motor fuels, and the example is also used to introduce the idea of covariance. It is shown how the results themselves can be made to supply whatever correction is appropriate for the effect of a concomitant variate. Stress is laid on the unity of experiments, their plan, operation, analysis, and final interpretation.

INTRODUCTION.

SIR CHARLES DARWIN, Director of the National Physical Laboratory, has remarked on the need "to inculcate in people's minds the idea that every number has a fringe, that it is not to be regarded as exact but as so much plus or minus a bit, and that the size of this bit is one of its really important qualities." ¹ After quoting this in his review of the "A.S.T.M. Manual on Presentation of Data," E. L. Grant added, "It is partly because many engineers have never been sufficiently aware of the inevitableness of variability that they have not informed themselves about the best methods of dealing with variability." ²

The position in petroleum technology is similar to that in engineering. Naturally, statistical methods have, in general, been used most where the need for them is most evident and where it is most difficult to reduce the uncontrolled variability in materials and conditions—for example, by closer specification; but whereas large numbers of engineers have now become acquainted with these methods through the use of quality control charts in production, petroleum technologists, dealing in the main with compara-

tively homogeneous materials in bulk, have not. Yet in testing petroleum products they daily have recourse to many special tests, including machine tests, the results of which may vary considerably and unpredictably. It is with methods of handling data of this kind, particularly where the number of observations is small, and also with the efficient experimental designs to which they have given rise, that this paper is primarily concerned. Its purpose is essentially introductory, however, and no attempt will be made to discuss in detail all the procedures involved in the analysis of data, which can best be learnt from one of the many text-books available.³⁻⁹

The very ease with which variation can be reduced in the exact sciences and in certain fields of technology has served to obscure, on the one hand, the practical impossibility of eliminating every vestige of variability entirely, and, on the other, the fact that its measurement is more important than its reduction, desirable as this may be. Thus, the view expressed by the late Thomas Midgley that the "basis of the scientific process is the reproducible experiment," and that "even logic is of secondary importance to the reproducible experiment,"¹⁰ appears somewhat unrealistic. It is precisely because reproducibility is not absolute, but relative, that some measure of the uncontrolled variation is always implied, even where it is least in evidence. The yardstick of experimental error is, indeed, crucial to the process of scientific inference by which results are interpreted. By focusing attention on the logical basis of this process, and in particular on the estimation of this reference yardstick, the modern application of statistical methods to experimental data has conferred a degree of definition on the term "scientific method" that was lacking hitherto. It is, in fact, less the reproducible experiment that is the basis of the scientific process than the devising of experiments appropriate to the testing of particular hypotheses postulated on the basis of existing knowledge. The degree of appropriateness is assessable by the extent to which, as a result of the experimental design, the interpretation of the data is necessarily unambiguous, and for this to be possible there must be adequate provision for estimating the magnitude of the experimental error.

If we consider a comparison of, for example, the octane numbers of two fuels, each rated several times, it is clear that we need to take into account the variation from one test to another on the same fuel as well as the mean results for each fuel. The conclusion that one fuel has a higher rating than another may well be unsound if based solely on the average results for the two fuels. It is possible for the two sets of test results to overlap considerably, though the mean values shows an apparent difference in favour of one fuel. It is essential to know whether such a difference may have arisen merely as a chance error rather than in consequence of a genuine difference of octane number between the two fuels. A test of significance based on the variability manifest in the data enables us to estimate how often this would happen on the average, or, to put it another way, the odds against it happening. Admittedly, for octane ratings, though not for all tests, the "Standard Methods" state the order of repeatability and reproducibility, in this case 0.5 and 1.0 O.N.¹¹ respectively; but these are merely general indications of the limits within which it is considered that determinations should lie when the directions of the method are properly observed; they cannot be regarded as accurate measures of experimental reliability, which

it is always preferable the test data should themselves be made to supply. No test of significance can have any validity, however, unless, in the course of the experiment, care is taken to randomize all errors that cannot be eliminated, so that they have an equal chance of affecting each fuel.

The conduct of an experiment, the analysis of the results, and their interpretation, are interdependent.

THE MEASUREMENT OF VARIATION.

TABLE I.

Octane Rating of a Fuel by 25° Motor Method in Different Laboratories.

99.6	99.3	99.0	98.8	98.7	98.5	98.2
99.5	99.3	99.0	98.7	98.6	98.5	98.2
99.4	99.2	98.8	98.7	98.6	98.2	Mean 98.7

Table I, taken from the Standardization Committee's C.F.R. monthly correlation data for May 1945, shows a series of octane ratings by the 25° Motor Method obtained in different laboratories. Although the reference fuel and the setting and operation of the C.F.R. engine have been closely specified in an attempt to eliminate all systematic errors, and the specification was adhered to, by no means all causes of variation have been excluded. The values fluctuate around the mean value of 98.7. The deviations are small, but may nevertheless be important; when fuels are blended in a refinery an error of 0.5 O.N. may waste many thousands of barrels of a valuable high-octane component. These fluctuations are typical of much experimental data, and can be regarded as due to the operation of a multitude of factors, in this case connected with the fuel, the engine, the operator, or external conditions, each small in itself, and each as likely, on the average, to pull in one direction as in the other, the combined effect of which in any determination accounts for the resultant error.

The assumption that the elementary errors contributing to the total occur at random is the basis on which Gauss derived his well-known Law of Error. This states that the probability of an "error" occurring in the

range of magnitude x to $x + \delta x$ is $\frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{x^2}{2\sigma^2}} \cdot \delta x$ where σ is a constant

of the distribution known as the standard deviation. This distribution is the basis of a large part of statistical theory and, although ideal, is one to which many actual data have been found to conform reasonably closely. In other cases it has been found that a simple transformation, such as from x' to $\log x'$ or to $\log(x' + 1)$, enables the properties of this so-called normal distribution to be made use of.

It is a fact of experience that the variation in a set of measurements made under essentially uniform conditions usually takes a form such that extreme values, low or high, are much less common than intermediate ones. A method of measuring variation may, therefore, be reasonably expected to be related to the frequency of occurrence of extreme values. The measure of variation found most useful in statistics is the standard deviation (σ), which is obtained by squaring the deviations of individual observations from the mean, dividing the sum of these squares by the number of the observations, and taking the square root. For the normal curve, an example of which is given in Fig. 1, this root mean square deviation from the mean

is numerically equal to half the distance between the ordinates through the two points of inflexion.

It is evident that it provides information about the spread of the distribution. Deviations from the mean of more than twice the standard deviation occur infrequently. Referring to Fig. 1, the area between the curve and the x axis outside the $+2\sigma$ and -2σ ordinates is about 4.6 per cent of the whole area bounded by the curve and the x axis. The probability of occurrence of deviations of more than twice the standard deviation is therefore expressed as 0.046. Deviations from the mean of more than three times the standard deviation occur in 0.3 per cent of cases—probability 0.003.

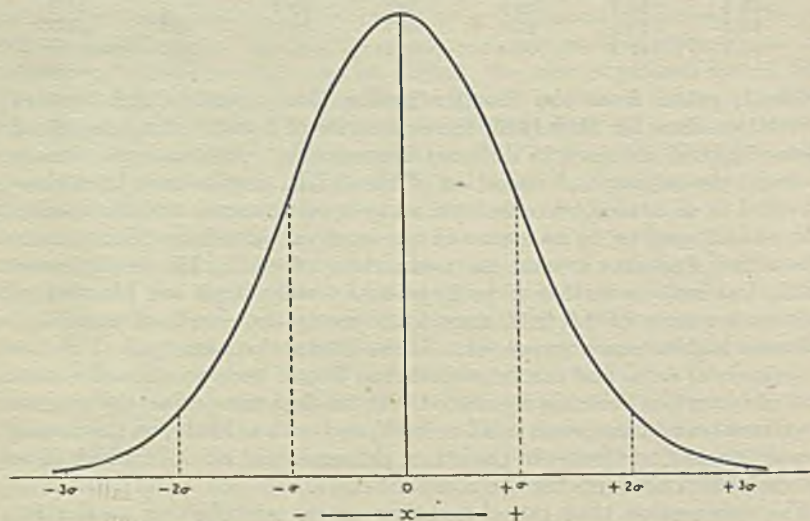


FIG. 1.

It is rarely, however, that the number of measurements encountered in experimental work is large enough for a smooth frequency distribution curve, similar to the normal curve, to be drawn. Often only a small number of results is involved, perhaps less than 25. These can be regarded as a sample of the population of results that would be obtained if the experiment were repeated a great number of times on similar material. We then take the mean and the standard deviation of our results, \bar{x} and s , as the best estimates at our disposal of the mean and standard deviation of the population, μ and σ ; the larger the sample the better these estimates became. This requires correction in one detail; it can be shown that

$$\sqrt{\frac{S(x - \bar{x})^2}{n - 1}} \text{ is a better estimate of } \sigma \text{ than } \sqrt{\frac{S(x - \bar{x})^2}{n}}$$

where n represents the number of results, x an individual result, \bar{x} the mean of n results, and $S(x - \bar{x})^2$ the sum of squares of deviations from the mean. In making the estimate of σ the mean of the sample is used as a reference point from which to measure the deviations, thereby reducing the effective weight of the sample by one. The number symbolized by $n - 1$ is known

as the number of degrees of freedom available for estimating the standard deviation.

Although the standard deviation is a satisfactory measure of variability its square, known as the variance, is a more suitable statistic to work with when variation due to more than one cause has to be split into parts attributable to particular factors. The additive nature of sums of squares of deviations and degrees of freedom forms the basis of variance analysis, a technique due to R. A. Fisher.³

GROUPED DATA.

Table II shows a series of ten Rich Mixture ratings by the British 3C procedure on each of two fuels designated A and B. These figures are taken from the M.A.P. monthly correlation data for October 1944.

TABLE II.
3C Rich Mixture Ratings of Fuels A and B.

Fuel A.	Fuel B.	Fuel A - Fuel B.
100.5	98.3	+2.2
99.8	98.5	+1.3
101.0	100.0	+1.0
100.5	99.5	+1.0
101.0	101.8	-0.8
101.4	100.5	+0.9
102.4	102.3	+0.1
99.5	99.8	-0.3
102.8	100.8	+2.0
103.6	102.0	+1.6
Mean 101.25	100.35	+0.9

It will be assumed that the results were obtained under essentially uniform conditions, free from bias, and that no result in the first column bears any special relation to any result in the second column. The ratings might, for example, have been obtained by one operator on one engine, the order of testing the fuels being random. Grouped data of this kind are common.

It is noticeable that, although there is some overlapping, the mean rating for fuel A is higher than that for fuel B by 0.9 of a rating. An analysis can be made to assess the reliability of this difference.

Table III shows the manner in which the total variation in the first two columns, due to all causes, can be split up.

TABLE III.
Analysis of Variance of Rich Mixture Ratings by 3C.

	Degrees of freedom.	Sum of squares.	Mean square.	Variance ratio.
Between fuels	1	4.05	4.05	2.2
Within fuels	18	33.31	1.85	—
Total	19	37.36	—	—

The figure in the first column is the number of degrees of freedom; this represents the number of independent comparisons between the members

of the group referred to at the beginning of the row; in general it is $n - 1$, where n is the total number in the group. Thus, there are two fuels giving one degree of freedom, ten results for each fuel giving $9 + 9$ degrees of freedom for the variance within fuels, and twenty results in all giving a total of 19 degrees of freedom.

In the second column are the sums of squares of deviations from the mean. The figure 33.31 is obtained by adding together the squares of deviations of each result from the fuel mean, *e.g.*, $(100.5 - 101.25)^2 \dots (98.3 - 100.35)^2 \dots$. The figure 4.05 is obtained in a similar way by adding together the squares of deviations of each fuel mean from the general mean; but in order to adjust the comparisons to the same "per item" basis it must be multiplied by ten to allow for the fact that each fuel mean is based on ten observations. Together, these two sums of squares, 33.31 and 4.05, equal the total sum of squares 37.36, obtained by summing the squares of deviations of each individual result from the general mean.

Two short cuts are possible in this calculation; first, working with a machine it is better to use the identity $S(x - \bar{x})^2 = Sx^2 - \frac{(Sx)^2}{n}$, and secondly, the "within fuels" sum of squares may conveniently be obtained by subtraction.

The third column gives the variance or mean square, *i.e.*, each sum of squares divided by the appropriate number of degrees of freedom.

The square root of the "within fuels" variance is the estimate of the standard deviation of the single population, from which it may be assumed, as a test hypothesis, that the two sets of results have been drawn. The question to be settled is whether means of ten ratings drawn from such a population would often differ by as much as 0.9 of a rating. This can be decided by comparing the "between fuels" and "within fuels" variances. The variance of the fuel means is only 2.2 times as large as the "within fuels" variance, and reference to statistical tables¹² shows that such a result would occur frequently, on the average about fifteen times in every hundred, by reason of random sampling alone if the hypothesis of a single population were correct. The hypothesis cannot therefore be regarded as disproved, and we must conclude that the data provide no trustworthy evidence that fuel A has a higher rating than fuel B. Naturally, further investigation with a large number of samples may supply such evidence.

This objective assessment of the results is clearly preferable to any assessment by inspection, but the conclusions of the analysis are valid only if the original assumption of uniform conditions free from bias is correct; on this account procedures of randomization occupy an essential place in experiments intended to be analysed by statistical methods.

PAIRED DATA.

The above analysis of the 3C ratings in Table II is based on a false premise, in that the data were actually obtained on ten engines, and each rating of fuel A is, in fact, related to the rating alongside it for fuel B. This fact has important consequences for the method of analysis. Some at least of the variation within fuels is attributable to differences between engines;

these may be due to small differences in engine parts, or in the way an engine is set by different operators, or in the reference fuels employed with the various engines, or to some other cause. The effect on the fuel ratings may be that engines differ slightly one from another but agree in the relative rating of the two fuels. This turns out to be the case. When the figures are analysed so as to take into account the consistent differences between engines, as in Table IV, it is seen that a considerable part of the

TABLE IV.

Second Analysis of Variance of Rich Mixture Ratings by 3C.

	Degrees of freedom.	Sum of squares.	Mean square.	Variance ratio.
Between fuels	1	4.05	4.05	8.54
Between engines	9	29.04	3.23	6.81
Error	9	4.27	0.474	—
Total	19	37.36	—	—

sum of squares 33.31 in Table III is removed from the error sum of squares, and the mean square for fuel differences is now appreciably higher than that for uncontrolled variation or error. The new variance ratio is 8.54 : 1, and reference to tables shows that this would have occurred by chance in less than 2 per cent of trials if the hypothesis of a single population were true. We therefore have good reason to believe that there is a genuine difference in the rich mixture performance of the two fuels.

The data can also be analysed by "Students'" Method of Pairs.

In 1908 "Student" worked out the distribution of $\frac{\bar{x}}{s}$, the ratio of the mean of a sample to the estimate provided by it of the standard deviation of the population.¹³ Later, he prepared a table of the distribution of $\frac{\bar{x}}{s_x}$ —known as *t*—the ratio of the mean of a sample to the standard deviation (or standard error) of the mean.¹⁴ The *t* test is not critical of small departures from the normal distribution, and the variance ratio test, of which it forms a special case, is in general still less critical.

The third column of Table II shows the difference in ratings between the two fuels in each of the ten engines. If, as a hypothesis, we postulate that the mean for the population of differences between one fuel and the other, of which the ten results + 2.2, + 1.3 . . . + 1.6 are a sample, is zero, we can proceed to estimate how frequently ten results from a population of the degree of variability indicated by the sample would produce a mean as different from zero as 0.9 of a rating. To do this we calculate the value of *t* for the observations and compare it with values set out in tables. Here *t* = 2.92, and reference to the table shows, as before, that on the average such a value would turn up by chance sampling less than twice in every hundred trials. The differences can therefore be regarded as significant.

Differences are said to be significant if the odds are heavy against their occurrence by chance as a result of random sampling, but there is no

absolute standard of significance. The customary limits are 19 : 1 and 99 : 1. Results that are significant only at the lower standard must clearly be regarded as more tentative than those significant at the higher level, but, equally, to insist on the higher standard is to risk overlooking real effects. The fact that the level of significance depends essentially on the agreement between parallel tests can be illustrated by means of the differences between fuel *A* and fuel *B* shown in the third column of Table II. Had the first difference $+ 2.2$ been $+ 4.2$, the average difference between the two fuels would have been greater, but the level of significance of the results would have been lower.

Instead of setting up the hypothesis that there is no difference between the rating of the two fuels, and testing the significance of the observed difference of 0.9 of a rating, we can advantageously find the limits within which the difference in rating between the two fuels must lie for significance at a particular probability level. These boundaries have been termed the fiducial limits of the parameter. To find them we take the limiting value of *t* at $P = 0.05$, for example, in this case 2.26, and multiply by the standard error of the mean, ± 0.308 , giving ± 0.7 . We can then say that there is a fiducial probability of 90 per cent that the mean of the population of differences between the two fuels lies between 0.9 ± 0.7 , *i.e.*, between 0.2 and 1.6 ratings.

The statistical approach to research problems has led to proper attention being given to the subject of experimental design, and many efficient arrangements have been developed, principally by Professor R. A. Fisher and his associates.⁴ These include randomized blocks, balanced incomplete blocks, Latin squares, factorial arrangements, and others.

RANDOMIZED BLOCKS.

In the randomized block design the experimental material is so arranged that the effects of major causes of heterogeneity impinge on entire units or blocks in which the main factors to be investigated are all represented. These factors, allocated at random within blocks, can then be compared independently of any differences from one block to another.

Table V gives the results of a series of burning tests on Pool Burning Oil carried out over four days with wicks subjected to seven solvent extraction treatments and to no extraction. This work, which was part of a programme carried out for the I.P. Kerosine Burning Test Panel in 1945, was intended to investigate the effect of the wick-extraction treatments on both the level and repeatability of the char value of a kerosine, but for the purpose of this example consideration will be restricted to the effect on the level of the char value.

Thirty-two wicks were equally divided without bias amongst the eight treatment groups. After extraction a wick from each treatment was burnt on each of the four days in a lamp randomly selected from a set of eight.

It will be seen that the char values exhibit considerable variation, part of which is attributable to the wick treatments and part to burning on particular days; the remainder represents uncontrolled variation and provides a valid estimate of experimental error.

The total variability shown by these results can be split up in the manner

TABLE V.

I.P. Burning Test Results.

Consumption in grams. Wt. of char in milligrams. Char value in milligrams per kilogram.

Wick treatment.		Days.				Totals.	Means.
		1.	2.	3.	4.		
1	Consumption	486	426	447	417	1776	444.0
	Cons./hr.	20.25	17.75	18.63	17.38	74.01	18.50
	Wt. of char	9.6	10.8	10.0	10.4	40.8	10.20
	Char value	19.8	25.4	22.4	24.9	92.5	23.12
2	Consumption	455	427	432	432	1746	436.5
	Cons./hr.	18.96	17.79	18.00	18.00	72.75	18.19
	Wt. of char	6.2	9.0	8.6	9.0	32.8	8.20
	Char value	13.6	21.1	19.9	20.8	75.4	18.85
3	Consumption	460	434	453	412	1759	439.8
	Cons./hr.	19.17	18.08	18.88	17.17	73.30	18.32
	Wt. of char	6.0	9.0	8.6	7.6	31.2	7.80
	Char value	13.0	20.7	19.0	18.4	71.1	17.78
4	Consumption	465	442	423	427	1757	439.2
	Cons./hr.	19.38	18.42	17.63	17.79	73.22	18.30
	Wt. of char	7.4	7.0	9.0	7.4	30.8	7.70
	Char value	15.9	15.8	21.3	17.3	70.3	17.58
5	Consumption	423	417	433	451	1724	431.0
	Cons./hr.	17.63	17.38	18.04	18.79	71.84	17.96
	Wt. of char	8.4	10.0	9.6	10.4	38.4	9.60
	Char value	19.9	24.0	22.2	23.1	89.2	22.30
6	Consumption	444	416	465	382	1707	426.8
	Cons./hr.	18.50	17.33	19.38	15.92	71.13	17.78
	Wt. of char	6.6	7.6	7.4	7.6	29.2	7.30
	Char value	14.9	18.3	15.9	19.9	69.0	17.25
7	Consumption	495	448	406	436	1785	446.2
	Cons./hr.	20.63	18.67	16.92	18.15	74.37	18.59
	Wt. of char	6.0	8.2	7.0	8.0	29.8	7.45
	Char value	13.3	18.3	17.2	18.3	67.1	16.78
8	Consumption	436	445	436	426	1743	435.8
	Cons./hr.	18.17	18.54	18.17	17.75	72.63	18.16
	Wt. of char	5.8	7.4	8.0	7.8	29.0	7.25
	Char value	13.3	16.6	18.3	18.3	66.5	16.62
Totals	Consumption	3664	3455	3495	3383	13,997	—
	Cons./hr.	152.69	143.96	145.65	140.95	583.25	—
	Wt. of char	56.6	69.0	68.2	68.2	262.0	—
	Char value	123.7	160.2	156.2	161.0	601.1	—
Means	Consumption	458.0	431.9	436.9	422.9	—	437.4
	Cons./hr.	19.09	18.00	18.21	17.62	—	18.23
	Wt. of char	7.075	8.625	8.525	8.525	—	8.19
	Char value	15.46	20.02	19.52	20.12	—	18.78

described on page 470 for the 3C ratings; the analysis is given in Table VI.

