Summary.

1. Deerfield bituminous coal yields, by vacuum distillation, a number of hydrocarbons, mostly of the series C_nH_{2n-4}, resembling the hydrocarbons that compose the neighboring Mahone petroleum.

2. Utah Gilsonite gives members of the series, C_nH_{2n} and C_nH_{2n-2} that resemble the same hydrocarbons in petroleum, also a series of unsaturated hydrocarbons. It contains in large proportion the nitrogen compounds that are found in all petroleum, which demonstrates its organic origin.

3. Grahamite gives a series of hydrocarbons resembling those from Gilsonite.

4. As above mentioned, there is a no more urgent and promising field of investigation than the composition of the natural bitumens on an adequate scale with a sufficient outlay of expense and expert labor.

[CONTRIBUTION FROM LABORATORY OF THE OFFICE OF SOIL FERTILITY, THE BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE POSSIBILITIES AND LIMITATIONS OF THE DUCLAUX METHOD FOR THE ESTIMATION OF VOLATILE ACIDS.

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Received June 18, 1917.

Introduction.

The different members of the volatile fatty acid series differ in properties only in slight gradations and the separation of the individual acids occurring in a mixture must be effected by some method of fractionation. The procedures which have been employed with a certain degree of success are: (*a*) Fractional distillation; (*b*) fractional precipitation of their salts; (*c*) fractional liberation from their salts; (*d*) fractional crystallization of their salts; and (*e*) fractional extraction of the barium salts with alcohol. All of these procedures are very laborious and give at best only partial satisfaction.

Many of the fatty acids are natural products occurring either in the free state or as esters and are of great theoretical and technical importance. The value therefore of a rapid and accurate method for their detection and estimation is patent. The method which has yielded the most satisfactory results is the one devised by Duclaux,[6] which is an indirect method based upon the behavior of the acids during distillation from dilute aqueous solution. He used this method in estimating the volatile fatty acids in wines and various fermentations and other biological products.

The method has since been used extensively by numerous investigators with more or less success. Only a few will be mentioned. Jensen[11] Suzuki, Hastings and Hart[17] and Currie[3] have used this method in estimating the volatile acids in cheese; Dox and Neidig[4] and Hart and Williman[10] have used it in their researches on corn silage; and Harden[9] and Seliber [16] have used it in estimating the volatile acids produced by pure cultures of bacteria.

The Duclaux method consists[6] in distilling a dilute solution of free volatile acids made up to a definite volume (110 cc.), collecting the distillate in 10 equal fractions (10 cc. each) and titrating the acid in each fraction. This process is applied first to solutions of the pure acids, and then to unknown mixtures. From such observations Duclaux was able to judge the qualitative composition of the acid mixture. In his study of wines[6] he concluded that in most cases only two acids were present and he calculated from the same observations the quantities of each present. In his first work on the subject[5] he made no such calculations. Later he suggested[6] a method of calculating the quantities for mixtures of three acids; this method involved the use of least squares. He did not find it necessary to carry this out for the analysis of wines and as far as we know neither he nor any one else ever carried out the suggestion.

The method Duclaux gave[6] for directly calculating the quantities of volatile acids present in a mixture of two was not given by him in its simplest form, as he left it at such a stage that the use of algebra is required each time the results of an analysis are calculated. It seems that he did not discover how simple the method becomes if the algebraic work is completed once for all, so that only simple numerical work is required for each analysis. He suggested and used a method employing what we may call auxiliary tables, which each investigator is to prepare anew from distillations of mixtures of various acids taken two at a time and in various proportions, and he not only states that this is more convenient if many analyses are to be made, but later, in his book[7] he omits any reference to a direct calculation.

We find that a number of investigators have tried to apply the Duclaux method to mixtures of three or more acids without being aware that a direct method of calculation is possible. They have calculated their analyses indirectly by forming first a preliminary estimate of the kinds and quantities of volatile acids present, from an inspection of the curve plotted from the distillation figures, and from the odor of the fractions, then calculating in the way suggested by Duclaux what the distillation figures should have been, finally adjusting and readjusting the estimate until they felt that the agreement between the calculated and observed distillation figures was sufficiently close. Sometimes, having already proved or assumed the presence of three acids, they have had no hesitation in assuming the presence of a fourth acid not detected chemically, in order to improve the agreement, without being able to show (for lack of a direct method of calculation), that as good an agreement could not have been reached merely by a more fortunate adjustment of the quantities of the three acids first assumed. In some cases no attempt was made to see whether the discrepancies persisting when the smaller number of acids was assumed were really greater than the experimental error.

A paper has recently appeared by Upson, Plum and Schott[18] in criticism of the Duclaux method as carried out at present. They show that by the "cut and try" method of calculating the results of analyses very incorrect results may be obtained. They also point out that the errors of analysis may be qualitative as well as quantitative if incorrect assumptions are made; we show below, however, that such errors are not so serious if direct methods of calculation such as are presented below, which utilize all the observations, are used instead of the cut and try method.

It is obvious that many of the difficulties which most investigators have experienced in the practical application of the Duclaux method have been due to lack of suitable procedures for calculating the results; and we hope that the calculations which we have developed, together with our study of the possibilities and limitations of a single Duclaux distillation, will suffice to make the method as generally useful as the originator believed it to be.

Laws Employed in Applying the Duclaux Method.

The method is based on certain laws which Duclaux gave in a general form. Since at least some of the difficulty hitherto experienced in developing the method seems to have come through a misunderstanding of the laws on which it is based, we prefer to give the laws in two more specialized formulations, as follows:

If 110 cc. of a dilute solution of a given volatile acid are distilled and the distillate collected in 10 equal fractions of 10 cc. each, then the quantity of this acid distilling in the first 10 cc. is a definite percentage of whatever quantity is taken for distillation, and so for the first 20 cc., etc., and furthermore the same quantity of this acid will be collected in any given fraction whether or not other acids are distilling at the same time. This is a statement of the principles utilized in constructing and applying Duclaux's "Table I."[6] Our Table I is constructed in the same way. We find Table I convenient for calculating the distillation figures for a known mixture.

The principles underlying Duclaux's (and also ours) "Table II" are formulated as follows: If the acid solution is distilled and the distillate is collected as just prescribed, then for any one acid, irrespective of the presence of other volatile acids, a definite percentage of the quantity of acid distilling over in 100 cc. comes over in the first 10 cc., a certain (different) percentage comes over in the first 20 cc. and so on; and these percentages are not dependent on the quantity of acid taken for the distillation, but are constant for the given acid. Table II was preferred by Duclaux for calculating the results of the analysis of an unknown mixture. The use of Table II seems to effect a certain compensation of errors, as we ourselves have calculated the results of a few analyses, using both Tables, and have obtained more accurate results by the use of Table II. We shall therefore use only Table II for this purpose in this paper.

Richmond[15] has given expressions for the rate of distillation of the pure acids in aqueous solution for both simple distillation and for distillation at constant volume; these expressions would not hold for acids contaminated with other volatile acids. They are obtained by integrating a differential equation which includes the principles stated above.

The principles underlying Table I and Table II, if true for pure acids, must also be true for mixtures. If x is the quantity of one acid appearing in a given fraction when A is the quantity of this acid taken for distillation (or the quantity of acid appearing in 100 cc. of distillate), then $x = k\,\mathrm{A}$. For a different acid

$$y = k'\,\mathrm{B}.$$

The quantity of both acids for the mixture A and B is

$$x + y = k\,\mathrm{A} + k'\,\mathrm{B}.$$

Now if we double the quantity of the mixture, there will be collected in the given fraction twice the quantity collected before, for

$$2\,k\,\mathrm{A} + 2\,k'\,\mathrm{B} = 2\,x + 2\,y = 2(x + y).$$

In other words, the quantity collected in any fraction will be proportional for a mixture to the quantity taken for distillation (or the quantity appearing in 100 cc. of distillate).

Apparatus and Experimental Technique.

The apparatus used is shown in Fig. 1. The ground-glass joint was polished somewhat with jewelers' rouge in oil. No grease is used on the joint, but it is cautiously secured with wire to avoid accidents. It has not leaked and we have had no trouble due to sticking or breaking, provided the whole is permitted to cool before taking apart. The capacity of the flask is about 200 cc. The open end of the condenser tube is somewhat oblique but permits a drop or two of liquid to be held while changing the cylinders used for collecting the distillate.