It is evident from a comparison of the sums of squares that the subdivision of the burning test into four separate days, each treatment being included on each day, was of benefit in increasing the precision of the comparisons of treatments. About one-third of the total sum of squares was attributable to the effect of different days burning; had this not been eliminated it would have swollen the error sum of squares, making the error mean square about 7 instead of 2.36, and the effect of the wick treatments would have appeared less marked. As it is, the mean square for treatments is 10.8 times that for error, a ratio that is highly significant.

From the error mean square we can calculate the minimum difference between the means of two treatments that will reach a particular level of

TABLE VI.
Analysis of Variance of Burning Test Results.

	Degrees of freedom.	Sum of squares.	Mean square.	Variance ratio.
Between treatments	7	178.96	25.57	10.8
Between days	3	119.36	39.78	—
Error	21	49.58	2.36	—
Total	31	347.90	—	—

significance, such as the 5 per cent or 1 per cent level, and so assess objectively the apparently superior effectiveness of some extraction treatments in lowering the char value. The minimum difference for significance at the 5 per cent level is 2.26 mg/kg, and at the 1 per cent level 3.07 mg/kg. Thus, the mean for treatment 7, for example, is significantly lower than the means for treatments 1 and 5, but not significantly different from the mean for any other treatment.

In addition, the analysis of variance shows that the day effect is significant at a very high level, a matter of some importance for the improvement of the kerosine burning test, since the differences brought about by burning on different days may be large. F. W. H. Matthews and W. H. Thomas have also referred to this day-to-day variation.¹⁵ They have reported char values on two kerosines by :—

- (a) the I.P. method, and
- (b) the I.P. method with the S.I.L. char estimation procedure.

The 114 results were set out to show any effect attributable to lamps and chimneys, but none was apparent. When their values are re-arranged and an analysis of variance is carried out, ignoring chimneys, a similar day-to-day effect is evident.

As an example, Table VII shows the char values obtained by one operator with lamps 3 and 4 on six days using the I.P. method, and on five days using the I.P. method with the S.I.L. procedure for char estimation.

The analysis of variance in Table VIII shows the day effect to be significant at the 1 per cent probability level, but its cause is as yet uncertain.

Matthews and Thomas consider that it is due to the presence in the wick of oily material removable by extraction with solvents. This explanation appears improbable, however, since the randomized block experiment shows that the effect is general to all wicks extracted and unextracted.

The analysis of the burning-test results of Table V was in terms of char value, expressed as milligrams of char per kilogram of fuel burnt, the

TABLE VII.

Char Values in mg./kg.

(Kerosine V data of Matthews and Thomas (Tables IV & VI).¹⁵)

	I.P. method.							I.P. method with S.I.L. char estimation procedure.						Total.
	Days.						Total.	Days.					Total.	
	6/12.	15/12.	5/1.	8/1.	23/1.	25/1.		11/12.	12/12.	19/12.	21/12.	10/1.		
Lamp 3	8	11	9	6	6	6	46	11	9	6	7	8	41	87
Lamp 4	9	7	9	6	8	7	46	11	10	6	8	7	42	88
Total	17	18	18	12	14	13	92	22	19	12	15	15	83	175

approved medium in which to compare char formation allowing for differences in consumption. This allowance for varying consumption is the obvious correction to make, and, though arbitrary, is preferable to one derived from data obtained on some other occasion perhaps under different circumstances. A comparison of kerosines in this medium is entirely legitimate, but, nevertheless, the correction may not be the best that it is possible to

TABLE VIII.

Analysis of Variance of Char Values in Table VII.

	Degrees of freedom.	Sum of squares.	Mean square.	Variance ratio.
Methods	1	2.19	2.19	—
Days within methods	9	48.27	5.36	4.70
Error	11	12.50	1.14	—
Total	21	62.96	—	—

make. A supposition that increments in weight of char formed are directly proportional to increments in consumption at all levels of consumption within the range observed may be unwarranted and false. A better correction, free from the defect of complete arbitrariness, and supplied by the results themselves—and hence of unquestionable applicability—can be arrived at by means of an analysis of covariance, which combines ordinary variance analysis with the methods of regression, the dependence of one variate on another.

When the figures for weight of char and consumption are so analysed it is found that they reveal no significant trend of char weight on consumption over the range recorded. The relative effectiveness of the wick extraction treatments can therefore be justifiably compared in terms of weight of char directly; in this case, however, it turns out that the conclusions of the previous analysis of the char values remain unaltered. A more interesting example of the usefulness of the covariance technique is provided by the experiment described below.

THE LATIN SQUARE.

The Latin square design is an extension of the randomized block arrangement, and was originally developed in agricultural research to give control of error in two directions at right angles. Treatments are arranged in rows and columns of a square, the number of treatments being the same as the number of rows and columns, and the randomization is subject to the restriction that a treatment can only occur once in any row or column. The Græco-Latin square is an arrangement along the same lines, possible with certain types of Latin square. It is such that a pair of letters, one Greek and one Latin, may be assigned to each cell of the square, so that each Latin letter appears once in each row and each column, and each Greek letter appears once in each row, once in each column, and once with each Latin letter.

The following experiment is an example of a 7×7 Græco-Latin square, and was intended to compare the consumption in m.p.g. of seven motor fuels. It was realized that a precise and closely controlled comparison could be made by means of a bench test in the laboratory, but this procedure carried with it the severe disadvantage that the results would apply strictly only to laboratory conditions, and not necessarily to ordinary road usage. Accordingly, it was decided to compare the seven fuels under actual motoring conditions by using them to propel a motor car of popular make over a route of twenty miles involving diverse gradients. Seven drivers were selected, and asked to drive the car in what seemed to them a normal manner, and, without using any artificial means of ensuring it, to be reasonably consistent. These instructions were preferred to a tight driving schedule at fixed speeds for the same reason that a road test was preferred to a bench test, and it was aimed to take account of differences in consumption attributable to differences in driving speed by making a correction for the average speed of the test run. The time of each run was recorded, and observations were also made of oil pressures and of air, water, and oil temperatures. The experiment was planned to cover seven days and seven periods of the day from 10 a.m.—11 a.m. to 4 p.m.—5 p.m., each fuel being tested by one of the seven drivers each day; in this way any differences attributable to days, periods of the day, or drivers could be eliminated from the comparisons of the fuels.

At the commencement of each day's testing it was arranged that the car should be driven for a few miles so that the oil temperature was 110° F. when the car was returned to the starting point, twenty minutes before the beginning of the first test run at 10 a.m. This was done to ensure that, though not properly warmed up to equilibrium temperatures, the engine was

not completely cold, but, in spite of this, it was found in preliminary tests that on cold days it was frequently necessary to use the carburettor strangler; a "warm-up" run of approximately $1\frac{1}{2}$ miles was therefore incorporated in the test procedure. This run was carried out five minutes before each test period, on a subsidiary can containing a small quantity of the next fuel to be tested. This precaution represented a compromise between covering the whole range of temperatures met with in motoring and warming up completely so that the car always ran at the maximum oil and water temperatures. It enabled drivers to avoid using the choke, but retained some diversity in the conditions, and preserved the influence of both days and periods of the day on the rate of cooling of the engine.

The experimental arrangement, chosen at random from the set of orthogonal 7×7 squares, will be clear from Table IX, which sets out the results for consumption, in the inverse units of m.p.g., and speed in m.p.h. Fuels are designated A-G, and drivers 1-7 in the cells of the square. The column of Table X headed "Sum of Squares (m.p.g.)" shows the straight-forward analysis of variance of the consumption results. It will be seen from an inspection of the adjacent column headed "Mean Square" that differences of fuel means are not significant, the error mean square for fuels

TABLE IX—Part I.

Speed and Consumption Results of Road Test.

Period.		Days.						
		1.	2.	3.	4.	5.	6.	7.
1		A.2.	B.6.	G.1.	C.3.	D.7.	E.4.	F.5.
	m.p.h.	33.36	40.11	39.34	37.50	34.80	35.23	38.38
	m.p.g.	35.74	31.45	30.65	30.84	31.98	33.28	31.76
2		C.7.	E.5.	D.4.	A.6.	F.1.	B.3.	G.2.
	m.p.h.	34.03	37.40	36.36	41.40	42.40	36.14	25.22
	m.p.g.	34.86	30.84	32.43	30.68	29.39	31.31	37.53
3		D.6.	G.4.	C.2.	B.1.	A.5.	F.7.	E.3.
	m.p.h.	38.32	36.55	30.89	44.78	36.00	37.50	39.96
	m.p.g.	31.05	31.73	36.61	29.26	33.26	32.36	31.83
4		E.1.	F.2.	A.3.	D.5.	C.4.	G.6.	B.7.
	m.p.h.	34.75	32.49	38.71	36.46	33.49	42.58	36.49
	m.p.g.	33.76	35.89	31.84	32.43	34.26	29.13	33.26
5		B.4.	A.7.	F.6.	E.2.	G.3.	C.5.	D.1.
	m.p.h.	34.43	33.69	40.45	25.65	37.21	34.52	41.81
	m.p.g.	34.17	33.02	31.25	38.32	32.18	34.01	29.22
6		F.3.	C.1.	B.5.	G.7.	E.6.	D.2.	A.4.
	m.p.h.	37.89	34.53	35.89	36.64	42.15	25.26	39.67
	m.p.g.	31.91	31.83	34.94	31.29	30.31	38.22	31.03
7		G.5.	D.3.	E.7.	F.4.	B.2.	A.1.	C.6.
	m.p.h.	34.47	35.64	34.57	32.97	28.31	44.44	42.63
	m.p.g.	32.64	29.92	33.85	32.97	38.87	27.88	28.92

TABLE IX—Part II.
Mean Speeds and Consumptions.

Days.			Period.			Drivers.			Fuels.		
Day.	m.p.h.	m.p.g.	Period.	m.p.h.	m.p.g.	Driver.	m.p.h.	m.p.g.	Fuel.	m.p.h.	m.p.g.
1	35.32	33.45	1	36.90	32.24	1	40.29	30.28	A	38.18	31.02
2	35.77	32.10	2	36.13	32.43	2	28.74	37.31	B	36.50	33.32
3	36.00	33.08	3	37.71	32.23	3	37.58	31.40	C	35.37	33.05
4	36.49	32.26	4	36.42	32.94	4	35.53	32.84	D	35.52	32.18
5	36.34	32.89	5	35.39	33.17	5	36.16	32.84	E	35.07	33.17
6	36.52	32.31	6	36.00	32.79	6	41.09	30.40	F	37.44	32.22
7	37.74	31.93	7	36.15	32.15	7	35.39	32.94	G	36.00	32.16

being very little more than that for error. The differences between drivers, however, are extremely marked. The analysis of variance of the m.p.h. results in the column of Table X headed "Sum of Squares (m.p.h.)" shows that in terms of speed also drivers alone differ significantly. Moreover, the mean speeds and consumptions of Table IX suggest strongly that part at least of the m.p.g. differences between drivers may be due to differences

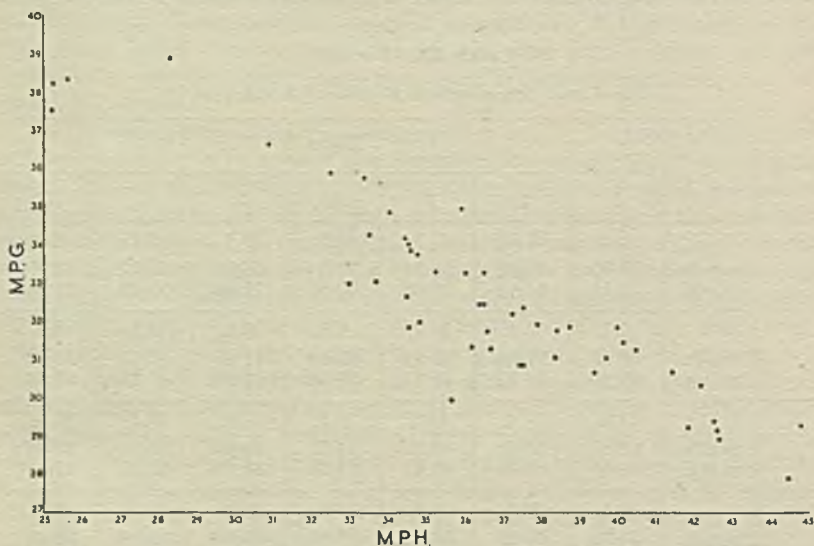


FIG. 2.
CONSUMPTION IN M.P.G. v. AVERAGE ROAD SPEED IN M.P.H.

in mean driving speed, high speeds being associated with low m.p.g.; such a relationship was, of course, expected. But the influence of driving speed on m.p.g. covered all test runs, and was not restricted to consistent differences between drivers. Indeed, when the consumption results of Table X are plotted against speed, as in Fig. 2, it is evident that the speed effect is so great as to make it useless to look for differences of m.p.g. between fuels without making an allowance for the mean speed associated with each fuel mean.

TABLE X.
Covariance Analysis of Results of Road Test.

Source of variation.	Degrees of freedom.	Sums of squares and products.						Errors of estimate.		
		Sum of squares (m.p.h.).	Mean square.	Sum of products (m.p.h. × m.p.g.).	Sum of squares (m.p.g.).	Mean square.	Reduction due to regression.	Sum of squares.	Degrees of freedom.	Mean square.
Periods . . .	6	23·4032	3·9005	— 7·5219	6·4079	1·0680	2·4176	3·9903	5	—
Days . . .	6	23·8829	3·9805	— 10·3160	13·4808	2·2468	4·4559	9·0249	5	—
Drivers . . .	6	693·4787	115·5798	— 402·1992	238·4596	39·7433	233·2648	5·1948	5	—
Fuels . . .	6	47·6883	7·9480	— 12·5840	14·1139	2·3523	3·3207	10·7932	5	—
Error . . .	24	172·1467	7·1728	— 67·9673	37·1664	1·5486	26·8350	10·3314	23	0·4492
Total . . .	48	960·5998	—	— 500·5884	309·6286	—	260·8670	48·7616	47	—
Fuels + error . . .	30	219·8350	—	— 80·5513	51·2803	—	29·5154	21·7649	29	—
Difference for testing adjusted fuel means								11·4335	6	1·9056

The column of Table X headed "Sum of Products (m.p.h. \times m.p.g.)" sets out the analysis of covariance obtained from the products of the m.p.h. and m.p.g. results in a manner analogous to that already explained for the analysis of variance. The total sum of products divided by the total sum of squares for speed gives the slope of the line of best fit for the points plotted in Fig. 2; this is the familiar Method of Least Squares. But both the sum of squares and the sum of products are heterogeneous, and it is clear that an appropriate correction for speed must be based on the trend "within periods, days, drivers, and fuels." It is therefore from the error terms in the two columns that the average effect on consumption of unit change in speed must be derived. In this case the figures show a decrease of 0.395 m.p.g. per unit increase in m.p.h. The sum of squares corresponding to this regression is obtained by squaring the error sum of products and dividing by the error sum of squares for speed. The quotient 26.8350 is the quantity to be deducted from the error sum of squares for m.p.g., and a comparison with the error mean square 0.4492, derived from the remainder 10.3314, shows it to be highly significant.

The marked gain in precision arising from the use of this adjustment for speed is shown by the fact that some 73 per cent of the error sum of squares for m.p.g. has been removed. The significance of differences between the adjusted fuel means may be tested by comparing the appropriate mean square 1.9056 with the error mean square 0.4492, which has been reduced by the correction to 29 per cent of its former value. The variance ratio 4.24 : 1 exceeds the 1 per cent limiting ratio of 3.71 : 1, and the differences of m.p.g. between fuels, previously obscured by the effect of the concomitant variate, are now seen to be highly significant.

The fuel means before and after adjustment are set out in Table XI. Individual comparisons of adjusted means may be made with the approximate yardsticks ± 0.74 m.p.g. and ± 1.01 m.p.g., the minimum differences for significance at the 5 per cent and 1 per cent levels respectively.

TABLE XI.
Mean m.p.g. for Road Test Fuels.

Fuels.	Before adjustment.	After adjustment.
A	31.92	32.02
B	33.32	33.40
C	33.05	32.64
D	32.18	31.83
E	33.17	32.88
F	32.22	32.63
G	32.16	32.01

In all the examples given in this paper discussion has been confined to the function of the analysis in providing an objective and proper assessment of the experimental data. The correct interpretation of the results in terms of chemistry and physics, usually the ultimate aim, is possible only when these foundations are soundly laid.

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DISCUSSION.

THE CHAIRMAN (Mr J. S. Jackson): The subject is one of fundamental importance and interest to all the members of the Standardization Committee in particular, and to everybody who is concerned with the planning of investigations. It is hoped, therefore, that this paper will arouse a keen discussion.

In the first place I am impressed with the fact that if one starts off with the intention of applying these statistical methods to a series of experiments one is forced from the very start to design the experiments thoughtfully and carefully; that introduction of a systematic method of approach is in itself a tremendous advantage. Even if one has doubts about the assumptions involved in statistical methods there can be no possible doubt about the advantage derived from designing the experiments along the systematic lines illustrated in the paper.

The conventional experimental method has been, of course, to study the effect of one variable at a time. This involves carrying out a very large number of experiments, and may involve a great deal of waste of time and money. It is possible, on the other hand, to design a neat, compact series of experiments involving all the variables that can be anticipated and if the effect of these variables can be picked out and analysed in the way suggested by Dr Davies, then the economy effected may be enormous; the ability to select certain factors, estimate their effect and eliminate them from our considerations, is very striking.

Just how far we can accept all the assumptions made I do not know. In the experiments dealing with char value, for instance, the large effect due to the different days on which the tests were carried out is quite striking. I should like to ask the author just what assumption has been made in this case. Is it that the different days involved different atmospheric conditions? Is not the manipulative skill of the operator also involved? Is it a fair assumption that the manipulative skill of the operator was

constant for each day? Was the variation in results due, not to the fact that the tests were carried out on different days with different climatic conditions, but to the operator having removed the char with a different degree of skill on different days?

If it is possible to pick out the effect of each variable, evaluate it in terms of mathematical values, eliminate the variables which are not of interest and concentrate upon those which are essential, then the whole method represents a fundamental change in our approach to many investigations.

MR PETER KERR : Dr Davies has done the Institute much service in drawing his examples either from the Institute's own work or from subjects in which the Institute is interested.

Even a brief consideration of the tables he has given shows how impossible it would be to digest and understand them by any mere inspection or unsystematic study. Dr Davies has shown that, by the methods he has discussed, variations which would otherwise be obscure can be analysed and allocated—and allocated quantitatively—to their various sources.