The heating elements are of bare nichrome wire, 0.018 inch in diameter. The side element (resistance 57 ohms), is wound on a six-legged frame built of two iron tripods, the legs being insulated with asbestos paper secured with asbestos cord. In constructing the bottom element (40 ohms) a spiral coil about $^1/_4$ inch in diameter was coiled and laid on a thin sheet of asbestos paper on a flat board and secured with pins, alundum cement was applied in as small a quantity as possible, the whole well dried (if electrically, then by a weak current!) and the pins removed. The two heating elements are connected in series; operated on 210 volts the combination passes 2 amperes. The power is about 0.24 kilowatt in the side and 0.18 kilowatt in the bottom element. The removable top and side insulating mantle does not extend to cover the flask completely but leaves a space uninsulated about $1^1/_4$ inches upwards from the bottom of the flask. While it is well to prevent condensation, it would be inadvisable to insulate so completely that too many spattered drops of acid solution are entirely volatilized on the superheated side of the flask, as such portions of the solution undergo no fractionation whatever. A distillation, with the accompanying titrations, is finished in about 50 minutes from the time of turning on the current, about 5 minutes elapsing before the distillate begins to collect.

Two 10 cc. graduated cylinders have been used alternately for collecting the acid. The titration of one 10 cc. portion of distillate proceeds while the next portion is being collected. Only one operator is required. The cylinders have not been rinsed; they were graduated to deliver 10 cc. The acid has been determined by titration with 0.1 *N* sodium hydroxide in the presence of phenolphthalein, and after titration of one portion of distillate the buret is not refilled to the zero mark but the next portion is added to the titration flask and the titration continued. No special precautions have been taken to exclude atmospheric carbon dioxide. The technique which we have used is by no means unusually precise, and we think, therefore, that by using care others should be able to obtain as satisfactory results. A little skill is required to collect exactly 10 cc.

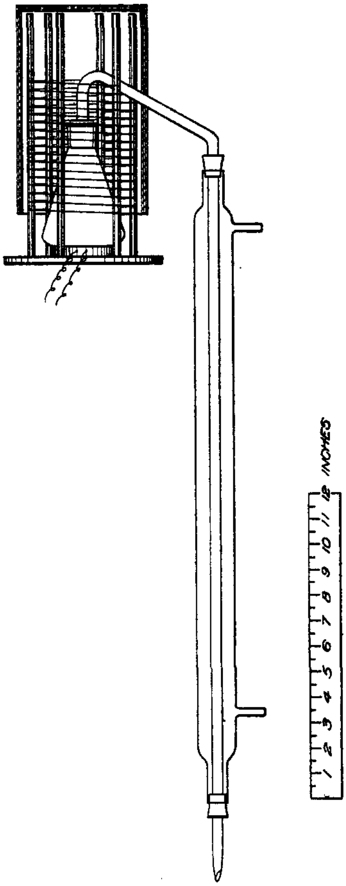

Fig. 1.—The distillation apparatus.

The same apparatus and technique were used for all the work described in this paper. All quantities of acid are expressed in cubic centimeters of 0.1 *N* solution. We wish to state that we have always taken for distillation solutions containing nothing but volatile acids; we have avoided the introduction of any salts of strong fixed acids.

Determination of the Distillation Constants.

The following acids have been used: Formic and acetic acids, bought as "chemically pure" and the acetic acid further purified by the method of

Bousfield and Lowry,[1] propionic acid "highest purity," and normal butyric acid, both from high grade firms. We have not prepared all the acids in a known state of high purity, and we give our distillation figures for the pure acids (the so-called "distillation constants") not because they are necessarily better than those given by Duclaux, but because they are somewhat different and are the basis for calculating all the results presented in this paper. It appears at present advisable for each investigator to prepare his own Tables I and II from distillations of pure acids made with his own apparatus.

With regard to the purity of the acids used for determining the distillation constants, *i. e.*, their freedom from mutual contamination, we have shown above that if the quantities of acid collected in various volumes of distillate when a mixture of pure acids is distilled can be calculated from the constants of the pure acids, the results of a distillation of a mixture of impure acids can also be calculated from the constants of the individual impure acids, for the impure acids are mere mixtures and the principle underlying the calculation is simply extended. Experiment confirmed this. We mixed acetic acid with a nearly equal amount of propionic and butyric acids and determined the constants of this contaminated acetic acid. We then mixed pure acetic acid with the contaminated acid, applied the usual Duclaux procedure and obtained a satisfactory estimation of the two acids: pure acetic and contaminated acetic acid. From this it follows that acids of a high degree of purity were not required in the present study of the method. Furthermore, since the errors of analyses by the Duclaux method will be found below to be rather large, if calculated as percentages of the quantities taken, it appears that for the practical application of the method there would be no advantage in the use of acids of extraordinary purity for determining the constants.

For determining the constants, 30 to 40 cc.* of 0.1 *N* acid were made up to 110 cc. for the distillation. The distillations were not done in duplicate. The calculated results are given in Tables I and II. Table I contains the percentages obtained by dividing the number of cc. of standard sodium hydroxide solution required to neutralize each fraction in turn by the number of cc. which would be required to neutralize the quantity of acid taken for distillation and then multiplying by 100. Table II contains the percentages obtained by dividing the number of cubic centimeters required for each fraction in turn by the number required for the total 100 cc. of distillate and multiplying by 100.

* The quantities of acid mixtures subsequently taken for analysis by distillation were usually about 40 cc., or less, of 0.1 *N* acid; only rarely were they as great as 50 or 60 cc. The actual amounts taken are recorded in the tables.

TABLE I.

Acid collected in various volumes of the distillate when 110 cc. of dilute solution are distilled, stated as the percentage of the quantity taken for distillation.

Volume of distillate in cc.	Formic.	Acetic.	Propionic.	Butyric.
10	4.2	6.4	11.2	16.4
20	8.5	13.0	22.2	31.2
30	13.2	19.7	32.7	44.8
40	18.2	26.7	42.9	56.6
50	23.4	34.1	52.7	67.3
60	29.3	41.6	62.0	76.2
70	36.0	49.9	70.9	84.0
80	43.6	58.7	79.1	90.1
90	53.0	68.5	86.7	94.8
100	65.3	79.9	93.6	97.8

TABLE II.

Acid collected in various volumes of the distillate, when 110 cc. of dilute solution are distilled, stated as the percentage of the quantity finally collected in 100 cc. of distillate.

Volume of distillate in cc.	Formic.	Acetic.	Propionic.	Butyric.
10	6.5	8.0	12.0	16.7
20	13.0	16.3	23.7	31.9
30	20.2	24.6	34.9	45.7
40	27.8	33.5	45.8	57.9
50	35.9	42.7	56.3	68.8
60	44.8	52.1	66.2	77.9
70	55.2	62.4	75.7	85.8
80	66.8	73.4	84.5	92.1
90	81.2	85.7	92.6	96.8
100	100.0	100.0	100.0	100.0

Experimental Verification of the Laws Underlying the Duclaux Method.

If we distil 110 cc. of an aqueous solution containing, for instance, 10 cc. each of 0.1 *N* acetic and propionic acids, then as we find from Table I, 6.4% or 0.64 cc. of 0.1 *N* acetic acid and similarly 1.12 cc. of 0.1 *N* propionic acid will be collected in the first 10 cc. of distillate; and in the same way 1.30 cc. 0.1 *N* acetic and 2.22 cc. 0.1 *N* propionic acid will be collected in the first 20 cc. of distillate. Thus the total amount of acid passing over in each fraction is easily calculated. We calculated in this way what the titration figures should be for a number of our mixtures after having determined the titration figures by actual distillation. The distillations were not done in duplicate. The results are compared in Table III.

Examination of Table III shows that in some cases the agreement is extremely good. An occasional large difference occurs. Most of the larger differences (from 0.3 to 0.4 cc.) are not isolated, but seem to result from a gradual accumulation of small errors during the course of the distillation; this may have been due in some cases to a persistent error in

TABLE III.—OBSERVED TITRATION FIGURES AND THOSE CALCULATED FROM TABLE I, FOR VARIOUS MIXTURES OF FORMIC, ACETIC, PROPIONIC, AND BUTYRIC ACIDS.