We are left in no doubt as to the value of the methods which he has applied. Those methods are relatively new, but no one to-day can afford to neglect the possibilities they offer of more economical and more intelligent preliminary design of research and experimental work.

Dr Davies will perhaps correct me if I am wrong in thinking that the chief advantage of the method is that measurement can be substituted for the control which was previously essential. The results he discusses are all quantitative; are there similar methods available for obtaining purely qualitative results?

DR DAVIES : A query has been raised by the Chairman as to whether the day effect in the char value results is in fact a matter of atmospheric conditions, or whether it may be due merely to changes in the operative skill of the person estimating the char value. I have made it clear in the paper that the actual explanation of this effect, which I have called the "day effect," is not yet known; at any rate I do not know it, and I am not satisfied with the explanations that have been suggested. He is right in saying that the cause could in this case have been a difference of operative skill as between one day and another in the actual estimation of the char value. But we have other results, which were obtained in a different way, where that is unlikely. However, it must be understood that the term "day effect" is merely a descriptive term, relating to the variation between the mean results for columns 1-4 of Table V. It has been employed because the individual results making up these means were all obtained at the same time; it must not be regarded as implying any particular cause, such as a fluctuation in atmospheric temperature, pressure and humidity. Undetected differences, of some other kind may have existed between days 1, 2, 3, and 4. For example, although I do not think it was so in this case, the amount of dust in the atmosphere, or in the fuel, may have differed from day to day.

There is, in fact, no special assumption involved regarding the cause of the variation. We are merely considering sets of results obtained on different days, and we refer to the difference between the means of each

set as a day effect. We can call it a group effect if we like, but I think it is clearer if we call it a day effect.

I agree with Mr Kerr that the measurement of error, rather than its control, is very much at the core of these methods, and there is no doubt that it is more important to be able to measure variation than to control it. I believe that ease of control has often held back the use of these methods. In fields of technology where it is fairly easy to control variation one usually finds that methods of measuring it are not in common use. I prefer both measurement and control; but I insist that measurement cannot be dispensed with.

Mr Kerr asked whether we can do anything about purely qualitative results. I think we have to distinguish between two cases, first, where it is possible only to place the results in order, secondly, where it is possible to employ some rough assessment, such as a method of scoring. If only the order can be settled, Kendall's rank correlation coefficient may be used; but that is comparatively crude, as is to be expected if only the order of the results can be set down. If six oils are compared for ring sticking, and one can do no more than say that the order is B, C, D, A, E, F, it is not surprising that statistical methods can give very little help. They are essentially methods for dealing with numbers. If, on the other hand, some rough assessment can be made by a method of scoring, one can carry out an analysis of variance of the scores. But the limitations of the original results must be borne in mind; they are only scores, and they are not infinitely variable but discontinuous.

MR J. G. WITHERS: I think it is rather remarkable that the residual error in Table VI is so small. If there is a large day-to-day variation, I think we should expect quite a large variation within one day, depending on the time at which the experiment was started. I wonder if Dr Davies would agree that the reason for such a small error must be either that all the experiments were started at the same time, or that there is, perhaps, an operator error coming in, which changes after the operator has had a good night's rest.

Coming to the analysis of the road fuel consumption and speed tests, I believe that this may be to some extent misleading. The author states that he wished to obtain fuel consumption results uninfluenced by restrictions in the way the car was driven, in which case I think the analysis should be directed to obtaining the significance of differences irrespective of the covariance corrections. I think that this simpler analysis would give a better indication of the significance of any differences to the group of drivers. If the covariance corrections are applied an adjustment is made for the effect of speed, but would it not be better to eliminate speed in the first place, if that is what is desired? Should it not be the policy in an experiment to control all disturbing variables from the beginning, rather than to eliminate them through the analysis?

In Table X, under errors of estimate, the difference for testing adjusted fuel means is obtained from the difference between the fuels plus error and the error terms. Is there any reason why a direct comparison should not be made between the fuel term and the error term? In the case considered, the answer so obtained differs very little from that given, but there must

be some reason for having " Fuels plus Error " as a separate line in the Table.

Finally, the author has stated that the sum of the squares is additive. That does not seem to apply to the covariance analysis.

DR DAVIES : AS I have already mentioned, what is called the " day effect " in respect of the burning test results probably involves a number of different factors; it is just a term referring to the difference between one set of results and another set of results obtained on different days. So far as I can remember offhand, these particular results were obtained over four days in such a way that there was probably an hour's difference in the time of starting a test as between day 1 and day 2, day 2 and day 3, and so on. But I shall have to look up the records in order to be absolutely certain that that was so all the way through. Naturally, all the eight tests were started together on each of the four days.

Instead of referring to the difference as being between " days," shall we say as between " periods of 24 hours in which the burning tests were carried out " ?

MR KERR : I would point out that 11.30 p.m. is very nearly the next day.

DR DAVIES : I think there is some misconception. In this connection, when I refer to a " day " I do not mean a particular date, as, for example, November 28; I mean the period of 24 hours in which the eight tests were carried out. Differences due to those periods, plus differences due to variable technique in char estimation from one day to another, and any others not yet spotted, all go to make up the difference between one set of results obtained together and another set of results obtained together.

As to Mr Withers' remarks on the covariance correction, I certainly do not agree. He suggests that in a test of this kind speed variation should be eliminated in the first place. If it is so eliminated that must mean fixing the speed of driving; if you do that, you are certainly not getting a result that refers to average road conditions, for you are causing the car to be driven in a highly artificial way. I think it is far preferable to allow the drivers to drive a car as they normally drive. That was done in this case. The instructions were to drive in what seemed to them to be a normal manner and to be as consistent as possible without using any special means of ensuring it, such as making a point of driving only between 30 and 35 m.p.h. The correction for speed was introduced in the analysis. I think that was right; I do not agree that the straight analysis of variance, without correction for speed, is the method which best gives results that can be called average road results, just because this difference of speed was associated with the individual drivers. Had there been any speed difference associated with fuels, it would have been a proceeding of very dubious validity to have introduced the correction and to have compared two results at the same speed, knowing that the fuels had very much affected the difference in speed actually observed. In this case the fuels themselves did not affect the speed of driving, as can be seen from the analysis of variance for m.p.h.

MR KERR: Could you limit a car to a certain speed and so eliminate one variable factor from the experiment?

DR DAVIES: I was about to point out that one obtains additional information by the method I have described. It is not only a question of whether causes of variation are allowed to operate; one can gain information about the extent of their effect, and at the same time—and in spite of the fact that these other causes of variation are present—one can still make the comparisons that the experiment is intended to make.

Mr Withers' question regarding the "Fuels plus Error" term is rather difficult to answer. The sums of squares of errors of estimate, other than the error sum of squares, have been included in Table X for completeness and also because they are interesting from some special points of view. They represent the extent to which the m.p.g. variation for particular factors, such as fuels, are not accounted for by the regression of the m.p.g. means for those factors (*e.g.*, fuel means) on the corresponding m.p.h. means. The comparison of the sums of squares or mean squares for fuels and for error in the errors of estimate section is not one that is appropriate to the purpose of the experiment. The trend "within periods, days, drivers and fuels" supplies the true measure of the influence of m.p.h. on m.p.g., and in consequence it is the effect of this regression that needs to be subtracted in order that the residual fuel and error terms can properly be compared. By working with the Fuels plus Error totals, as in the penultimate line of Table X, we are enabled to leave in as a genuine fuel effect the extent to which the regression of the fuel means differs from the error regression. This is precisely as it should be.

I would refer you to text books in which these methods are explained in detail, such as that of R. A. Fisher and others mentioned in the "References" at the end of the paper.

The sum of squares for the "Errors of Estimate" are not additive.

MR C. S. WINDEBANK: I should like to make a point regarding the amount of work associated with the use of the methods described. There is a tendency among the uninitiated to regret the amount of effort that it is necessary to put into an experiment based on the Græco-Latin square, or one of the other patterns which Dr Davies has touched upon. After the limited experience I have had, I am well satisfied that this effort is worth putting into the job. Rarely would we be satisfied, in more usual and less well planned experiments, to base any real conclusions on less than perhaps half these number of tests, and I really think the additional effort of the complete experiment is well worth while, (*a*) for the increased accuracy obtained thereby, and (*b*) for the benefit of establishing how significant the results really are.

That is, I think, the real point about these methods. So frequently, because of the expense and time involved—and this applies particularly to engine test work, in which I am closely interested—one is apt to restrict the amount of experimental work in order to get some sort of result quickly. We have always realized that there is a wide margin necessarily attached to the data that we get—a wide margin of experimental accuracy, or inaccuracy. But I think that rarely have we realized how wide this is, and

I think we may be well advised in the future to look very closely into the level of significance of our results, more particularly in such work as the engine testing of lubricating oil. I have used the conventional term "significance," but perhaps "insignificance" would prove to be a better word to use!

MR E. THORNTON : I would like to support the remarks of Mr Windebank. I agree that the paper does bring up the "insignificance" of our results. I am reminded of the old story concerning the man who confidently stated that "figures cannot lie," and got the reply : "No, but liars can figure."

It is appalling that the results of any allegedly standard tests should show such wide apparently uncontrolled variations. It does look as if some of our limited figuring may lead us very wide of the truth in tests of this kind. It is particularly appropriate that the Chairman of the Standardization Committee should be the chairman of this meeting, because it is apparent that some careful scrutiny by statisticians would be of advantage when reviewing our so-called standard tests to see that, at least, we do not deceive anyone but ourselves when we sit back in the confident belief that any test is "standard" if in reality it is capable of giving variations of the order indicated by the figures quoted by the author in connection with the kerosine burning test.

The answer to all this is surely twofold : on the one hand, if after statistical review of this character we discover unsuspected variations, we must hammer away at achieving the removal or control of the conditions of test giving such variability and, in cases where this is obviously not possible, then we ought to indicate for such difficult tests a minimum number and optimum arrangement of test results which would give a reasonable answer when assessed by statistical methods.

MR R. J. BRESSEY : I think a paper of this sort is very long overdue so far as the Institute of Petroleum is concerned. Statistical methods have been making very great progress in their application to many sides of science; but I think this is the first occasion on which the subject has been brought forward in this Institute, and now that the ice has been broken I hope there will be more papers dealing with the application of statistical methods to the analytical, testing and sampling problems with which technologists are faced. We live in a statistical world, and need to be reminded of it.

With regard to the "day effect," I am in the fortunate position of knowing nothing whatever about "char"—it is just a cup of tea to me! But when I learned that this paper was to be read, I re-read a lecture on "What is Probable Error?" which was presented to the Institute of Chemistry in 1931, by Dr J. F. Tocher, and I was struck by a very interesting section on the cyclical character of the results of successive analytical determinations, which may possibly have some bearing on the matter. It was shown that in one particular series of determinations* by various workers the mean of their first to fourth determinations were lower than the observed

* Actually of fibre in animal feeding stuffs. This example and others will be found on page 27 of the lecture.

means for the whole series. From the fifth to the tenth determinations the means were above the overall mean, while after the tenth determination the means fell again. In this particular series the workers were nearest the overall mean about the fourth or fifth determination. A similar rhythmical movement—a tendency for high values, following a tendency to have low values, was demonstrated in other cases and Dr Tocher commented: "Tell us why it is that highly skilled men engaged in scientific work of any kind stagger from side to side like drunken men along a straight road, despite all efforts to keep straight. Must we conclude that Man in all his best efforts takes a similar irregular course?"

I think there is food for thought there!

That leads me to the next point, that if, in a long series of determinations of a single characteristic, you get all this variation, what is the significance of a single determination or even duplicate determination of that characteristic? Leading on from that, what is the significance of these single or duplicate results in relation to specification limits? For example, when it is specified that the octane number of a gasoline shall not be below a certain limit, what does it mean? What do we really mean, we who sit on B.S.I. committees and make specifications, when we say, for example, that the maximum sulphur content of a diesel fuel shall be not more than 1 per cent. or some other figure?

With regard to books on the application of statistical methods, I notice that Dr Davies gives a list. But, in my rather limited experience, most of the books I have seen have treated the subject either from a purely mathematical standpoint or with particular reference to the biological sciences. Is there a book available which deals with the subject in such a way that it is "respectable" mathematically, yet puts the subject forward so that the comparative tyro can understand it and its application to some of the things in which he is directly interested as a physicist or chemist or engineer?

It seemed to me, when reading this paper, that some of the procedure, apart from the mathematics, is just applied common sense and I think we ought to enter a caveat against the danger of over-complicating matters so that they become incomprehensible to the average worker, with the result that his interest and co-operation are lost.

DR DAVIES: I have at home a reprint of Dr Tocher's paper, and I must look up this matter of the cyclical trend of results. I can hardly swallow at the moment the suggestion that that is universal. He may have found this oscillation for a particular set of results, probably in dairy chemistry concerning total solids or solids-not-fat, but if it is suggested that this cyclical trend is observable in all analytical determinations, of any kind, then it seems to me at the moment to be incredible. There may be some simple explanation. Though I can easily imagine that particular operators, who experience marked fatigue in carrying out some process, will obtain results which vary according to whether they are fatigued or rested, I can hardly believe that that would be so in all analytical determinations. Such an effect might be very pronounced in certain cases, as, for instance, in psychological tests where the operator has to dot points on a strip of paper moving at high speed, but not evident at all in other cases.

On the question of the significance of results, such as for ratings or fuels, it is probably a good thing to stress that more results should be obtained than are usually obtained, as indeed Mr Windebank has stressed. Having increased the number of results, one is in a very much better position to make estimates about the mean of the population. This is not to say that the only solution is to do an immense number of tests. What methods such as these can do is to indicate how many tests should be carried out in order to give a result with a certain degree of reliability.

With regard to books, I have not found that the biological bias is a serious drawback except in one or two cases. The book by Snedecor, which I have mentioned in the paper, seems to me to be one that can very easily be used even by workers in other fields than agriculture. After all, though designs like randomized blocks were first used in agriculture, their application to other sciences is a comparatively simple matter; after that the analysis is quite straightforward and independent of the particular subject on which the worker is engaged.

MR H. R. HOLMES : Do these methods depend on the distribution being normal, and how far is this a serious limitation ?

DR DAVIES : I think the answer is that, for exactness, the methods do depend on the distribution being normal; they give exact results when the distribution is normal. But, as I mentioned earlier, they are essentially aids to common sense, and do not in any way supplant it. It is found that small departures from normal distribution are not serious. The means of several results tend much more closely to be normally distributed than do individual results, when there is some departure from normality.

Secondly, the *t* test and the *z* test—the *t* test being “Student’s” test, and the *z* test being the test developed by Fisher and embodied in the analysis of variance—are not critical of departures from the normal distribution unless those departures are very large, and it is probably safe to use the methods unless there is a definite contra-indication. If you have a positive reason for believing that the distribution is nothing like the normal, that it is, for example, either J-shaped or U-shaped, then obviously you will have to re-consider the matter. Fisher deals with this to some extent in his book “The Design of Experiments.” Using some data of Darwin’s he gives there the results of making a test on the assumption (a) that the distribution is normal and (b) that it is entirely random, and he shows that the conclusions are very little different in the two cases. In a later part he mentions the work Eden and Yates carried out at Rothamsted. There again the conclusions derived from the *z* test very closely verified conclusions derived on the basis of complete randomness in material that was very far from normal.

In addition, I call to mind the fact that in the A.S.T.M. “Handbook on the Presentation of Data” the committee mention that they have not come across any distributions in which deviations from the mean of three or more times the standard deviation occurred in less than 96 per cent. of cases, the value given by theory being about 99. The departure from normality was thus comparatively slight.

MR H. L. WEST : On this “day effect” problem, would it not be better

if you applied the covariance correction to the rate of consumption, because there seems to be a relation between the char value and the rate of consumption of the kerosine? I wonder if that effect is not possibly obscuring the so-called day-to-day variation.

DR DAVIES: I quite agree about the desirability of using the covariance method with the results of the burning test and, in fact, working in terms of weights of char and fuel consumptions. I have mentioned, below Table VIII in the paper, that when the figures for weight of char and consumption are analysed in that way they reveal no significant trend of char weight on consumption over the range recorded. (The range, especially of consumption, was very small, so that it is not surprising that these particular figures do not show any trend.) As they do not show any trend, it is perfectly justifiable to compare the results in terms of weight of char directly. When you do that you find that the conclusions of the analysis using char values are unaltered. They are unaltered just because the consumptions were not very widely different; otherwise, dividing the weight of char by the consumption would almost certainly have given different conclusions from those derived by working in terms of weight of char alone. But I am certainly not very happy about using this arbitrary correction for differences of consumption and expressing the weight of char in mg./kg. I think it would be better to take steps to restrict the consumption even more than is done already and then work in terms of weight of char, rather than to use the assumption of a linear trend over the range.

DR W. E. J. BROOM: I should like to congratulate Dr Davies on having presented this paper; it is very welcome here. I also feel that I should like to congratulate him on having organized the experiment he described for investigating fuel consumption. Quite apart from any statistical questions, it does require quite a bit of organization to run off such tests at appointed periods of the day, with different drivers and different fuels.

There are one or two matters on which I should like his advice. I gained the impression, from what he said at the beginning, that these methods were developed mainly in agricultural experiments. I take it that in effect that means that where we are doing experiments in which there is a very great number of variables and where the conditions are uncontrollable, the assessment of the results by these analytical methods is absolutely essential.

That surely represents one end of the scale, where control is very difficult. At the other end of the scale we have, for example, the determination of octane number, where all concerned have done their best to introduce every sort of control that can be conceived. To what extent should we introduce control when we are endeavouring to assess accuracy or fine differences? Dr Davies' analysis of the two sets of rich mixture results did show that, although the two fuels were fairly close together in actual values, there was a real difference. His analysis confirmed the averaged engine data.

All our methods of testing in the industry are based on applying as strict a control as possible. Our Chairman, Mr Jackson, is also the Chairman of a sub-committee of the Institute which is concerned entirely with apparatus, and which stipulates the most minute details in regard to that

apparatus in order to ensure that we do obtain results which are comparable as between one laboratory and another.

So we cannot abandon control in favour of statistical analysis in every case, although there are many cases in which the application of analysis will show up unexpected sources of error. We have discussed the "day-to-day" effect in the kerosine burning experiments, which effect may be due to various obscure reasons; but the point is that this analytical method has shown that there is some obscure effect. If we applied it to some other well known tests we might be somewhat surprised to find other sources of error which we have not thought about.

The one great pity about this method is that we need a lot of results in order to apply it; and it is unfortunate that our most costly experiments are those of which we have the smallest number of results. It seems to me that those experiments are the ones we must control most.

DR DAVIES : I agree about endeavouring to control those experiments which are most expensive. But the question as to what is a large number of results and what is a small number obviously depends very much on how long the test takes, what it costs in money and effort. The extension of statistical methods to experimental work is essentially that of applying it to comparatively small numbers of results, such as less than 25, whereas in the past those methods were restricted in their application to vast numbers, such as arose in the course of State business, running into thousands or millions. But, whatever the number of results, you can at least make some estimates from them. If you have only a small number, the estimates will not be very well based, and naturally the reliability will be lower than with a larger number. I would always look at the results from that point of view.

The question as to how far we can abandon control is somewhat difficult. I would not favour the abandonment of control; for many purposes I would be in favour of maintaining it and even of extending it where the effort involved is not very great. So long as it involves no restrictions that are undesirable—as, for instance, restriction of the basis of application of the results, as would have been the case, in my opinion, had we carried out the road tests at one fixed speed—there is almost everything to be said for it. It is then a question of how much effort is involved. But you must always have some measure of variation, whether or not you have control, because even if you introduce a fair degree of control, as is done with many of the methods set out in the book of "Standard Methods," it is impossible to eliminate every single cause of variation. The main argument for having a closely specified method is undoubtedly that you will be able to make comparisons between results obtained in different laboratories and on different occasions. The 3C ratings, which have been analysed in two ways, show that you can have differences between one engine and another, but agreement as to which fuel gives the better performance. That is quite satisfactory if you want to ascertain merely whether one fuel is better than another, and roughly how much better. But from the point of view of the Institute of Petroleum and correlation work between laboratories, it is clearly a good thing if engines can be specified in respect of their manufacture and operation so that they will give as nearly as possible

the same answer, as well as agreeing that fuel A is better than fuel B. One can appreciate that there is a good deal to be gained if two laboratories tell the same story about fuel A, so that agreement is not confined merely to the fact that fuel A is better than fuel B.