Mixture No.	Composition of mixture in cc. 0.1 *N* acid, diluted to 110 cc. and distilled.				Total number of cubic centimeters 0.1 *N* acid collected in various volumes of distillate.										
	F.	A.	P.	B.	Volume of distillate in cc.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100.
1	...	3.50	39.20	...	Observed	4.65	9.15	13.55	17.80	21.90	25.80	29.50	33.05	36.40	39.45
					Calculated	4.61	9.16	13.51	17.75	21.85	25.76	29.54	33.06	36.38	39.49
					Difference	0.04	—0.01	0.04	0.05	0.05	0.04	—0.04	—0.01	0.02	—0.04
2	...	17.30	19.60	...	Observed	3.30	6.60	9.80	13.00	16.50	19.30	22.45	25.55	28.75	32.05
					Calculated	3.30	6.60	9.82	13.03	16.23	19.34	22.53	25.66	28.84	32.17
					Difference	0.00	0.00	—0.02	—0.03	0.27	—0.04	—0.08	—0.11	—0.09	—0.12
6	...	15.00	16.20	17.90	Observed	5.70	11.10	16.20	21.05	25.60	29.90	33.90	37.60	41.15	44.50
					Calculated	5.71	11.13	16.27	21.09	25.70	29.92	34.01	37.75	41.29	44.65
					Difference	—0.01	—0.03	—0.07	—0.04	—0.10	—0.02	—0.11	—0.15	—0.14	—0.15
8	...	34.60	19.60	4.05	Observed	5.10	10.10	15.10	20.00	24.85	29.70	34.60	39.55	44.65	50.15
					Calculated	5.07	10.11	15.04	19.94	24.85	29.63	34.56	39.46	44.53	49.95
					Difference	0.03	—0.01	0.06	0.06	0.00	0.07	0.04	0.09	0.12	0.20
11	...	19.20	10.20	2.20	Observed	2.75	5.45	8.15	10.85	13.50	16.20	18.90	21.60	24.40	27.40
					Calculated	2.73	5.45	8.10	10.75	13.40	15.99	18.66	21.32	24.08	27.04
					Difference	0.02	0.00	0.05	0.10	0.10	0.21	0.24	0.28	0.32	0.36

15	2.20	7.70	15.30	22.00	Observed	5.90	11.45	16.60	21.50	25.95	30.10	33.90	37.30	40.50	43.30
					Calculated	5.90	11.45	16.66	21.47	26.01	30.10	33.96	37.40	40.56	43.43
					Difference	0.00	0.00	—0.06	0.03	—0.06	0.00	—0.06	—0.10	—0.06	—0.13
16	2.20	15.35	25.50	11.00	Observed	5.70	11.30	16.55	21.70	26.60	31.30	35.80	40.10	44.30	48.45
					Calculated	5.74	11.27	16.58	21.66	26.59	21.22	35.77	40.05	44.22	48.33
					Difference	—0.04	0.03	—0.03	0.04	0.01	0.08	0.03	0.05	0.08	0.12
17	2.20	14.40	5.10	22.00	Observed	5.20	10.05	14.65	18.90	22.90	26.60	30.05	33.20	36.20	39.10
					Calculated	5.19	10.06	14.65	18.88	22.92	26.56	30.07	33.27	36.31	39.23
					Difference	0.01	—0.01	0.00	0.02	—0.02	0.04	—0.02	—0.07	—0.11	—0.13
18	21.95	14.40	8.15	2.20	Observed	3.10	6.20	9.25	12.50	15.70	19.05	22.55	26.25	30.35	35.30
					Calculated	3.12	6.23	9.38	12.58	15.82	19.15	22.71	26.45	30.65	35.62
					Difference	—0.02	—0.03	—0.13	—0.08	—0.12	—0.10	—0.16	—0.20	—0.30	—0.32
19	11.30	17.30	19.60	16.20	Observed	6.40	12.60	18.55	24.25	29.75	35.05	40.20	45.20	50.20	55.35
					Calculated	6.43	12.62	18.57	24.25	29.78	35.00	40.21	45.18	50.19	55.39
					Difference	—0.03	—0.02	—0.02	0.00	—0.03	0.05	—0.01	0.02	0.01	—0.04
19	11.30	17.30	19.60	16.20	Observed	6.45	12.65	18.60	24.30	29.85	35.10	40.20	45.20	50.20	55.35
					Calculated	6.43	12.62	18.57	24.25	29.78	35.00	40.21	45.18	50.19	55.39
					Difference	0.02	0.03	0.03	0.05	0.07	0.10	—0.01	0.02	0.01	—0.04

collecting a little more than 10 cc. in each fraction, as an error of one drop is to be expected in any case. The average difference, without respect to sign, is 0.07 cc., which is about the error of titration; the mean difference is minus 0.002 cc. The differences are largest for mixtures No. 11 and 18; and for both mixtures, when the percentages, reckoned on the quantity of acid in 100 cc. of distillate, were calculated from the observed titration figures, we found that they agreed well with the percentages calculated from the quantities of acid taken. We conclude that Duclaux's laws as given above in our two formulations, hold within the experimental error over the range of concentrations such as we have used.

We have not studied the behavior of the acids over a wide range of concentrations, but Richmond[15] has found that the rate of distillation of formic acid increases with increasing concentration, and that this is true to a smaller extent of acetic acid; higher acids not being studied. This means that the numbers of Table I are not perfectly independent of the concentration, at least for these two acids, but increase somewhat as the concentration is increased. The numbers of Table II, which are used for calculating the results of analyses, should vary less than those of Table I, because of the compensation involved in referring the percentages to the quantity of acid in 100 cc. of distillate.

Algebraic Methods for Calculating the Results of Analyses: Mixtures of Two Volatile Acids.

The meaning of Table II is this: If in 100 cc. of distillate there should be present, for instance, 20 cc. of 0.1 N acetic acid and 15 cc. of propionic acid, then the first 10 cc. of distillate would contain 8% of 20 cc. or 1.6 cc. of 0.1 N acetic acid and 12.0% of 15 or 1.8 cc. propionic acid, and thus the total amount of acid passing into each of the fractions can be calculated. No further chemical or physical ideas are involved in calculating the results of analyses; the rest is purely mathematical. Suppose we have originally present in the distillation flask x cc. acetic and y cc. propionic acid, expressed always in this paper as 0.1 N, then from Table I we see that 100 cc. of distillate will contain $0.799\,x$ cc. acetic and $0.936\,y$ cc. propionic acid, and the total quantity in 100 cc., which we shall call Q_{100}, equals the sum of these two quantities. Now the quantity of acetic acid collected in the first fraction is 8.0% of the quantity of acetic acid in 100 cc. of distillate, or $8.0 \times 0.799\,x/100$ cc., and that of propionic acid is similarly represented, so that the total quantity of acid in the first 10 cc. fraction, which we shall call Q_{10}, is $8.0 \times 0.799x/100 + 12.0 \times 0.936\,y/100 = Q_{10}$. The percentage, reckoned on 100 cc. of distillate, which comes over in the first 10 cc. is $100\,Q_{10}/Q_{100}$ and we shall call its numerical value R_{10}. Therefore $8.0 \times 0.799\,x/Q_{100} + 12.0 \times 0.936\,y/Q_{100} = R_{10}$ and it is convenient to introduce new symbols a and p for the quotients, so that the equation takes the simpler form

$$8.0\,a + 12.0\,p = R_{10}.$$

In similar fashion we shall have for the corresponding percentage coming over in the first 20 cc.,

$$16.3\,a + 23.7\,p = R_{20},$$

where a and p are the same a and p as before, and we shall have also eight other equations which never need be written out. In order that what follows may be more typical, let us replace in the 10 equations the numbers that were obtained from Table II by appropriate letters: for acetic acid A_{10}, A_{20}, etc., and for propionic acid P_{10}, etc. The 10 equations are then of the form

$$A_{10}\,a + P_{10}\,p = R_{10}, \text{ etc.}$$

Since $0.799\,x + 0.936\,y = Q_{100}$ it follows that $a + p = 1$. The 10 equations then become reduced in number to 9 if we substitute for p its value $(1 - a)$, and each of the new equations contains only one unknown quantity.

$$(P_{10} - A_{10})\,a = P_{10} - R_{10};\ (P_{20} - A_{20})\,a = P_{20} - R_{20}, \text{ etc.}$$