There will be many opportunities of improving the correlation work of the Institute of Petroleum by the use of these methods.

MR R. J. BRESSEY : I should like to return to the question of cyclical variations. It does seem to be very well authenticated in the paper by Dr Tocher, who quotes several different examples observed in technical and pure scientific work. The phenomenon appears to have been first noticed by Pearson and to have been confirmed by "Student" and others, and there seems no reason for casting doubt on its existence.

DR DAVIES : I am very interested, and I will take the first opportunity of looking it up. I was really querying how universal was the cyclical variation; but in the face of the evidence you have just mentioned, I will withdraw my objections.

THE CHAIRMAN : We have had an excellent discussion, and I would like to thank Dr Davies on behalf of the meeting. He has presented a very thought-provoking paper, and one which I hope will have very important repercussions. I should also like to congratulate him on the easy, confident, and pleasant manner in which he has dealt with all the questions. The discussion serves as a very great compliment both to the author and his paper and I invite you to express your appreciation in the usual way.

(The vote of thanks was carried with acclamation, and the meeting closed.)

MR. R. J. BRESSEY, in a subsequent written communication, directed attention to a recently published monograph on "Industrial Experimentation" by K. A. Brownlee (H.M. Stationery Office, 2s. net). This is a guide to modern statistical methods written entirely from the practical point of view and should be particularly valuable to those who have no time or inclination for the underlying mathematical theory. Each statistical method discussed is illustrated with practical examples worked out in detail to show what exactly is involved in its use, and the only mathematics involved is simple arithmetic.

THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute of Petroleum was held at 26, Portland Place, London, W.1, on Wednesday, May 8, 1946, the Chair being taken by Mr. A. Beeby Thompson, O.B.E.

THE CHAIRMAN: I have great pleasure in introducing Dr. George Sheppard to speak about the geology of Ecuador. I must confess that I have no personal acquaintance with Ecuador, but I was one of the pioneers in exploring part of the same belt of country in Peru in 1904, when really serious exploitation of the Peruvian oilfields was initiated. Since then a great deal has been learnt about the geology of the country that extends from the northern part of Peru into Ecuador, about which latter Dr. Sheppard is to speak. I am sure he has some very interesting things to tell us, and I hope he will say something concerning the future oil prospects in the part of Ecuador on which he is about to talk.

THE GEOLOGY OF THE GUAYAQUIL ESTUARY, ECUADOR.

By GEORGE SHEPPARD, D.Sc., Ph.D. (Fellow).

GUAYAQUIL, the principal port of Ecuador, is situated about seventy miles from the Pacific Ocean, at an elevation of but a few feet above mean sea level. Its early inhabitants, the Huancavilcas, were conquered by the first Spanish invaders under Sebastian Benalcazar in the year 1535. Later followed a series of minor hostilities, and finally the city of Guayaquil was founded in 1537, by Francisco Orellana, the discoverer of the River Amazon. The Spanish occupation lasted until 1820, and the city declared its independence on October 9 of that year.

Most of the city is built upon the estuarine silts and muds of the River Guayas, and forms part of the same regional territory, in common with other parts of the west coast of South America, which is slowly emerging above sea level.

The conspicuous range of rounded hills, actually forming a picturesque background to the north (Fig. 1), is the chief feature of geological interest. The same hills outcrop across the river, but within a few miles they pass beneath the silts, an enormous level stretch of land which continues eastwards to the foothills of the Andes. The Guayaquil Hills form part of the Cordillera de Chongon, and follow a direction generally east and west (Fig. 2).

Dr. Robert Cushman Murphy,¹ describes the estuary of the River Guayas as follows:

“The Gulf of Guayaquil is the relic of an ancient, larger estuary, now bordered with long islands of silt consolidated by mangroves, and penetrated by innumerable creeks through which the current of the river does not flow. The large island of Puna, however, is not a delta formation, but is a recently detached portion of the sandstone plateau of Santa Elena. Inland around the shores of

the Gulf are successive zones comprising (1) the manglares (mangrove swamps) where the flooding tide covers the roots, (2) the savannahs, which are above the high tide line, but are inundated by rainwater during the 'invierno' (January to May), and (3) agricultural land."

GENERAL OBSERVATIONS ON THE GEOLOGY.

Table of Formations.

(1) Recent Deposits :

- (a) Fluvial, etc., including shoals and manglares ;
- (b) Scree accumulations.

(2) Tertiary Formations :

- (a) Chongon Sandstones and Shales ;
- (b) Guayaquil Group :
 - (1) San Eduardo Limestone ;
 - (2) Guayaquil Argillites and Cherts ;
 - (3) Moreno Sandstone ;
 - (4) Tres Cerritos Breccias.

RECENT DEPOSITS.

The low-lying lands bordering the River Guayas consist essentially of recent accumulations which can be described conveniently under two headings. The first are fluvial in origin, and include the finer muds and silts which have been brought down from the interior by the innumerable small streams and rivers which make up the greater part of the Guayas drainage system (Figs. 3 and 4). This process has been in intensive operation since the close of the Quaternary period, and there is no doubt that the enormous quantities of detrital material thus removed by the steeply graded streams from the western slopes of the Cordilleras have been distributed over the plains, and have formed, in effect, the vast areas of agricultural land which occur in the vicinity of the estuary.

In addition to the normal activities of atmospheric erosion, which, in a tropical climate, are considerable when applied to terrain consisting of loosely compacted volcanic material, the frequent occurrence of landslides in the highlands during the rainy season adds an appreciable amount to the overloaded water-courses which flow towards the Guayas basin. The great bulk of the heavier rock material, boulders, and coarse gravel, is deposited at the foot of the mountains, and the finer detritus is distributed over a much larger area which, in a geographical sense, includes the whole of the estuarine zone.

Mudbanks and shifting shoals are naturally more active during the rainy season, by reason of an increased quantity of mobile sediments transported from inland, and which, upon impact with the tidal waters of the estuary, accumulate almost to the water level. Deposits of this nature are well exemplified in the creeks or "esteros" around Guayaquil, and they consist principally of dark-coloured muds which usually support a profuse growth of manglare vegetation. They are also infested by colonies of small crabs and other crustaceans, and various semi-aquatic forms of life.

References to "floating islands" are common in the descriptive literature of this part of Ecuador, and are applied to the flood-waters of the River Guayas during the wet season, when large masses of aquatic vegetation, dislodged by the flooding of certain parts of the country, are carried out into the waters of the Gulf. Here they are subject to the tidal currents, until they finally disintegrate and disappear, and so add their quota to the humic constituents of the silts, or river muds.

Shoals of considerable extent can be seen near the island of Puna. These, in the course of time, become overgrown with vegetation, and form dangerous obstacles to ocean-going steamers. From the generally turbid state of the river water all the year round, it must be assumed that large quantities of suspended detritus are carried to the ocean, and a great proportion of this is deposited in the lower reaches of the estuary itself. The scree accumulations are usually derived from two sources: (a) the slopes of the western Andes; and (b) the Cordillera de Chongon and the Guayaquil Hills. It is possible that the whole area underlain by the plain which extends from the Andes to the river consists of rounded boulders and gravels which have been derived primarily from the steep slopes of the mountains. They are found also near the estuary, beneath a covering of river silt, and include lavas and other volcanic material.

In the immediate Guayaquil district, however, the deposits resulting from recent denudation consist of limestones, argillites, flinty shales, etc., which are local in origin. The scree is fairly thick near the respective escarpments, but grade into finer gravels and sand in the lower sections of the region.

THE TERTIARY FORMATIONS.

Chongon Sandstones and Shales.

The arenaceous deposits known collectively as the Chongon Sandstones and Shales have an extensive regional distribution, and, whilst occurring as type sections in the district of Chongon, they are found also within a few miles of Guayaquil, where they appear to rest conformably upon the San Eduardo Limestone.

The series is probably of Miocene or upper Oligocene age, and though no fossils have yet been recorded from the formations, they are similar lithologically to the known Miocene strata of the Bajada region farther to the south-west, and they no doubt form an easterly extension of the same facies. The sediments include dark-coloured, coarse to fine-grained sandstones with shales, all of which are loosely compacted and porous. The sandstones are usually thin-bedded, with separations of iron oxide along the bedding-planes. In other localities they are tabular in habit and are dark green in colour, this being due either to glauconite, or to the inclusion of some admixture of decomposed pyroxenic material.

The shales are present in more or less lenticular bands of close-grained sandy silt, being light buff to brown in colour. Some varieties have the appearance of bentonite, with dendritic markings on their weathered surfaces, and have a wax-like texture.

Outcrops of these formations are found between Chongon and the first limestone outcrop about five miles from Guayaquil, on the main road to Salinas (Figs. 5 and 6).

The Guayaquil Group.

The Guayaquil Group has been divided into four sections, which will be described separately, as under :

- (a) San Eduardo Limestone (Fig. 7);
- (b) Guayaquil Argillites and Cherts (Figs. 8, 9);
- (c) The Moreno Sandstone (Fig. 10);
- (d) Tres Cerritos Breccias.

The above classification applies only to the outcrops found in the Guayaquil region proper, where they have been mapped and studied in

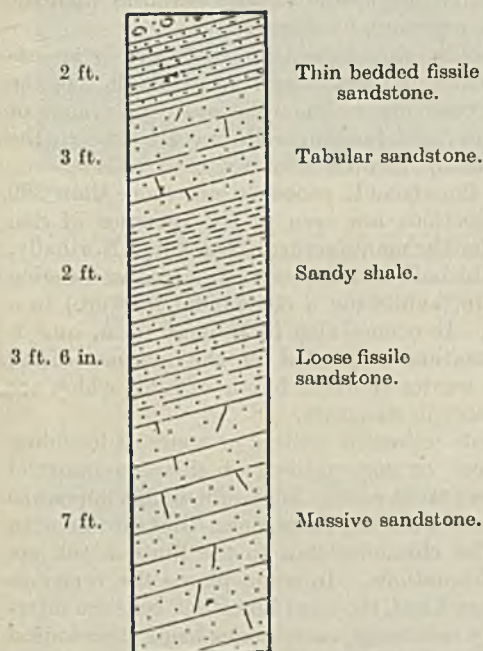


FIG. 5.

SECTION IN MIOCENE SANDSTONE NEAR KM 21
GUAYAQUIL-SALINAS ROAD.

General dip S.W. at 15.



FIG. 6.

SECTION IN LOWER PART OF MIOCENE WEST OF FIRST OUTCROP OF SAN EDUARDO LIMESTONE, KM 18 GUAYAQUIL-SALINAS ROAD.

detail. Similar formations have been observed in other parts of the same hill range—namely, at Colonche, and in several localities in the province of Manabi. It is quite possible, therefore, that the formations in the north may have the same lithological characteristics, and indeed may form part of the same group, as those about to be described.

The four subdivisions enumerated above appear to belong to one stage of sedimentation, though it must be noted that the upper one—*i.e.*, the San Eduardo Limestone—is a distinct facies, and is a true limestone which carries a foraminifer fauna. The whole development of the Guayaquil Group probably attains a thickness of some 1000 feet in this region. Fossils, apart from the foraminifera, are scarce. A few imperfect casts, however,

were found in the neighbourhood of Mongon, and they were described as follows by Mr. A. A. Olsson.²

“The fossils are too imperfect and indefinite for me to decide their true nature. They are apparently not molluscan, but I strongly suspect that they are the remains of barnacles. One specimen in particular is quite similar to figures of the wall-plates of certain barnacles, but the material is altogether too meagre for me to be sure.”

Though this description, which applies only to the fossil evidence seen during the course of this work, adds nothing to what we already know regarding the geological age of the formations, it is clear that the deposits, as a whole, are of relatively shallow origin, and as such conform with the known Tertiary formations of the region under discussion.

(a) *San Eduardo Limestone*. The San Eduardo Limestone is an exceptionally pure form of calcareous sediment, and in places it has the appearance of a typical hard, Cretaceous chalk. Siliceous concretions, or separations, almost like true flints, add further to its resemblance to the recognized chalk formations of Europe and elsewhere.

In the Guayaquil district the limestone is probably not more than 300 feet in thickness, and typical sections are seen in the quarries of San Eduardo, where the rock is used for the manufacture of cement. Normally, its colour varies from white to light buff, and the rock has a texture ranging from that of a compact porcelain (exhibiting a conchoidal fracture) to a coarser-grained, softer material. It occurs also in tabular form, and is occasionally massive. The formation is jointed in the manner of all limestones, and certain horizons carries sporadic bands of flint, which are either tabular, spheroidal, or ramose in structure.

There is no doubt that the flints represent centres or zones of leaching, and indicate either accumulations or segregations of siliceous material which have been derived from the parent rock. Such flint-bands appear to be slightly porous at their contact with the limestone; they are grey to brown in colour, and have similar characteristics to the flints which are found in Cretaceous limestone formations. In some places the rock has the texture of marble; on the other hand, the hard limestone beds are inter-laminated by layers of an earthy substance, such zones being discoloured by iron oxide and other materials. Veins of a honey-coloured calcite are common, and usually occupy the joint-planes of the tabular strata.

In San Eduardo and other places where the limestone is found, the texture of the rock varies considerably, and the different kinds have been classified as :

- (a) compact, cream-grey, fine grained limestone, with a porcelain-like texture;
- (b) coarse-grained rock, with foraminifera and shell fragments very comminuted, and has the appearance of marble;
- (c) soft, earthy layers—coloured pink to light brown—with a separation of limonite;
- (d) flints, tabular, spheroidal and ramose. These occur principally in (b).

In addition to the siliceous segregations, which do not actually occupy joint or other planes, but appear sporadically distributed throughout the



Courtesy.]

[*Government of Ecuador.*

FIG. 1.

AERIAL PHOTOGRAPH OF CITY OF GUAYAQUIL SHOWING THE LOW HILLS OF THE GUAYAQUIL ARGILLITES AND CHERTS IN THE FOREGROUND. THE CITY OF GUAYAQUIL IS BUILT UPON A MARGINAL DETRITAL ACCUMULATION OF THE RIVER GUAYAS, THE ISLAND OF SANTAY AND THE EASTERN CORDILLERA OF THE ANDES IN THE BACKGROUND.



FIG. 2.

LOW SWAMPY TERRAIN NEAR CHONGON AT THE FOOT OF THE CORDILLERAS DE CHONGON (BACKGROUND).

[*To face p. 496.*



FIG. 3.



FIG. 4.

VIEWS OF THE DISTRICT AROUND GUAYAQUIL SHOWING THE TOPOGRAPHICAL NATURE OF THE LOW-LYING "MANGLARES," WITH THE OUTCROPS OF GUAYAQUIL ARGILLITE, ETC., NEAR THE CITY.

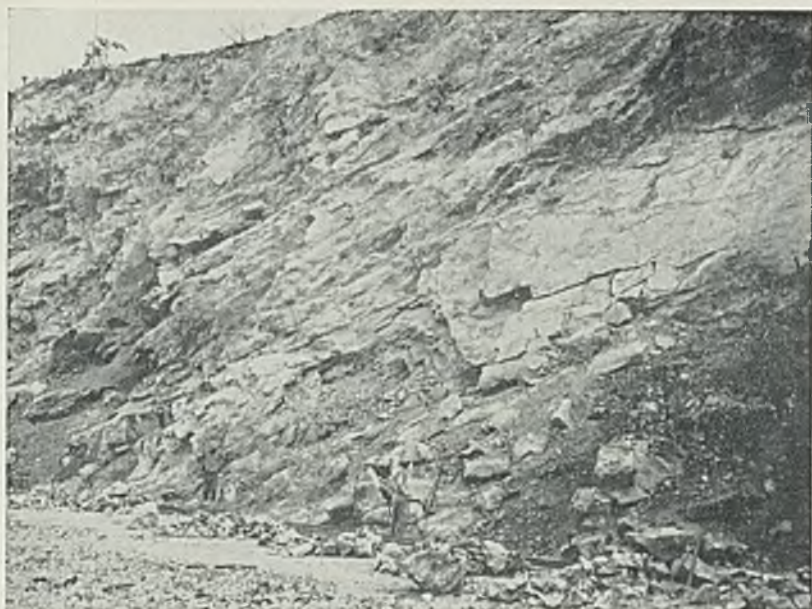


FIG. 7.

SAN EDUARDO LIMESTONE (QUARRY OF THE SAN EDUARDO CEMENT FACTORY, GUAYAQUIL).



FIG. 8.

SECTION IN THE GUAYAQUIL SERIES (60 FT IN HEIGHT), MUNICIPAL QUARRY, GUAYAQUIL.



FIG. 9.

QUAYAQUIL ARGILLITES AND CHERTS (NEAR BRIDGE ACROSS THE ESTERO SALADO).



FIG. 10.

THE MORENO SANDSTONE, WITH GLAUCONITE INCLUSIONS AND GREEN GLAUCONITIC SHALES.

Roadside quarry about 2 miles along the road from Guayaquil to Salinas.



FIG. 11.

SECTION IN THE GUAYAQUIL SERIES NEAR THE ESTERO SALADO, GUAYAQUIL.

parent rock, there are other vein fractures of calcite, and in these cases the vein-walls are altered to a softer form of vari-coloured limestone material. The latter clearly indicates a condition which has resulted from a local process of leaching, and may be indeed associated with regional metamorphic action.

From analyses supplied by the San Eduardo Cement Company it appears that the percentage of lime carbonate is high, and includes from 83 to 96 per cent of the rock. Four specimens of limestone from this locality have yielded the following results :

SiO ₂ , per cent	1.70	6.70	9.60	11.80
Al ₂ O ₃ , per cent	1.00	1.20	0.80	4.00
Fe ₂ O ₃ , per cent	0.20	0.20	0.70	0.80
CaO, per cent	53.50	50.70	49.60	46.50
MgO, per cent	0.80	0.70	0.42	0.63
Loss, per cent	42.80	40.10	39.10	37.27
CaO ₃ , per cent	96.25	91.75	88.00	83.00

The age of the San Eduardo Limestone (the Guayaquil limestone of previous publications) has been a subject of controversy since 1892, when Wolf³ described the formation as Cretaceous by reason of the identification of certain *Inocerami*. No such fossils have been found in the rocks of the Guayaquil district since that date, but more recently Wayland Vaughan concluded, from a study of the foraminifera, that the deposits were Eocene.⁴

In Dr. Wolf's book, under the chapter entitled "The Cretaceous Formations of the Coast Belt," we read :

"The following rocks have been found in great variation in the quarries and cuttings near Guayaquil, Chongon, Pacuales, etc., beds of limestone, siliceous slate or shale, quartzite, yellow and green sandstones, and shales which alternate the above strata. They are usually thin-bedded and occur in relatively thin strata, and differ considerably in different places. The limestone is but rarely pure, though beds sufficiently calcareous for burning into lime are found near Pacuales and Chongon. The limestone is nearly always impregnated with silica, and the percentage of the latter increases in many cases so that a pure siliceous shalo results, which contains but little calcium carbonate. All the grey, buff-coloured and similar rocks which are found in the quarries near Guayaquil are of the siliceous variety. I have made analyses of many specimens, and these vary from 5-40 per cent of calcium carbonate.

The fine, white or cream-coloured rock of texture semi-crystalline, which has been obtained for many years from a quarry between Chongon and Guayaquil for paving the river front, occurs in thick, massive layers, and this limestone dissolves almost completely in hydrochloric acid.

"There are other varieties of siliceous limestone, however, which are dark-coloured, and almost black, and this colour may be due to the presence of bituminous substances. The sandstone layers, which alternate the calcareous or siliceous strata, are well-exposed in Las Penas to the north of the city. They are always dark-coloured, generally green or grey.

"In addition to the quartz grains, the chief mineral, there is considerable glauconite, which iron silicate gives the green colour to the rock when the mineral is fresh.

"When decomposed, however, the red or brown colour is due to oxide of iron. Usually the quartz grains are small, but at times they are larger, and the whole deposit assumes the texture of a breccia or a conglomerate. According to my observations, the sandstones are found usually in the lower part of the section, whilst the limestones are above.

"The disposition of the Cretaceous rocks is very irregular. Horizontal beds are never found, but the strata are inclined at varying angles. The beds in front of the Estero Salado are almost vertical. In several places it is seen that the rocks have been violently contorted, producing undulations, ripples and faults. The latter can be seen quite clearly in the quarries near Guayaquil."

The great advances in the science of palæontology since the beginning of the century have led to modifications, or rectifications, in the nomenclature of many geological formations, especially in regard to their age and the conditions under which they were deposited. The researches of Professor H. B. Geinitz during the latter part of the nineteenth century, for example, afforded a notable stimulus to the study of Cretaceous formations all over the world, and in Ecuador we have seen that considerable tracts of country were, at that time, mapped as Cretaceous, upon evidence which could not be accepted by the palæontologist of to-day.

Apart from the fossil content of a formation, a fair amount of reliance was placed upon lithological similarities, and this often led to confusion and incorrect diagnosis. In addition to the formations found in the Guayaquil district, Wolf described an extensive zone in the interandine basin of Cuenca—namely, that of the Azogues Sandstone. This was stated to be of Cretaceous age, an opinion which was based upon the identification of certain fossil forms, by Geinitz, who considered them to belong to the Wealden (Lower Cretaceous) of Europe.

Thus, in Wolf's book on the geology of Ecuador, we read :

"For the determination of the geological age of the Azogues Sandstone, we are indebted to the discovery of fossils from Paccha. I found here near a small stream, several large blocks of strata which were composed entirely of fossils, finely-cemented by a ferro-calcareous substance. Unfortunately, I was not able to find this rock in place, but there is no doubt that it occurs in the immediate vicinity. I forwarded the specimens to Prof. H. B. Geinitz, of Dresden, and he recognized a great similarity between these fossils, and those of the Wealden of Europe. He determined for certain *Cyrena*, *Cyclas* and *Paludina*.

"If we take this palæontological evidence in conjunction with the petrographical nature of the sandstone, viz., the coals and asphalts, there is no doubt that we have a contemporaneous formation to the Wealden, namely, the oldest section of the Cretaceous group."

A few years ago the same fossil locality was visited by the present writer, and a collection of specimens taken from the sandstone formations *in situ*. These were subsequently examined by Drs. Marshall and Bowles, of the United States Natural History Museum, who found that the material yielded three new genera, each represented by one new species, and a new species of *Pomacea*.⁵

In the paper referred to, the authors state

"at present there are no reliable data to establish the age of the deposits, but as none of the species and none of the genera, except *Pomacea*, occur in the recent fauna, it is probable that the age cannot be later than Pliocene, and it may be earlier."

The shales and sandstones in which the above fossils were found lie in the interandine belt near the town of Cuenca, situated between the two main ranges of the Andes. The fossil beds are highly inclined, with a general northerly strike, and hence they give some idea of the approximate age of the orogenic movements which were associated with the Andean uplift in this country.

In common with the Leaf Beds of the Loja basin, the deposits of Paccha are of fresh-water origin, and were most probably laid down in a lake, or ancient river valley, which occupied the depression between the existing mountain ranges. Of major importance, however, is the fact that the Azogues Sandstone is folded steeply in accordance with the general direc-

tion of the Cordilleras, and therefore the final stages in the uplift of the Andes in Ecuador must have taken place in either Miocene or early Pliocene times.

Nevertheless, Cretaceous rocks have been recognized and described by Messrs. Wasson and Sinclair, from the Oriente of Ecuador—*i.e.*, to the east of the main Andean range.⁶

According to this publication,

“the age of the Napo Limestone has been determined, from the fossils collected, as Middle Comachean to Upper Cretaceous, Middle Albian to Turonian of the European section. These fossils are largely of Turonian age, equivalent in the United States to Eagle Ford, or Benton, of the Texas and Rocky Mountain sections respectively.”

With regard to the Guayaquil series (Fig. 11), we find that Messrs. Sinclair and Berkey⁷ made one of the first scientific investigations of these rocks in the year 1921, and examined many of the type specimens under the microscope.

The rocks are described collectively as cherty limestones by the above authors, and a type example collected from Guayaquil, is as follows :

“Specimen E. 1.—This is a compact rock, almost white, with microfine structure and almost amorphous, which original framework was later slightly modified by replacement and silicification. The primary and essential constituents are microscopic organic forms which, containing both silica and lime carbonate, include Radiolaria and Foraminifera. Silica is the principal substance introduced. The formation was originally composed almost entirely of micro-organisms, fragments of shells, probably both calcareous and siliceous, thus giving the present rock a varied composition.

“The greater part of the matrix is calcareous, but the principal fossil traces are siliceous, both being present in approximately equal quantities. Thus the rock is not simply calcareous, neither is it a true chert, but its origin and character are unmistakable. Such a rock would probably have the simple composition of a chert in some places, and in others almost pure carbonate of lime. Also there would be specimens where the one form would grade into the other. Its origin is organic, and is classified as a cherty rock composed of Infusoria and Foraminifera.”

The authors state further :

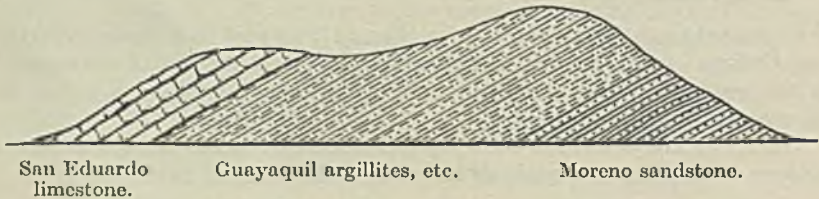
“We do not know of other cherts in Ecuador except those of the Santa Elena Peninsula. These cherts have been described in a previous publication.”⁸

Another important extract from the above paper, and which will be discussed in a later section of the present article, is of considerable interest in connection with the geology of the Guayaquil formations :

“In all their essential aspects, the cherts of Santa Elena and Guayaquil are petrographically the same. They have the same general origin, and are in essentially the same condition, they have passed through the same stages of formation. The organic forms are similar in their principal details, and we are impressed by their similarity in origin, history and formation. They are the same in all these points, almost to the fact that in certain strata occur angular fragments of recent clastic materials, *e.g.*, ash, also in the difference in the filling of the vein cavities, the formation of breccia, and the different stages of deformation. The calcareous examples of the districts of Guayaquil and Santa Elena contain a foraminiferal fauna with identical genera, and prove that the rocks from both places are approximately of the same age, and were deposited under similar conditions.”

(b) *Guayaquil Argillites and Cherts.* The hills to the immediate north of Guayaquil consist entirely of the Guayaquil Argillites, all of which are

well exposed in the different quarries now being opened by the municipal authorities (Fig. 12). The group is a complex one in a lithological sense, and the term "argillite" can be used only in a general way, since other stages of sedimentation are represented, such as sandstones, cherts, slates, and true argillites. All are highly silicified, and perhaps to the majority of the subdivisions the term "silicified shale" would be equally appropriate and applicable. As a rule, highly compacted siliceous mudstones make up the bulk of the section, and they are thin-bedded, also tabular, and occur occasionally in a massive form. The latter include coarse-grained sandstones with interbedded layers of a greenish, siliceous shale. It is of



SECTION NORTH FROM SAN EDUARDO ACROSS EASTERN END OF THE CORDILLERAS DE CHONGON, NEAR GUAYAQUIL.
Length of section, 3 km.

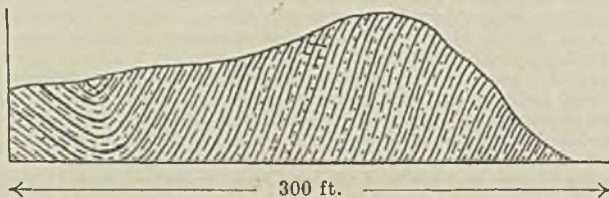


Fig. 12.

GENERALIZED SECTION IN THE GUAYAQUIL ARGILLITES, ESTERO SALADO, GUAYAQUIL.

interest to note that the above-mentioned greenish deposits are found in the hills of the same range to the east of Colonche, and hence the series may be similar in the northern part of the province of Manabi.

In some places the strata are completely replaced by silica, either in the form of chert, or in some other amorphous variety. Where veined, the rock contains blue chalcidonic silica, almost opalescent, nodules of compact iron pyrites, and fairly thick veins of quartz. In others, the respective strata are green, grey or light buff in colour, and their exposed surfaces weather to a bright vermilion colour, which is due no doubt to the presence of secondary iron oxide.

In a normal succession the flinty argillites pass downwards into a coarse, brown sandstone—possibly a basal deposit—which contains angular fragments of a dark, olive-green material, which has been identified by the British Museum authorities as glauconite,⁹ this being a confirmation of the diagnosis made by Dr. Wolf many years ago.

Another section in this vicinity has the appearance and constitution of a slate, though it is thin-bedded, and includes lenticular strata of hard, coarse-grained sandstone, the more massive parts of which exhibit

spheroidal forms on the exposed surfaces (Fig. 13). The latter phenomenon, however, is a result of tropical weathering, and has been observed in other parts of the country, such as the Cuenca district, and the Oligocene sandstones of the Santa Elena Peninsula.

The contact between the basal sandstone and the siliceous argillites shows a formational transition by the presence of occasional layers of green shale, which appear to pass upwards into the argillites proper. The above sandstone has been named the Moreno Sandstone, in order to distinguish it from the Miocene sediments which are found in the same region.



FIG. 13.

● 60 FT. SECTION IN GUAYAQUIL SERIES NEAR GUAYAQUIL.

Hard siliceous argillite, thin bedded (grey-green). Includes lenticular massive sandstone layers, which weather in a spheroidal manner.

(d) *Tres Cerritos Breccias*. This varied series of arenaceous deposits outcrops in the district known as Tres Cerritos, about two miles north of the city, and near the Municipal Aerodrome.

The formation occurs in tabular and massive layers, and consists of a dark, olive-green to brown breccia, which passes locally into coarse sandstone, with thin tabular strata towards the top of the section. The massive beds weather in a spheroidal manner, and contain abundant angular pieces of glauconite, and decomposed volcanic ash. This heterogeneous deposit was formed most probably from the rapid denudation of a basic igneous terrain, in which lavas and tuffs were common. The Tres Cerritos Group represents the oldest sedimentary rocks exposed in the

Guayaquil area, and may be homotaxial with certain breccias found at Ancon Point, in the Santa Elena Peninsula.

GENERAL OBSERVATIONS ON THE STRUCTURE AND ASSOCIATED OCCURRENCES OF IGNEOUS ROCK.

The Guayaquil Hills constitute a block of altered sedimentary strata which, though inclined steeply in places, indicate a general declination to the south or southwest. The same structural trend continues across the river eastwards for a few miles, whilst towards the west these formations are succeeded by a series of loosely-compacted sandstones and shales, which are most probably of late Oligocene or Miocene age.

The argillite sections near the Estero Salado are almost vertical, and exhibit minor folds which are incidental to the general structure.

To the northwest of Chongon, however, about twenty miles distant from the city, a reversal of dip is apparent in the Miocene deposits, and it is quite possible that a large synclinal fold occurs here, which may have some structural relation to the regional anticline which is found in the same formations near the village of Bajada.

The tilting of the clastic deposits, however, has been induced from the east, or northeast, and the principal tectonic movement was doubtless associated with the regional uplift of the western range of the Andes. The isolated outcrops of east-west orientation near Guayaquil dip generally southwards at an angle of 20 degrees. Towards the west the angle steepens, with local folding, to about 40 degrees, and in some places the strata are actually vertical. As referred to above, the basal formation is a coarse brown sandstone with included greenish shale, and is probably an upper phase of the breccias or tuffs exposed at Tres Cerritos.

The chief elevations of the range are known as Cerro del Carmen and Cerro Santa Ana, and they rise to an altitude of approximately 300 feet above the river level. A more extensive development of the same escarpment occurs about a mile to the west of the above, and this forms the beginning of the Cordillera de Chongon proper. This is an important tectonic unit in the region under discussion, and it continues towards the Pacific Ocean for a distance of about 85 miles to the northwest of Guayaquil, and, in some places, reaches a height of some 2000 feet above sea level.

Similar deposits to the above, with intruded igneous rocks, are found to the east of Colonche in the same cordillera, and the dip in this case is to the south or southwest at about 25 degrees.

The Gulf of Guayaquil, the largest inlet of its kind along the west coast of South America, presents many features of geological interest. Although the majority of the islands which are found dotted all over the estuary are simply mudbanks covered with mangrove swamps, the Island of Puna, the largest, consists of Tertiary formations superimposed by a thin deposit of Quaternary "raised beach" or tablazo. Both these formations are found on the mainland to the north, but it is important to note that not only are volcanic lavas present in the Tertiary beds, but at least one boss, or outcrop, of biotite gneiss.

Wolf, in 1881, found a series of volcanic types in the Island of Puna,

and according to him they occurred on the east coast of the island. They were described as large masses of compact lava, some in part porous (probably scoriaceous), and others cemented together. Wolf was of the opinion that the rocks are true lavas, like those recent types which are found in the Andes at the present time, and may have resulted from a submarine eruption. Quite recently, a mass of igneous rock was found by G. H. S. Bushnell (1937) in the same locality, and this has since been identified by the British Museum (Nat. Hist.) as a biotite gneiss, a plutonic type which appears to have an unusual field relationship to the recent lavas and Tertiary sediments.

A petrographical examination of the gneiss, by the authority above cited, is as follows :

"The slide shows the following minerals, quartz, orthoclase, microcline, plagioclase (andesine), biotite, muscovite, apatite, zircon and magnetite. Apatite and zircon show idiomorphic boundaries. The remaining minerals have interfered with each other's development and are allotriomorphic. In some places, the texture is almost granular. Evidence of stress is furnished by the undulose extinction of the quartz, and by discontinuous and bent albite laminae. Some secondary twins seem to have been induced by stress in some feldspar grains. The andesine is sometimes altered to mica or a saussuritic mineral aggregate. Other crystals are quite fresh. This alteration often affects only one part of a particular andesine crystal. The mica is mainly biotite, which shows a tendency towards a rough parallel arrangement of flakes. Microcline is very abundant, together with potash feldspar showing a micropertthitic intergrowth.

"The rock is a biotite-gneiss."

Specimens of a decomposed biotite gneiss, or granite, have been found at Punta Piedra, about half-way up the River Guayas from Puna to Guayaquil, and these are associated with reddish, siliceous argillites which are similar in appearance to those found near Guayaquil. Boulders of gneiss are very common also in the Quaternary beds of the Santa Elena Peninsula, and it is quite possible that they may have been derived from some pre-existing outcrop of this material, during the deposition of the Quaternary formations.

A large syenite mass, surrounded by argillites and siliceous shales, is found at Pascuales to the north of Guayaquil, whilst many of the smaller topographical elevations in the same region consist of diorite, and are probably intrusive masses of the same geological age as those which occur in the Andes proper.

The distribution of both plutonic and volcanic forms of rock, which follows the general direction of the Gulf of Guayaquil, indicates that we have here a complex geological problem, the solution of which may throw light upon the history of the Gulf itself. Granites and similar forms are of relatively rare occurrence in the Andean region of Ecuador, and their outcrops, where found, are usually indicative of the ancient core of this great mountain chain.

The Andes in Ecuador consist of two roughly parallel ranges, following the line of the Pacific Coast from south to north, Suess says :

"The great range of Ecuador consists of a western chain, the continuation of the Cordillera Occidental, formed chiefly of intrusive and effusive rocks of Mesozoic age, and an eastern chain, corresponding to the Cordillera Central, which is composed of pre-Cambrian rocks. These are separated by the Interandine region, which is bordered on both sides by recent volcanoes, and cumbered by their ejectamenta."

The same authority also states :

“Towards the sea (*i.e.*, in Ecuador) the Cordillera Occidental is bordered by a plain, but isolated bosses of syonite and diorite emerge from the Inoceramus Limestone of Guayaquil, and on the east coast of the Island of Puna Wolf observed a breccia of andesitic lava. . . . Granite, however, occurs on the River Tumbes near Lat. 4. S and phyllite with a north strike near Paita. They probably form offshoots of the Amotape Mountains.”

The following observations were made also by Suess upon the geology of this region, and it will be noted that he assumes the correctness of the Cretaceous age of certain formations, which have since been proved to be younger :

“From the southern boundary of this state to about Lat. 2. S. the Andes consist of two parallel cordilleras which are frequently united in the south. The eastern cordillera is composed of granite, mica-schist, chloritic schist, and other ancient crystalline rocks, these strike, like the cordillera itself, from south to north, their extension towards the east is unknown. The western cordillera, on the other hand, is formed of ancient eruptive rocks of great variety, which are described as ‘porphyries and greenstones,’ some granite masses also crop out amongst them. Towards the north, conglomerates and rocks resembling Flysch appear as an additional member. On the west side of the western cordillera, Cretaceous deposits appear in the direction of the sea, the Gulf of Guayaquil restricts the region they occupy, but to the north of it they reappear with imposing breadth, and extend thence far to the north. Eruptive greenstones accompany the Cretaceous, especially in the provinces of Guayas and Manabi.

“The boundary region between the eastern and western cordillera runs between the Meridians 79 and 80, and is termed by Wolf the intra-andean region. It is of the greatest tectonic importance. Within it, south of the town of Loja and also near the town itself, lie two depressions filled with recent leaf-bearing beds. Somewhat further to the north, near the headwaters of the River Jubones, there appears in this intra-andean region, succeeding each other along a line running from south, somewhat west, to north, the first fore-runners of the great volcanoes of northern Ecuador.

“These are formed chiefly of andesite. They appear in three regions, on the upper Jubones, then south of Cuenca, and lastly north of this town in Azuay. Between the last-named volcanic masses there appears northeast of Cuenca in the intra-andean region, a curious mass, the ‘Aronisca de Azogues,’ which consists of sandstones with quicksilver. It is bluish grey in colour, weathers spheroidally, is bleached by the alteration of iron, and is accompanied by shales. The stratification is very much disturbed, the strike corresponds to that of the intra-andean region. Crossing southern Ecuador from east to west, we thus meet in the east, with gneiss and ancient crystalline rocks, then in the intra-andean region leaf-bearing deposits, the first masses of andesite and the patch of sandstone with asphalt and quicksilver, and in the west, various porphyries and greenstones which are succeeded towards the sea by the Cretaceous formation. The continuation of these chains towards the north may be traced by observations given in the works of Reiss.

“The eastern cordillera in this region also consists of gneiss and other ancient rocks which, in the case of a few summits, reach a height of 4500 metres, and on the Sara Urcu in the north, even of 4800 metres. The intra-andean region of the south is here represented by the high plateau of Riobamba, Latacunga and Quito, covered with lavas, tuff and ash. The western cordillera is formed of soft, chiefly black, shales, traversed by various greenstones, and of massive beds of sandstone.

“Towards the west it descends steeply to the sea. . . .”

Igneous intrusions of a dioritic nature are well distributed in the Gulf zone; they are found towards the east of the Cordillera de Chongon, and have been observed in the same range as far north as Colonche. Similar dykes and sills of post-Tertiary and pre-Quaternary age are common throughout the coast belt of southwestern Ecuador, and have been described in a previous publication.¹⁰

Hence we may infer that, in addition to the recent types of lava found in the Andean region proper, there is a second and slightly older series, which have been intruded through the early group of Tertiary sediments, but has not yet been recorded as penetrating the Quaternary formations. To this series must be added the intrusive rocks of the coast-belt and, in the case of Puna, there is evidence of contemporaneous lava-flows in several places where the Tertiary sediments are exposed.