We therefore compute from Table II the differences P — A for each of the first 9 fractions. For any unknown mixture assumed to be acetic and propionic acids calculate from the titration figures its distillation percentages R_{10}, R_{20}, R_{30}, according to the form of Table II and then find the differences $P_{10} - R_{10}$, $P_{20} - R_{20}$, etc. The values of a are then given by the following quotients, which may be found by means of a slide rule:

$$\frac{P_{10} - R_{10}}{P_{10} - A_{10}},\ \frac{P_{20} - R_{20}}{P_{20} - A_{20}} \cdots\cdots\cdots\cdots \frac{P_{90} - R_{90}}{P_{90} - A_{90}}.$$

Of the nine values of a the mean is to be taken as the most probable and p is found by subtracting the mean value of a from 1.*

Finally x and y are obtained from the formulas

$$x = a\,Q_{100}/0.799 = 1.252\,a\,Q_{100}.$$
$$y = p\,Q_{100}/0.936 = 1.068\,p\,Q_{100}.$$

In general, for mixtures of a *more* volatile acid, whose distillation constants are M_{10}, M_{20}, ... M_{100}; with a *less* volatile acid,† whose distillation constants are L_{10}, L_{20}, ... L_{100}; the values of l, the fraction of less volatile acid in 100 cc. of distillate, are given by

$$\frac{M_{10} - R_{10}}{M_{10} - L_{10}},\ \frac{M_{20} - R_{20}}{M_{20} - L_{20}} \cdots\cdots\cdots\cdots \frac{M_{90} - R_{90}}{M_{90} - L_{90}},$$

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* In this way, p is determined by difference. Indeed, whether in mixtures of two, three, or four acids, the quantity of the most volatile acid is always determined by difference. The errors of the analyses do not, however, affect the acids so determined more than the others, in fact examination of Table IV below shows that the errors are as a rule smallest for such acids.

† These designations, *more* and *less* volatile, refer to the volatility of the acids from aqueous solutions, and not to the volatility of the pure, moisture-free acids. As a general rule the more volatile moisture-free acids, formic, for instance, are the less volatile from dilute aqueous solution.

where the R's have the same meaning as above, and the value of m, the fraction of more volatile acid in 100 cc. of distillate, is 1 minus the mean value of l. The quantity of any acid in 100 cc. of distillate is found by multiplying the fraction (l or m) by the total quantity of acid collected in 100 cc. of distillate, and the quantity of the acid originally present in 110 cc. of solution is finally found by dividing by the fraction (given in Table I as *percentage*) of the pure acid which appears in 100 cc. of distillate.

Mixtures of Three Volatile Acids.

If a third volatile acid is present, for instance, butyric acid, in addition to acetic and propionic acids, then the 10 equations are of the form

$$\mathrm{A}_{10}\, a + \mathrm{P}_{10}\, p + \mathrm{B}_{10}\, b = \mathrm{R}_{10}, \text{ etc.},$$

where B and b refer to butyric acid. The 10 equations could be reduced in number to 3 "normal" equations containing three unknown quantities (a, p and b) by the method of least squares, and the normal equations then solved. This is the procedure suggested by Duclaux. We have found that the work is enormously lessened, however, if we operate rather on the 9 equations which result if we eliminate b by substituting its value $1 - (a + p)$.

Each of the nine new equations contains only two unknown quantities:

$$(\mathrm{B}_{10} - \mathrm{A}_{10})\, a + (\mathrm{B}_{10} - \mathrm{P}_{10})\, p = \mathrm{B}_{10} - \mathrm{R}_{10}, \text{ etc.}$$

the last one being,

$$(\mathrm{B}_{90} - \mathrm{A}_{90})\, a + (\mathrm{B}_{90} - \mathrm{P}_{90})\, p = \mathrm{B}_{90} - \mathrm{R}_{90}.$$

We therefore prepare from Table II a table containing the differences B — A and B — P for each of the first 9 fractions. These differences are known numbers and may better be represented by single (italicized) characters: thus $\mathrm{B}_{10} - \mathrm{A}_{10} = A_{10}$, $\mathrm{B}_{10} - \mathrm{P}_{10} = P_{10}$, etc. For each analysis we compute the nine differences B — R and call them R_{10}, etc. To illustrate we give in Table IV our values of A and P together with the values of $S = A + P$ which are useful in controlling the least square calculation. We give also the values of R for the case of one of our mixtures, No. 9.*

TABLE IV.