The presence of plutonic forms, however, as at Pascuales and Puna, is difficult of explanation; they may be of the same age as the diorites, but it seems more likely that they form a much older phase of igneous activity, and perhaps represent an ancient core to the cordilleran system.

Though it is not considered that the stratigraphical formations near Guayaquil and Colonche are Cretaceous, but are Eocene in age, and that so far no Cretaceous rocks have yet been discovered west of the Cordillera Occidental of Ecuador, it must be remembered that an extensive region in the Oriente—*i.e.*, to the east of the Andes in the Amazon basin—consists very largely of Cretaceous formations, these having been described in detail by Messrs Wasson and Sinclair from 1921 onwards. Cretaceous rocks occur also in the Amotape Mountains of Peru, and form part of the same series as those found in the Oriente region of Ecuador.

THE SANTA ELENA REGION OF ECUADOR.

With regard to the Santa Elena region of Ecuador, which forms the northern part of the Gulf of Guayaquil, a considerable amount of geological information has been acquired within recent years, and thanks to the work of the geologists of the oilfields, and others, it has been possible to compile a comprehensive summary of a few important facts which have been ascertained both from the mapping, and from drilling. General descriptions of this complicated geological zone have been published, but the present account will be confined to a description of the igneous and metamorphic rocks which are here found, their association with petroleum, and their correlation with the normal sedimentary formations which are found in the same region.

The complex geological structures found in certain parts of the Tertiary coastbelt of Ecuador have given rise to considerable conjecture, and diversity of opinion, regarding their origin and distribution. The problem is fundamentally a regional one, and it is often difficult, and at best unsatisfactory, to put forward a theory regarding the structure of a special area, without considering the greater regional whole of which the discussed area forms but a minor part.

According to the present state of our knowledge, therefore, we must attribute the general structure of this part of South America to one, or to a combination of, the following factors :

- (1) Regional tectonic movements, plus seismic influences, associated with the main uplift of the Andean chain ;
- (2) The local influence of hypabyssal or volcanic intrusions ;
- (3) Gravitational sliding, caused by the overloading of sediments on a sloping continental platform.

At the outset, the writer would like to pay a tribute to the valuable paper published by Mr. R. A. Baldry.¹¹

The contemporaneous formations of Ecuador, however, which form part of the same geological unit as northern Peru, do not form a good parallel, neither in a stratigraphical nor in a structural sense, and although, without quite appreciating the physical reason why sediments should gravitate to a lower level after consolidation rather than before, or why we should assume the presence of a relatively steep depositional platform, or to attach too much importance to the so-called Pacific Fault in this connection, the evidence recorded in reference to low angle slipping is of considerable interest.

The late Dr Bosworth's theory regarding regional faults of great throw appeared to be a satisfactory explanation of the structure of northern Peru, yet it must be remembered that he had not the advantage of Mr. Baldry's knowledge of the detailed subsurface mapping.

One important difference, however, must be noted regarding the two countries, and that is, the presence of certain igneous rocks which are found in association with the sedimentary formations of Ecuador, and also the cherts and altered sedimentaries, which, apparently, have not yet been recorded from the coastal zone of Peru.

References and descriptions of these igneous rocks and cherts have been published,¹² but the igneous areas probably underlie great tracts of country, and, as such, have undoubtedly had some effect on the structure of the sedimentary formations they have invaded.

As a general rule, the igneous rocks found in this part of the country include an intermediate form of basic magma, probably a quartz dolerite, and the actual outcrops are offshoots (in the form of apophyses or dykes) from some igneous platform which occurs at depth.

Chert masses are associated with the igneous rocks, and it is possible that the phenomenon of "chertification" is the result of a complicated series of hydrothermal processes which have been caused primarily by the intrusion of igneous material.

Thermal waters, or vapours charged with siliceous compounds, the raising of temperature by igneous contact, the circulation of heated gases through the sediments of the contact zone, each or all may have contributed to the silicification of the original sedimentary formations, the results of which we now recognize as cherts, argillites, or siliceous shales.

There appears to be abundant evidence in support of the suggestion that the secondary silicification of a shale causes a local increase in volume, this phenomenon being indicated by the intense crushing found in the lesser altered zones in contact with the larger chert bodies. On the other hand, a chert outcrop usually has a sharp and clearly defined contact with the unaltered sedimentary formations, a fact which has led many observers to assume that faulting has taken place.

The probability is, however, that although the principal phase of igneous activity in this region was of post-Oligocene pre-Quaternary age, there may have been several stages in the hypabyssal movement of the viscous igneous rock, which continued over a considerable time in the above geological interval. Thus, an already silicified, or partly silicified mass of shales, resting normally upon an igneous platform, or low angle dyke,

may be still further moved or dislocated by the intrusion of a later igneous body, and hence may have the appearance of a faulted unit.

There appears to be little doubt that the complex structure which is a characteristic feature of the "disturbed belt" of southern Ecuador has been caused largely by the action of igneous rocks, their movement under, and in contact with, the sedimentary formations.

The southern part of the coastal zone—namely, the northern arm of the Gulf of Guayaquil—consists chiefly of Tertiary formations, with a thin development of Recent and Quaternary deposits. The region can be divided into at least four geological units :

- (1) The Eocene-Oligocene belt which extends from the River Guayas almost to Bajada. This includes also the Guayaquil Hills;
- (2) The Miocene-Oligocene tract of San Jose de Amen;
- (3) The Eocene zone of the Ancon oilfield;
- (4) The Santa Elena Peninsula proper.

It seems probable that the principal structural trends which have been recognized so far in this region indicate a general northwesterly orientation, and they are represented specifically by the low-dipping anticlinal fold of Bajada and San Jose, formed essentially of Miocene and Oligocene sediments, the faulted monoclinial or collapsed anticlinal of the Ancon oilfield, and the gentle structure near Colonche.

It is of interest to note that in both the units (1) and (4) the Tertiary formations are of a complex order, and include cherts, argillites, metamorphosed sediments and igneous intrusions, whilst in units (2) and (3) neither igneous rocks nor cherts have been yet recorded.

Correspondingly, whilst surface indications of petroleum are widespread in the most disturbed structural area—viz., that of the Santa Elena Peninsula—there are few evidences of this nature elsewhere.

The complicated disposition of various lithological types, all of which are associated with contemporaneous or post-Oligocene intrusions, or include the altered members of the Oligocene formations, has led more than one observer to consider the whole region as a structural "imbricate," or shatter-zone, in which it is almost impossible to recognize definite trends in any direction. Regional "sliding" on a large scale has been also suggested as an explanation of the different phenomena which are found in this zone, and the possibility of "rock-sheet" movements (H. G. Busk) on a regional scale must not be overlooked in order to account for the structural conditions which have been revealed by the surface mapping. More recently, C. Barrington Brown has considered this gravitational theory in relation to the peninsular area of Santa Elena, and has described many of the interesting geological features which are found here.¹³

In the district known as Ahuquimi the dolerite occurs as a sill, with attendant dykes. It is certain also that offshoots and stringers of the same material extend upwards from the principal mass, and form apophyses in close association with the cherts and altered shales. The upper surface of the igneous platform is invariably fissured, and is, to a certain extent, porous. For this reason it often forms an ideal container for the accumulation of petroleum which has migrated from below. Crush-breccias are found near its contact with the chert, in which the individual fragments

of igneous rock appear to have been "rolled," and are usually coated by altered chloritic deposits. The cherts are also intensely shattered near their contact with the igneous rock. In several of the wells drilled in this area the dolerite sill has been penetrated, and both cherts and altered shales have been found below.

The area called Santa Rita Achallan forms part of the disturbed zone of the Santa Elena Peninsula, where the stratigraphy has been complicated by the many lithological types which have been formed primarily by igneous intrusion, and where the structure is very confused. Post-Tertiary, or perhaps Tertiary dykes and sills are a feature of this zone, especially in the northern part. In the southern sector—viz., where the Oligocene sandstones and shales predominate—igneous intrusions do not form outcrops. The mapping has revealed the presence of crush zones and shatter belts; these, however, alternate with considerable areas of more normal sedimentaries, such as the Achallan Sandstone, where the strata are block-faulted, and are possibly duplicated in accordance with the recognized trends of movement. In these areas the disposition of the respective formations is similar to the geological structure of most of the Ancon region, where minor faults or thrusts are common, but which, *per se*, have little influence from the point of view of oil production.

The southern half of the area is occupied largely by a soft, greenish sandstone with shales, the majority of which are highly inclined and faulted.

These formations include cherts and argillites, with normal sandstones and shales. In this especial area the sandstone is almost characteristic, it being greyish-green in colour, and has a tendency to include large spheroidal concretions. It belongs undoubtedly to the Oligocene (of the Ancon Point group), but the unusual greenish colour seems to be always associated with the sandstones which are found in the neighbourhood of the hand-dug oil pits. On the other hand, the green colour may be due to the inclusion of chlorite, or glauconitic products, and thus the rocks are similar to those already described from the Guayaquil district.

The occurrence of surface seepages of petroleum in their relation to the subsurface formations has not yet been satisfactorily explained in the present region. Three major factors, however, must be considered in this connection :

- (a) the lithological nature of the rocks through which the petroleum exudes to the surface;
- (b) the structure of the local formations in relation to any regional tectonic phase;
- (c) the influence of dykes or sills.

The exploited oil-pits in this zone are associated with altered cherts and igneous rocks, the latter having channelled the cherts to such an extent that the oil has found its way into the pits through joints or fissures. To the west, the "pit" zone follows a line roughly northwest, which corresponds to structural trend in the Tertiary formations. From an examination of most of the oil-pits in this area, one is led to the conclusion that the sedimentary deposits here found—there are no igneous nor cherts at the surface—form a crush zone which may be an example of extreme

tectonic compression resulting from the general structural forces which were initiated from the southwest in post-Oligocene times.

Large deposits of the so-called "tierra-brea," a heavily impregnated sand of inspissated petroleum, are found in this area. From the field evidence it seems possible that the actual "tierra brea" is a Quaternary deposit of uncompacted marine sand which covered the disturbed sandstones of the Oligocene at the beginning of the Quaternary period. Thus we may picture a belt of Achallan Sandstone, fissured and jointed, through which the oil gradually migrated upwards into a thickness of some 10 feet of soft, unconsolidated sands, which latter, in effect, provided an ideal container for this inspissated material. The "tierra brea" is thus a saturated sandstone of Quaternary age, though the oil itself is of Tertiary, or even older, origin. On the other hand, there is always the possibility that where defined patches of "oil sand" occur, the underlying sourcebeds have been partially depleted during past geological ages, and moreover, the oil itself, by contact with atmospheric agencies near the surface, and through the physical changes induced by the processes of upward migration and filtration in different geological media, has been deprived of its more valuable constituents.

THE CAUTIVO AREA.

The Quebrada Cautivo is one of the many minor stream courses which traverse the "disturbed zone" of Santa Elena in a general northwesterly direction, and the rock exposures found along its valley give an excellent idea regarding: (a) the nature of the geological formations; (b) the complexity of the structure; and (c) the occurrence and distribution of natural petroleum in association with both (a) and (b).

The quebrada itself is of the usual trench-like form, with level benches of tablazo (Quaternary raised beaches) forming the outer definition of the stream-course, whilst subsidiary river terraces, each of which most probably represents a flood year of abnormal intensity, are found at lower levels in the valley area.

Almost vertical banks up to 40 feet in height are common, and occasionally these are surmounted by small hanging-valleys, where the lateral drainage channels have been eroded through the tablazo limestone.

For the greater part of the year these quebradas are dry, though during the months from January to March the few showers of rain which usually fall are sufficient to cause a slight flow of water towards the sea.

The principal topographical features of the valley, however, have been sculptured during some bygone rainy season (which occur approximately at seven year intervals), and during these abnormal years the streams become torrential, and the enormous volume of water drained from the adjacent areas rushes with great velocity to the sea.

As a consequence, the erosion during these heavy rainy seasons is phenomenal, and the resulting modification of the existing topography is considerable.

In addition to the Recent and Quaternary formations, the principal sedimentary deposits are of Oligocene age, and include sandstones of various kinds, and soft, gypsiferous shales. There are also metamorphosed

representatives of the above sedimentary units, which are the cherts and silicified shales.

A large igneous mass, a form of quartz dolerite, occurs as an outcrop beneath the tablazo towards the west of the map area, and from what we know of the subsurface conditions in this zone, it can be assumed that the igneous body occurs beneath the greater part of the zone.

The igneous outcrops are undoubtedly offshoots from some platform of hypabyssal rock—probably a sill, with associated dykes—which is found at depth, not only in this area, but throughout the greater part of the Santa Elena region proper. The field relationships of igneous rocks with the Tertiary formations of the Ecuadorian coastbelt have been described in previous publications, and is a geological condition which is not found in the contemporaneous formations of Peru.

The Oligocene formations of the Cautivo area are usually of two kinds : (a) the massive, coarse-grained variety, passing locally to grits, with large spheroidal masses; and (b) the softer, light-coloured variety which has been described previously as the Ancon White Sandstone.

Cherts and silicified formations are found normally at the contact of igneous dykes, or in the proximity of deeper-seated hypabyssal masses.

There appears to be little doubt that the complex structure which is a constant and characteristic feature of the sedimentary and altered deposits in the Santa Elena region, has been influenced to a large extent by the intrusion of igneous rocks, and their movement under, and in contact with, the sedimentary formations with which they are now found associated.

From the field evidence we may assume that basic igneous rocks of a quartz dolerite type underlie most of the region under present discussion. Occasionally there are surface outcrops, as at La Puntilla, La Libertad, Cautivo, and San Vicente, but in the majority of cases the igneous body has been proved at varying depths by the drill. Igneous rocks of the above form are not confined only to the Santa Elena district of Ecuador, but are found all along the coast, at least as far north as Manta.

Drilling usually proves that an outcrop of chert rests directly in contact with igneous rock, and that the latter is usually in the nature of a low angle sill which has penetrated the Oligocene sediments.

Though it is considered that the majority of these intrusions are of post-Oligocene age, it must be remembered that there is always the possibility of contemporaneous igneous activity, and this, in itself, would perhaps account for the shattered condition of the cherts and for the general complexity of the structure which is found in all chert areas.

In the Cautivo section the igneous outcrop to the west of the map area abuts on a chert mass to the east, and appears to have a structural relation with the steeply dipping massive sandstones near the coastline. Thus, from an interpretation of the sequence we may consider that the uplift of the igneous which, though outcropping to the west, lies also below the chert, has caused a pronounced tilting of the Oligocene sandstone at the coast. At the same time, the shales overlying the dolerite became altered, ultimately assuming a siliceous phase which we now recognize as true chert. To the east, a succession of sandstones and shales is found which are inclined at varying angles, and in some cases the formations are vertical.

Slickensided, crushed and contorted shales are a constant feature of the geology of this region, and such zones always occur near the chert and igneous outcrops. These shales form considerable areas in the Peninsula, and have been termed collectively a "clay-matrix" by H. G. Busk, who considers that the huge isolated blocks of sandstone and chert have been displaced laterally through the medium of slip-planes in the softer shales. The clay-matrix, which is found not only in the Cautivo area, but in many parts of the Santa Elena Peninsula, indicates quite clearly that it has been a medium for the movements of larger and more solid lithological units. This material, however, must not be confused with the Clay Pebble Bed of the Ancon district, as this formation is of a different geological age, and has been formed undoubtedly under entirely different conditions. From the field evidence, therefore—*i.e.*, the presence of metamorphosed sedimentaries, and their sporadic or irregular occurrence in the clay shales—with a complete absence of recognizable structure (the whole series representing more or less a confused geo-breccia), it can only be assumed that the zone has been subjected to a regional tectonic movement, possibly towards the northwest, which was also associated with igneous activity. Apart from the influence of regional tectonics, it is the opinion of the writer that the general structure which characterizes the disturbed zone of the Peninsula can be explained only by the factor of subsurface igneous injection on a large scale, *viz.*, a major sill with its apophyses and attendant dykes or offshoots.

In this way the Oligocene formations would be dislocated or displaced in accordance with the movement, or flow, of the hypabyssal magma, and which, at the same time, would induce the formations of the cherts and other altered sediments.

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DISCUSSION.

THE CHAIRMAN : I am sure we are all grateful to Dr. Sheppard, not only for his very informative lecture, so full of interesting matter, but for the pleasing manner in which it has been presented. We are particularly pleased to have with us H.E. the Minister for Ecuador. I feel sure that he has been gratified to hear such a promising account of the oil prospects of his country and will share the hope of us all that further prospecting will lead to more oilfield discoveries.

Dr. Sheppard's paper raises so many interesting questions that it is difficult to single out any one for special mention. His description of the geology discloses extremely difficult and unusual factors bearing on the distribution of oil in the severely deflected and fissured Tertiary sediments in which it is found.

In Peru, structures are relatively simple, for drilling is undertaken in gently-dipping formations in which lenticular bodies of sand yield oil. Few wells fail to produce, and more or less defined sandy horizons are followed down-dip to increasing depths until a strike fault again raises the succession to readily-accessible depths. Unlike Ecuador there is no shattering of rocks by igneous intrusions, nor have the beds suffered silicification.

Among the many excellent pictures shown on the screen was one depicting a fault in section with displaced oil sands. This recalled a rather puzzling occurrence in the Negritos oilfield when an exceptionally large flow of oil was unexpectedly struck. On closing the well after much oil had been lost and preparing for production, it failed to yield when re-opened and, although cleaned out, it not only failed to give any more oil, but four other wells drilled in the vicinity also failed to give production. The only explanation I could conjecture was that the well struck an unsealed fault, making contact with perhaps more than one oil sand, and that, after shutting-in, loosened debris blocked the fissure so firmly that no more oil could reach the well.

The source of the oil in this Pacific belt has always been a subject of dispute. I was personally inclined to the view that the oil in flow had an indigenous origin, but others thought its source lay in deeper horizons. Dr. Sheppard's views on this question would be appreciated.

MR. R. R. TWEED : I should like to ask whether Mr. Sheppard does not consider that in Ecuador igneous rock is the final answer to drilling and that he means that you can go through it and find oil below. Igneous rock has always been held up to me as a great danger spot, and I have been told that below it there is nothing; but is that so in Ecuador?

DR. SHEPPARD : I think Mr. Tweed may be quite right. I am satisfied that in Ecuador igneous rock is not an obstacle. In the Cautivo area we have drilled right through the igneous and found oil, and we have also got good production out of igneous rock itself where the cracks have come through. You must not consider that where you get igneous rock in Ecuador drilling has to be stopped.

MR. T. DEWHURST : I would like to express my personal thanks to Dr. Sheppard for his delightful presentation of a geological paper on what is

obviously very difficult country. The only point I would like to raise is that of the age of the source rocks of the oil. In northern Peru, not far to the south of Ecuador, the main oil-bearing series, the Negritos formation, is Lower Eocene in age, while at Napo, in Ecuador, on the east side of the Andes, the oil series is of Cretaceous age. It is obvious that the oil occurrences described by Dr. Sheppard are due to upward migration along cracks formed by the igneous intrusions. I, therefore, wish to know whether Dr. Sheppard is inclined to correlate the oil source rocks of his area with the Lower Eocene source oil series of northern Peru or with the Cretaceous oil series of Napo on the east side of the Andes.

DR. SHEPPARD: This is rather a problem, but I am quite satisfied that the Eocene of northern Peru is the same homotaxial formation as in Ecuador. But in Ecuador we get oil in all the formations, Eocene and upwards, and even in the Quaternary where it is penetrated by the igneous. I think that all the oil of the coast belt—Ancon, Cautivo and other oil-fields—has a source in the Cretaceous—that is, in the Napo Limestone—and has migrated upwards into the container sands of the Tertiary. From my experience and knowledge of the country I am not yet satisfied that there are important source beds in the Tertiary rocks themselves. There is not a sufficient development of shale nor anything else which would account for the vast quantities of oil present, and the only reason with which I can satisfy myself, is that this oil has a source far deeper down, and has come possibly from the Cretaceous beds.

MR. F. G. RAPPOPORT: I should like to ask Dr. Sheppard—it is some years since I last saw him and discussed these points with him—whether he has formed any opinion on the reason for that big difference in the geology and oil-finding between the north-western part of the Ancon Peninsula and the eastern part, where we get oil in large quantities from the Atlanta sandstone. We are interested to know what is the position in the north-western part, where we only get oil at shallow depths, evidently oil that has seeped up from below.

DR. SHEPPARD: Do you refer to the area known as Ahuiquimi?

MR. F. G. RAPPOPORT: Yes; why do we get shattered rocks in the north-western part and more gentle stratigraphical conditions in the eastern part? What is the connection between the two? Is there any chance of getting that same deep oil in the northern part as in the eastern part?

DR. SHEPPARD: How deep do you drill in Ahuiquimi? What is your deepest well?

MR. F. G. RAPPOPORT: One thousand to fourteen hundred feet.

DR. SHEPPARD: That is not very deep for an adequate test. I rather think that if you had drilled deeper in the Ahuiquimi area you would have got quite a good well. I have always looked upon that area rather favourably. You should drill to between two and three thousand feet. If you

hit an igneous layer it is advisable to continue. If you go deep in that area, I think it would repay you. The shattered condition of the formation is quite good sometimes for having an accumulation of oil beneath.

MR. L. C. STEVENS: May I enquire whether the Napo limestone is within the reach of the drill in the Santa Elena area?

DR. SHEPPARD: I am afraid that I have no information on this point, but I feel that deep drilling by modern methods may reach the Cretaceous limestone. The Anglo-Ecuadorian Oilfields drilled a deep test over 8000 feet a few years ago, but they did not penetrate the Tertiary formations. Possibly, however, the strata may have been steeply inclined at depth, but I have no precise information on this problem.

H.E. DR. VITERI LAFRONTE, Ecuadorian Minister in London: Mr. Chairman, I thank you very much for the kind invitation of the Institute of Petroleum to attend this very interesting meeting and to hear Dr. Sheppard's lecture. I have heard his observations—scientific, serious and amusing—admired his illustrations, and I shall read the complete lecture with great interest. Dr. Sheppard has been working in Ecuador in the high position of official consultant to the Government. During the time he worked in my country he did really important work, and the people and the Government value highly the important publications—books, pamphlets and articles—that he has published about our geology. I am sure that he has not said his last word on the subject. He was in Ecuador for a long time, and I know that he loves and remembers the country, just as the people and the Government love and remember him. I am sure that we shall have the opportunity of reading in the near future new work like that which we have had the good fortune to hear to-day. I thank you very much.

THE CHAIRMAN: Thank you, your Excellency, for your very kind tribute to Dr. Sheppard and his work. I am sure it is the wish of you all to thank Dr. Sheppard for coming forward and giving us this very interesting lecture.

DR. SHEPPARD: Thank you very much, gentlemen. It has been a great pleasure to me to come here and talk to you.

ON THE COURSE OF THE REACTION AT 100° C IN THE SYSTEM AROMATIC-FREE MINERAL OIL/OXYGEN.

By D. J. W. KREULEN (Fellow).

SUMMARY.

The course of the reaction at 100° C in the system aromatic-free mineral oil/oxygen has been investigated. A new apparatus for the oxidation under standard conditions of mineral oils is described; this makes it possible to introduce oxygen into the oil at such a rate that real reaction velocities are measured.

The data obtained were analysed with the aid of the Kreulen-Ter Horst method. The underlying principles of this method are reviewed; it enables one to decide whether a substance is formed directly or via one or more intermediate stages.

It appears that peroxides represent the first, carbonyl-containing compounds the second, and acids the third reaction stage. As the second reaction stage appears to occur to a greater extent than the first reaction stage it is very probable that the peroxides exert a catalytic action (chain mechanism) during the oxidation.

During the oxidation of the oil the saponification number increases. It was found that this "saponification number" does not relate to esters or lactones but only to peroxides.

A linear relationship between dipole moment and oxidation time was found and explained.

A mode of procedure is described which enables the accuracy with which the dielectric constant can be measured to be improved. It is based on the linear relationship which was found to exist between density and dielectric constant.

INTRODUCTION.

OIL deterioration in technical practice is very complicated, the more so as both oxidation and cracking reactions play a part in it. Moreover, deterioration in use is often influenced by the actual engine conditions. For example, in lubricating practice it is often doubtful whether the observed deterioration results from abnormal engine conditions or from the character of the oil.

In other technical apparatus, for instance in transformers, deterioration is less complicated.

For the study of the deterioration of oil it is essential to eliminate as many confusing factors as possible. It is therefore necessary to investigate oxidation and cracking separately.

The present writer decided to simplify the matter still further and investigated primarily the oxidation of an aromatic-free mineral oil.

OUTLINE OF THE INVESTIGATION.

The apparatus used for this work was specially constructed at the physical laboratory of the Utrecht University. It is a modification of the apparatus introduced by R. Luther and J. Plotnikow for the study of reaction velocities.¹

In this apparatus (Fig. 1) gaseous and liquid phase form a closed system, isolated from the air by a mercury seal. To realize a constant oxygen pressure, the experiments were carried out under a slight excess pressure (5 cm Hg). A hollow stirrer is used, its lower part having the form of a Segner's waterwheel. This stirrer distributes the gas phase homogeneously

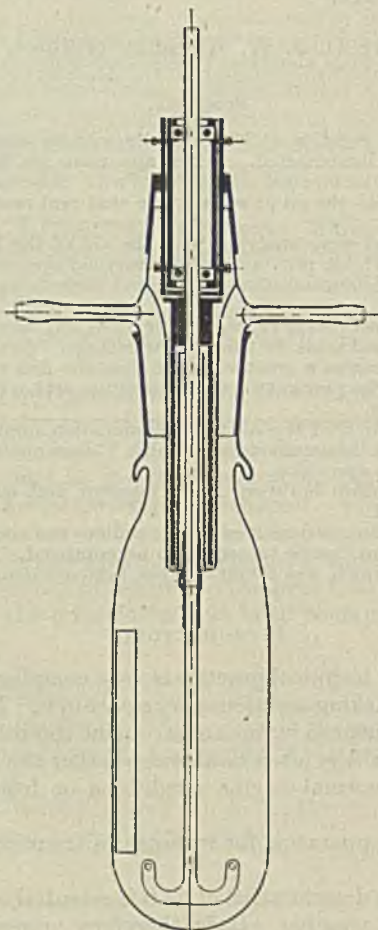


FIG. 1.

OXIDATION FLASK.

into the liquid. At the top of the stirrer a couple of small openings are present through which the gas enters. A glass strip prevents too much whirling in the liquid and consequently increases the dispersion of the gas.

As true reaction velocities are measured only when the liquid is constantly saturated with oxygen, that stirring velocity was chosen at which this requirement was fulfilled. From Fig. 2 it appears that this is the case at a stirring velocity of 1000 r.p.m.²

The oil used for oxidation was a "liquid paraffin."³ It showed the following constants: mol. weight 445; d_4^{20} 0.8833; n_D^{20} 1.4828; aniline point 109° C; surface tension at 20° C 32.1 dynes/cm and specific dispersion ($\times 10^4$) 158. From these constants the average composition is calculated as 0 per cent aromatic rings, 37 per cent naphthenic rings, 63 per cent paraffinic side chains, 5 extra tertiary carbon atoms and 2.8 rings per molecule.

During the oxidation of this oil the changes in density, dielectric constant, dipole moment, peroxide number, saponification number, carbonyl number, acid value and viscosity were measured, together with the amount of water which was liberated.

The mean dipole moment was calculated from the difference between the

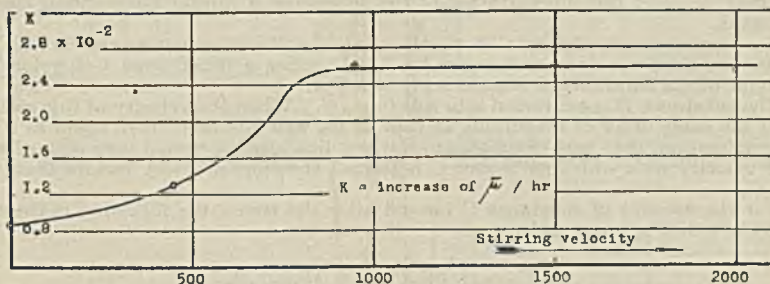


FIG. 2.

RELATIONSHIP BETWEEN REACTION VELOCITY (INCREASE IN DIPOLE MOMENT PER HR. OXIDATION TIME) AND STIRRING VELOCITY.

molecular polarization P and the molecular refraction P_0 according to the relation:

$$\bar{\mu} = 0.0127 \cdot 10^{-18} \sqrt{(P - P_0)T}$$

The application of the dilution method with benzene showed that association did not occur, even at oxidation periods of 77 hours. The peroxide number was determined by shaking 1 g of oil with a mixture of 20 c.c. of glacial acetic acid, 2 g K.I. and 2 c.c. of water for 15 minutes in an atmosphere of CO_2 and titrating with $n/100$ thiosulphate after dilution with 50 c.c. of water. 1 c.c. $n/100$ thiosulphate corresponds with 0.08 mg active oxygen or 0.16 mg peroxide oxygen. The results obtained with this method agree with those which are obtained with the SnCl_2 method of O. Hock and O. Schrader.⁴

The saponification number refers to neutralized solutions of the oxidized oil in a mixture of benzene and alcohol.

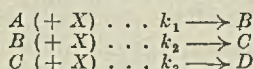
The carbonyl number was determined by the method of H. P. Kaufmann, S. Funke and Fu Ying Liu.⁵

In order to determine the quantity of water formed during the reaction we attached to the neck of the reaction vessel a basket of fine copper gauze containing dried silica gel or CaCl_2 . At successive intervals of oxidation the basket was removed and weighed. No absolute figures are obtained in this way, but the increase in weight of the basket is proportional to the amount of water which is formed during the reaction.

The course of the reaction was judged by the method of Kreulen and Ter Horst.⁶

Since it is possible to obtain with this method an insight into the course of slow reactions, such as generally occur in oil chemistry, the underlying principles of this method will be mentioned briefly.

Let us suppose that we have a substance A which, either directly or by reacting with a substance X (in the latter case the substance X is taken in excess), is converted into the substance B , and this in turn into C , etc., according to the scheme:—



We now determine the concentrations of the substances B , C and D after reaction times which are short compared with the time in which one half of the substance A (initial concentration C_A) has been converted. In this case as a first approximation we may consider the concentration of the substance A during the reaction time as constant.

As a consequence the rate at which substance B is formed is, also in the first approximation, constant and equal to $k_1 C_A$. After a short time t therefore the amount of the substance B formed is $C_B = k_1 C_A t$.

The substance B is converted into substance C . When the velocity of this reaction is of the same order of magnitude as that of the first reaction, then, again as a first approximation, that part of substance B which has been converted may be neglected. The velocity with which substance C is formed therefore at every instant is $k_2 C_B = k_1 k_2 C_A t$.

For the amount of substance C formed after the time t the following is therefore valid in a first approximation:—

$$C_C = \int_0^t k_1 k_2 C_A t dt = \frac{1}{2} k_1 k_2 C_A t^2.$$

In the same way, for the amount C_D of the substance D formed

$$C_D = \int_0^t k_3 C_C dt = \int_0^t \frac{1}{2} k_1 k_2 k_3 C_A t^2 dt = \frac{1}{6} k_1 k_2 k_3 C_A t^3.$$

In a first approximation the quantity of the first reaction product formed is thus proportional to t ($C_B = k_1 C_A t$), that of the second reaction product formed to t^2 ($C_C = \frac{1}{2} k_1 k_2 C_A t^2$) and that of the third reaction product to t^3 ($C_D = \frac{1}{6} k_1 k_2 k_3 C_A t^3$).

Since $\log C_B = a + \log t$, $\log C_C = b + 2 \log t$ and $\log C_D = c + 3 \log t$, a , b , and c being constants, it is found that upon plotting on a logarithmic scale the relation between reaction product formed and reaction time, the concentration of the product first formed is indicated by a line the tangent of whose angle of slope is unity, while the corresponding lines for the second and third products have angles of slope which are two and three respectively. For the reaction scheme:—



one finds in the same way for the amount of C formed:—

$$C_C = \int_0^t k_2 C_B^2 dt = \int_0^t k_2 (k_1 C_A t)^2 dt = \frac{1}{3} k_1^2 k_2 C_A^2 t^3,$$

thus C_C is proportional to t^3 . In this case on plotting on a logarithmic scale the line which indicates the concentration of the second product as a function of t would appear with an angle of slope whose tangent is three.

For longer times the effect of the decrease in concentration by conversion, which is neglected in the above, makes itself felt, so that a bending of the lines toward the t -axis occurs. It is therefore possible to decide from the slope of the line which, plotted logarithmically, indicates the relation between reaction product formed and reaction time, whether the substance in question is formed directly or via one or more intermediate products.

EXPERIMENTAL PART.

The experiments were carried out with 250 c.c. of oil to which, in order to reduce the length of the induction period, small quantities of copper filings

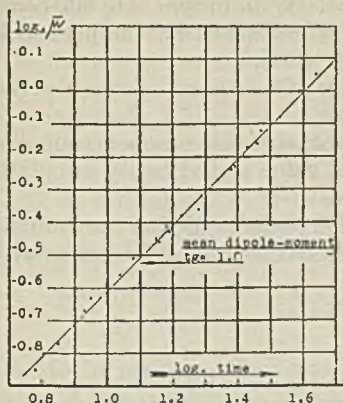


FIG. 3.

RELATIONSHIP BETWEEN DIPOLE MOMENT AND REACTION TIME.

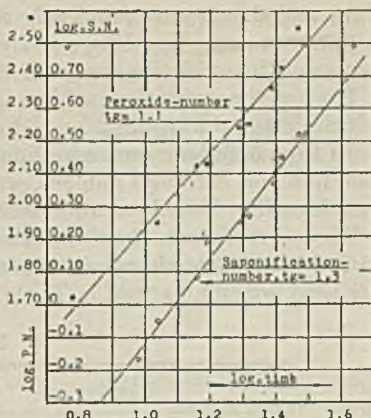


FIG. 4.

RELATIONSHIP BETWEEN PEROXIDE NUMBER, SAPONIFICATION NUMBER AND REACTION TIME.

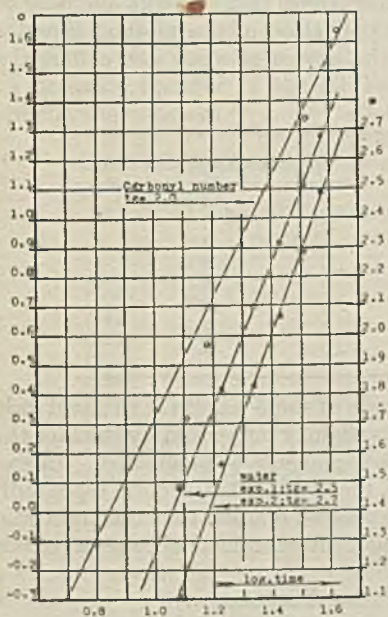


FIG. 5.

RELATIONSHIP BETWEEN CARBONYL NUMBER, WATER AND REACTION TIME.

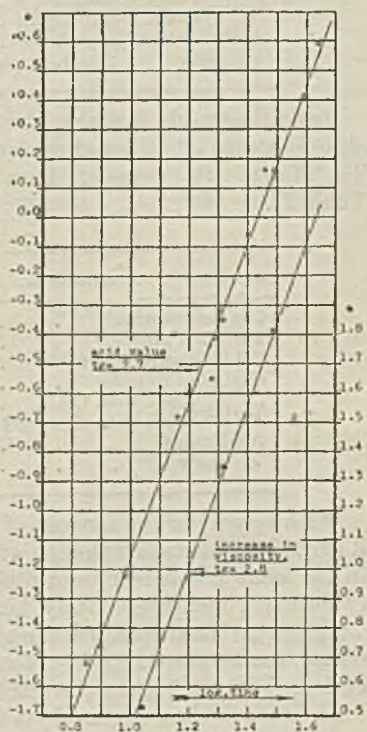


FIG. 6.

RELATIONSHIP BETWEEN ACID VALUE, INCREASE IN VISCOSITY AND REACTION TIME.

were added. It was previously found that the influence of quantities of copper not exceeding 10 g per 250 c.c. was negligible with respect to the course of the oxidation reaction of this type of oil.⁷

During the oxidation no increase in specific dispersion was observed, which means that cyclisation did not occur.

In Figs. 3-6 the increase in dipole moment, peroxide number, saponification number, carbonyl number, water, acid value and viscosity are plotted on a logarithmic scale as a function of time.

Time *O* represents the end of the induction period. Before the induction period is ended no change in constants could be observed. The units which are used are summarized in Table I.

TABLE I.

Increase in—	Unit.
Dipole moment	D ($1D = 10^{-18}$ e.s.u.)
Time	hrs.
Peroxide number	mg O ₂ per 100 g.
Saponification number	mg KOH per g.
Carbonyl number	mg KOH per g.
Water { exp. 1 (CaCl ₂)	mg H ₂ O per 100 g.
{ exp. 2 (silica gel)	mg H ₂ O per 100 g.
Acid value	mg KOH per g.
Viscosity	centistokes

From the graphs it is seen that for short times that straight line relationship exists which is required for the application of the method Kreulen-Ter Horst. The tangents found for the angles of slope are collected in Table II.

TABLE II.

Constant.	Tangent angle of slope.
Dipole moment	1.0
Peroxide number	1.1
Saponification number	1.3
Carbonyl number	2.0
Water { exp. with CaCl ₂	2.5
{ exp. with silica gel	2.7
Acid value	2.7
Viscosity	2.8

With respect to the tangent of the angle of slope found for the acid value it should be mentioned that this figure is slightly influenced by the fact that in the same graph results of different experiments are collected. In each of the experiments separately, however, the figure 3.0 was found repeatedly.

The experiments confirm the often expressed opinion that the succeeding stages, during the oxidation of an aromatic-free mineral oil, are peroxides, carbonyl-containing compounds, acids.

Thus the acids are formed via two intermediate stages.

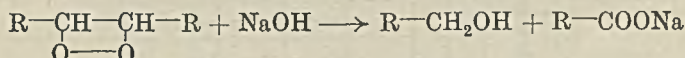
As to the formation of water, this corresponds with a fractional exponent. Thus water may be formed as well during the second as during the third oxidation stage.

The parallelism between the increase in acid value and viscosity is strik-

ing. Very probably these phenomena are closely related (tangents of angle of slope 2.7 and 2.8 respectively).

The value 1.3, found for the tangent of the angle of slope of the saponification number, needs further explanation. In literature on this subject the compounds, which are responsible for the saponification number, are often described as esters or lactones. If this were true a tangent of at least 4 should be found.

J. C. A. Yule and C. P. Wilson⁸ found that aqueous caustic soda immediately removes a small amount of the peroxides and that part of the remainder is gradually removed by continued shaking according to the scheme:



H. Hock⁹ mentions the decomposition of cyclohexeneperoxide by caustic soda. If this peroxide is treated with 0.25 per cent aqueous caustic soda it is completely destroyed after 24 hours heating, while during the treatment a lemon-yellow colour appears.

A similar lemon-yellow colour was observed by us after adding aqueous caustic soda to oxidized oils.

In order to investigate the parallelism between peroxide number and saponification number, the following experiments were carried out. 10 g of oxidized oil was treated with varying quantities of $n/10$ NaOH (from 0 c.c. up to 12.5 c.c.) in a nitrogen atmosphere, in the same way as in the saponification test. The amount of NaOH which was consumed was determined by titration. After adding 25 cm of water, the oil was recovered by shaking with petroleum spirit. The petroleum spirit was removed and the peroxide number of the oil was determined. The data collected in Table 3 was obtained.¹⁰

TABLE III.

C.c. of 0.1- n NaOH consumed per g.	Peroxide number of the recovered oil (c.c. $n/10$ peroxides per g).
Blank test	1.70 *
0.081	1.60
0.149	1.53
0.217	1.40
0.228	1.48
0.345	1.30
0.360 (saponification number)	1.28

* The untreated oil had a peroxide number 2.00. Thus heating only caused a decomposition of $0.3 \times 0.1 n$ peroxides per g.

In Fig. 7 the data of Table III are represented graphically. It appears that a straight line relationship exists between the consumption of NaOH and the decrease in peroxide number. This, together with the fact that the tangent of the angle of slope of the saponification number is about 1 proves that the "saponification number" of oxidized aromatic-free mineral oil indicates really nothing but the presence of peroxides. From Table III it follows that 0.360 c.c. 0.1 n NaOH corresponds with $1.70 - 1.28 = 0.48$ c.c. $n/10$ peroxides. Thus 1 peroxide corresponds with 0.75 acid. That one

molecule of peroxide is converted into one molecule of acid is in perfect agreement with the scheme given by Yule and Wilson.

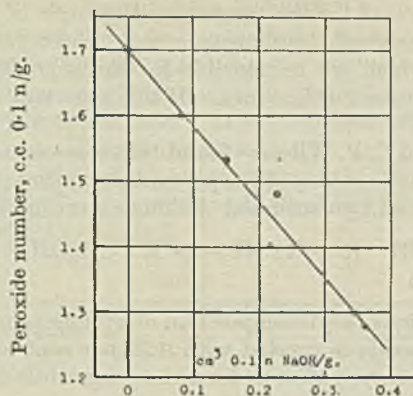


FIG. 7.

RELATIONSHIP BETWEEN C.C. 0.1-N NaOH CONSUMED AND PEROXIDE NUMBER OF THE RECOVERED OIL.

As to the dipole moment, it should be noted that the specific polarization is additive, which means that its increase is a direct indication of the amount of polar molecules which are formed. The non-oxidized oil used is non-polar, thus $P = P_0$. During oxidation P_0 remains practically constant, thus $\bar{\mu} = k\sqrt{\Delta P}$. Thus if, as in this case, the average dipole moment is found to be directly proportional to the oxidation time (tangent angle of slope = 1.0), this means that the concentration of polar molecules is proportional to the square of the reaction time.

In fact, the second oxidation stage of this oil appears to be predominant with respect to the formation of polar compounds, as is shown later (Table V).

On account of the linear relationship which exists between the dipole moment and reaction time, it seems interesting to express the tendency to oxidation of oils of this type in terms of increasing dipole moment (D per hour). In this way we found for our oil the value 2.6×10^{-2} , while for a hydrogenated gas oil of the composition 0 per cent of aromatic rings, 51 per cent of naphthenic rings and 49 per cent of paraffinic side chains (molecular weight 207) the value 2.0×10^{-2} was found. Apparently saturated mineral oils of different molecular weight and composition behave rather similar during oxidation.

As to the accuracy of the dipole moment, we would remark that density and refractive index are reliable to within one in a thousand, and the temperature to within 0.01°C . The accuracy of the molecular weight is rather poor ($\frac{1}{2}$ per cent), but it is calculated into both molecular polarization and molecular refraction and, moreover, it remains practically constant during oxidation. Thus it does not influence the increase in dipole moment.

The dielectric constant, which is of great influence, however, is at best reliable to within $\frac{1}{2}$ per cent. Its accuracy can be improved by the following procedure.

A simple linear relationship is found between the increase in density and that of the dielectric constant. Thus, if the dielectric constants which are obtained during a test are plotted as a function of the densities, we can draw the corresponding average straight line, which eliminates errors. Then we can calculate the dipole moment with that value of the dielectric constant which corresponds in this graph with the observed density. This procedure has, moreover, the advantage that in a series of

experiments with the same oil, the above mentioned graph being known, much time is saved.¹¹

In Fig. 8 the above-mentioned relationship between density and ϵ is shown for the oil investigated, while in Fig. 9 it is shown for a hydrogenated gas oil, xylene and toluene. In Table IV two more oils are mentioned.

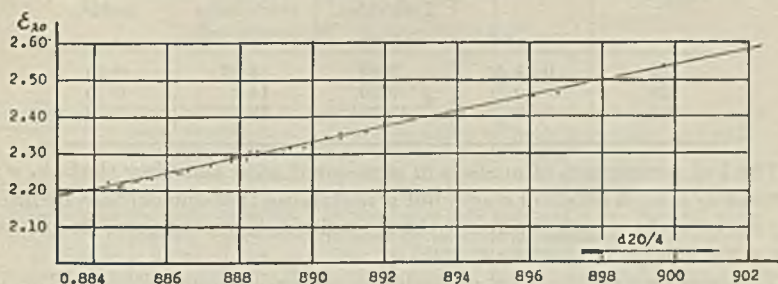


FIG. 8.

"LIQUID PARAFFIN." RELATIONSHIP BETWEEN DENSITY AND DIELECTRIC CONSTANT.

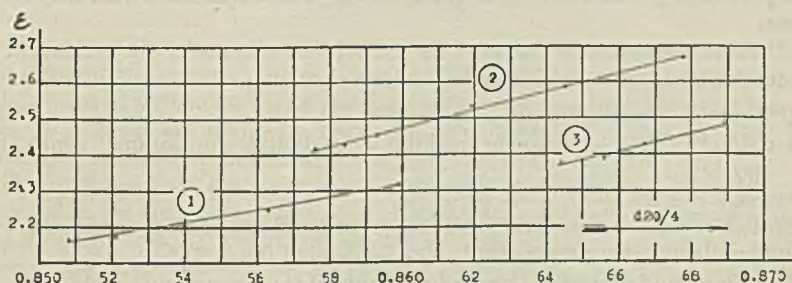


FIG. 9.

RELATIONSHIP BETWEEN DENSITY AND DIELECTRIC CONSTANT.

1 = hydrogenated gas oil; 2 = xylene; 3 = toluene.

TABLE IV.

Oil.	Mol. weight.	Density, 20/4.	" Ring analysis."			Increase in ϵ per 0.01 increase in density.
			A, per cent.	N, per cent.	P, per cent.	
Hydrogenated gas oil	207	0.8508	0	51	49	0.17
Xylene	106	0.8564	72	0	28	0.25
Toluene	92	0.8644	84	0	16	0.24
Lub. oil (naphthene base)	446	0.9352	13	34	53	0.32
" Liquid paraffin "	445	0.8833	0	37	63	0.21
Lub. oil (paraffin base)	436	0.8721	9	16	75	0.33
Gas oil (naphthene base)	215	0.8889	13	48	39	0.40

Thus the rate of increase in dielectric constant per standard increase in density varies between wide limits for different types of oil.

If the peroxides, carbonyl containing compounds and acids, which are present after varying times of oxidation are expressed on a comparable basis, *e.g.*, mg mol per 100 g of oil, we obtain the values which are given in Table V.

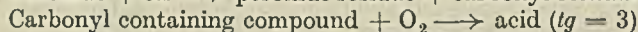
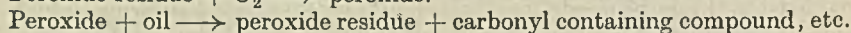
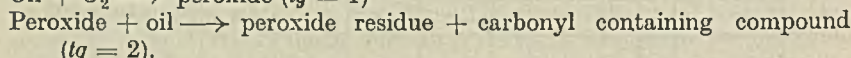
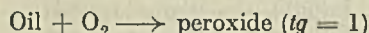
TABLE V.

Time of reaction, hours.	Dipole moment.	Mg mol per 100 g of oil.		
		Peroxides.	Carbonyl containing compounds.	Acids.
10	0.24 <i>D</i>	2.59	4.93	0.18
20	0.50 <i>D</i>	5.56	14.4	0.75
30	0.75 <i>D</i>	10.6	33.4	2.18

The low percentage of acids is in agreement with the view that they are formed as a third reaction stage, but it is striking that the carbonyl containing compounds, which represent the second reaction stage, are in excess of the peroxides (first reaction stage).

This can be explained by assuming a catalytic chain action of the peroxides during the oil oxidation. Then, the amount of peroxides increasing proportionally with time, their catalytic effect also increases with respect to time.

If this assumption is accepted as correct, the scheme of the oxidation of aromatic-free mineral oil may be written as :



where *tg* is the tangent of the angle of slope of the logarithmic plots.

Rotterdam, Laboratory for Coal and Oil Chemistry, 1946.

References.

- ¹ *Z. physikal. Chem.*, 1908, **61**, 513.
- ² This high stirring velocity does not improve our appreciation for technical tests in which oil is treated with quantities of oxygen varying from 2 up to 15 l/hr.
- ³ For sake of clearness we would emphasize that "liquid paraffin" is not a paraffin but an intramolecular mixture of naphthenic rings and paraffinic side chains.
- ⁴ *Brenn. Chemie*, 1937, **18**, 6.
- ⁵ *Fette u. Seifen*, 1938, **45**, 616.
- ⁶ D. J. W. Kreulen and D. Th. J. ter Horst. *Rec. Trav. chim. Pays-Bas*, 1940, **59**, 1165; W. P. Jorissen, Miss F. G. van Selms and D. J. W. Kreulen. *Ibid.*, 1942, **61**, 269.
- ⁷ D. J. W. Kreulen. *Rec. Trav. chim. Pays-Bas*, 1943, **62**, 512.
- ⁸ *Industr. Engng. chem.*, 1931, **23**, 1254.
- ⁹ 2e. Congrès Mondial du Pétrole, Paris, 1937.
- ¹⁰ Not all peroxides are destroyed under these conditions. They are distinguished between :—
 - (a) Peroxides which are destroyed by simple heating;
 - (b) Peroxides which are destroyed by caustic soda under the conditions of the saponification test;
 - (c) Peroxides which are destroyed during the refluxing of a mixture of 10 g of oil, 75 c.c. benzene-alcohol (2 : 1), 50 c.c. *n*/10 caustic soda and 750 mg of 40 per cent formaldehyde during 1 hour heating in an atmosphere of nitrogen.
 Under the condition (b) the peroxides of group (a) are also destroyed and under the condition (c) also those of group (a) and (b).
- ¹¹ When copper is present deviations occur as soon as the oil acquires a visible green colour. Then ϵ becomes higher than the value read from the graph.

ON THE COURSE OF THE REACTION AT 100° C IN THE SYSTEMS XYLENE/OXYGEN AND AROMATIC-FREE MINERAL OIL/XYLENE/OXYGEN.

By D. J. W. KREULEN (Fellow).

SUMMARY.

The oxidation of xylene and of mixtures of aromatic-free mineral oil and xylene has been investigated. The formation of both peroxides and aldehydes is linear with respect to time, while acid formation appears to increase with the square of the time. A gradual change in oxidation behaviour with increasing percentage of one of the components is observed in mixtures of xylene and aromatic-free oil. In this case less aldehydes are formed than might be expected, which is explained by some retardation effect.

If copper is present, the peroxides are destroyed during the oxidation and a corresponding increase in aldehydes is found. In the case of the oxidation of pure xylene an insoluble cuprous salt of toluic acid settles from the reacting liquid.

INTRODUCTION.

As a sequel to a study of the course of the reaction in the system aromatic-free mineral oil/oxygen,¹ the oxidation of the alkylbenzene xylene and that of mixtures of xylene and aromatic-free mineral oil has been investigated.

H. N. Stephens, and also Stephens and Roduta² found that alkylbenzenes are slowly oxidized at the α -carbon atom at 100° C.

The first recognizable stage is the formation of aldehydes and these are oxidized to the corresponding acids. Simultaneously water is formed which acts as an inhibitor. Peroxides are not mentioned by Stephens, but reference is made to experiments of Suida³ who found "activated oxygen" after the exposure of alkylbenzenes to actinic or ultraviolet rays.

EXPERIMENTAL PART.

The apparatus used in this investigation has been described previously.⁴ 300 c.c. of xylene was oxidized at 100° C with oxygen (stirring velocity 1500 r.p.m.). During the oxidation the increase in peroxide number, carbonyl number and acid value were measured.

It should be noted that fresh xylene sometimes shows no reaction, while xylene which has been kept in stock for some years always reacts. Apparently anti-oxidants are responsible for this phenomenon, for a treatment with KMnO_4 will generally remove the resistance of fresh xylene to oxidation.

It was originally intended to investigate also the oxidation of toluene. However, the rate of reaction of toluene is so slow (Table I) that this plan was abandoned.

TABLE I.

	Oxidation time, hours.	Total of peroxides + aldehydes + acids in mg mol per 100 g liquid.
Xylene . . .	10	7.1
" . . .	20	15.5
" . . .	30	22.8
Toluene . . .	100	5.7

The increase in peroxides (mg O₂/100 g), aldehydes (mg KOH/g) and acids (mg KOH/g) found during the oxidation of xylene is shown, on a logarithmic scale, as a function of time in Fig. 1. In Table II the increase

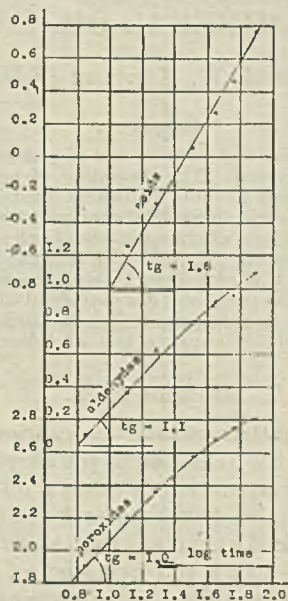


FIG. 1.

XYLENE. RELATIONSHIP BETWEEN PEROXIDES, ALDEHYDES, ACIDS AND REACTION TIME.

in peroxide number, carbonyl number and acid value is expressed on a comparable basis, *viz.*, mg mol per 100 g xylene.

TABLE II.

Time of reaction, hours.	Milligram-mol per 100 g of xylene.		
	Peroxides.	Aldehydes.	Acids.
13	5.0	4.2	0.5
32	11.7	10.7	2.1
57	17.1	16.2	5.1
77	20.0	22.6	11.1

Apparently about equal quantities of peroxides and aldehydes are formed.

From Fig. 1 it appears that both peroxides and aldehydes are formed linearly with respect to time. The linear formation of the aldehydes is further emphasized by the quadratical formation of the acids.

Now we previously found that during the oxidation of an aromatic-free mineral oil the aldehydes are formed quadratically and therefore complementary experiments were carried out with mixtures of such an oil and

xylene. A gradual change in properties was observed with increasing percentage of one of the components in these mixtures, therefore only the results which were obtained with a mixture of 25 per cent xylene and 75 per cent of aromatic-free oil are referred to.

The results are graphically shown in Fig. 2.

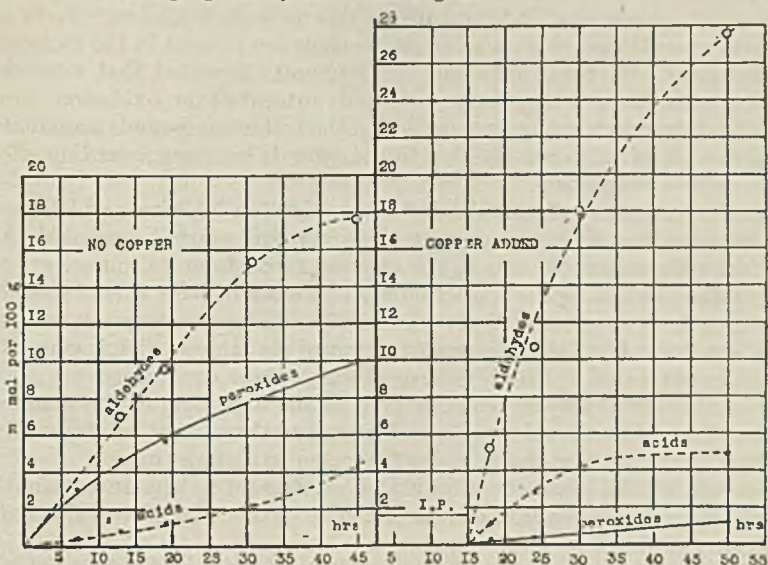


FIG. 2.

OXIDATION OF A MIXTURE OF 25 PER CENT XYLENE AND 75 PER CENT AROMATIC-FREE MINERAL OIL.

In Table III the peroxides, aldehydes and acids, expressed in mg mol per 100 g, present after 10, 20 and 30 hours oxidation time, are given.

TABLE III.

Oxidation time, hours.	Milligram/mol. per 100 g.			
	Xylene.	Oil.	Mixture 25/75 found.	Mixture 25/75 calculated.
10				
Peroxides . . .	3.5	2.6	3.8	2.8
Aldehydes . . .	3.3	4.9	5.2	4.5
Acids . . .	0.3	0.2	0.6	0.2
20				
Peroxides . . .	7.5	5.6	6.2	6.1
Aldehydes . . .	7.0	14.4	10.4	12.6
Acids . . .	1.0	0.8	1.2	0.9
30				
Peroxides . . .	11.0	10.6	7.8	10.7
Aldehydes . . .	10.0	33.4	15.0	27.5
Acids . . .	1.8	2.2	2.1	2.1

If in this table the quantities of aldehydes which are found are compared with those which are calculated from the pure components, it is seen that

less aldehydes are formed than might be expected. Apparently some retardation effect is present and in connexion with this the retardation effect mentioned by Stephens is remembered. But this effect is better related to certain aromatic compounds than to water, as during the oxidation of an aromatic free mineral oil, in which also water is formed, no retarding effect is observed. Moreover, in literature on this subject, inhibiting effects are frequently mentioned as soon as aromatic rings are present in the molecule. For instant, C. H. von Fuchs and H. Diamond⁵ reported that saturated hydrocarbons have a tendency to rapid autocatalytic oxidation while aromatic compounds act as anti-oxidants, the latter compounds apparently giving rise on initial decomposition to compounds having a retarding effect on the oxidation reaction.

These investigators distinguish between oxidation inhibitors which postpone reaction, but do not change its character once started, and oxidation retarders which affect the rate of the reaction throughout its course.

The influence of metallic copper on the oxidation of pure xylene was also investigated. It appeared that, when copper filings are present, no peroxides are formed. Even the small amount of peroxides which is generally present in untreated xylene is destroyed under these conditions.

An increase in aldehydes was observed at the beginning of the reaction, but the colour of the liquid soon turned green and therefore it was impossible to follow the formation of aldehydes for longer oxidation times.

However, when the observation with a mixture of xylene and aromatic-free mineral oil is taken into consideration, a further increase of aldehydes seems very probable.

In the case of pure xylene no increase of the acid value was observed, but an insoluble green compound settled from the liquid during prolonged oxidation. This compound appeared to be a cuprous salt from toluic acid for the corresponding acid of the salt showed a molecular weight of 140, the molecular weight of toluic acid being 136. From the copper content of the salt we would conclude that very probably also a small amount of the cupric salt of toluic acid is present.

For the results obtained during the oxidation of a mixture of aromatic-free mineral oil and xylene in the presence of copper we refer to Fig. 2. Here the most remarkable effect is the increase of aldehydes at the expense of the peroxides. Practically no peroxides remain, this being in distinct contrast to the high percentage of peroxides which is found after the oxidation of an aromatic-free mineral oil alone.

It is suggested that there is an analogy between this fact and the absence of peroxides during the oxidation of ordinary (aromatic ring-containing) mineral oil.

*Laboratory for Coal and Oil Chemistry,
Rotterdam, 1946.*

References.

- ¹ D. J. W. Kreulen, *J. Inst. Petrol.*, 1946, **32**, 515-524.
- ² H. N. Stephens. *J. Amer. chem. Soc.*, 1926, **48**, 1824, 2920; 1928, **50**, 2523. Stephens and Roduta. *Ibid.*, 1935, **57**, 2380.
- ³ Suida. *Monatsh.*, 1912, **33**, 1255.
- ⁴ Kreulen, *loc. cit.*
- ⁵ Fuchs and Diamond. *Industr. Engng. Chem.*, 1942, **34**, 927.