Values of A, P, and S used by us for calculating the results of analyses of mixtures of acetic, propionic, and butyric acids, together with the values of R for the analysis of Mixture No. 9.

Fraction.	*A.*	*P.*	*S.*	*R.*
10	8.7	4.7	13.4	6.5
20	15.6	8.2	23.8	11.7
30	21.1	10.8	31.9	15.6
40	24.4	12.1	36.5	18.0
50	26.1	12.5	38.6	19.3
60	25.8	11.7	37.5	18.4
70	23.4	10.1	33.5	16.7
80	18.7	7.6	26.3	13.1
90	11.1	4.2	15.3	7.6

* The composition of this mixture is given in Table V.

The nine equations now to be solved are easily kept in mind without writing them down, but for clearness here we state them as read off from Table IV.

$$\begin{array}{r} 8.7\,a + 4.7\,p = 6.5 \\ 15.6\,a + 8.2\,p = 11.7 \\ \hdashline \hdashline 11.1\,a + 4.2\,p = 7.6. \end{array}$$

To obtain the two normal equations by the method of least squares calculate the quantity (AA) by squaring A_{10}, A_{20} - - - - A_{90}, in turn and adding the squares; calculate the quantity (AP) by multiplying A_{10} by P_{10}, A_{20} by P_{25}- - - - - - A_{90} by P_{90} and adding the products; calculate in like manner the quantity

$$(PP) = P_{10}P_{10} + P_{20}P_{20} + \text{- - - - - - - -} P_{90}P_{90},$$

and also, for verification, (AS) and (PS). Then (AS) must equal $(AA) + (AP)$ and $(PS) = (AP) + (PP)$. All these calculations, in which it is unsafe to drop any significant figures, can be done in about thirteen minutes on one of that class of commercial calculating machines which multiply by a direct process. One of the most convenient operations to carry out on such machines is to form squares or products and add the results together as they are formed. That class of machines which can multiply only indirectly, by a process in which the operator punches keys say five times in order to multiply by five or fifty, would hardly be convenient. In the absence of a calculating machine Crelle's tables (2), which tabulate multiplications up to 999 times 999, may be used to marked advantage, but the work is laborious.

This work is done once for all for the case of mixtures of these three acids. When any particular mixture is analyzed, a little more least square work is required, as follows: Calculate the quantities (AR), (PR) and (SR). $(AR) + (PR)$ must equal (SR). The two normal equations need not be written out; the solution for a and p is as follows:

$$p = \left[(PR) - (AR)\frac{(AP)}{(AA)}\right]\frac{1}{(PP) - [(AP)/(AA)](AP)};$$

$$a = \frac{(AR)}{(AA)} - p\,\frac{(AP)}{(AA)}$$

In the solution many of the quantities are the same for all mixtures of these three acids; for our constants the solution was

$$p = 0.172{,}891\ [(PR) - 0.468{,}246\ (AR)];$$

$$a = 0.268{,}317\ (AR)/1{,}000 - 0.468{,}246\ p.$$

Then $b = 1 - (a + p)$; and x, y and z are finally obtained as shown above. It has proved useless to obtain the "probable error" for the case of mixtures of three (or more) acids. In applying the method to other combinations of three acids it may be convenient first to prepare a generalized scheme of work by substituting throughout in the foregoing directions L's for the A's (the least volatile), I's for the P's (the intermediate), and M's for the B's (the most volatile).

The numerical work required when a calculating machine is used is as follows for analysis of mixture No. 9, having already calculated the distillation percentages according to Table II from the titration figures and the differences R as given above in Table IV.

$(SR) = 3975.44$
$(PR) = 1269.45$ $\qquad = 1269.45$
$(AP) = 2705.99$ $\qquad 0.468{,}246\ (AR) = 1267.069$ $\qquad 0.268{,}317\ (AR)/1000 = 0.7261$
Difference $= +2.381$ $\qquad 0.468{,}246\ p = 0.1928$
$0.172{,}891 \times 2.381 = +0.411{,}65$ $\qquad a = +0.533$
$p = +0.412$
$a + p = 0.945$
$b = +0.055$

Q_{100}, the quantity of total acid collected in 100 cc. was 25.05 cc.
$25.05\ a = 13.359$ $\qquad 25.05 p = 10.313$ $\qquad 25.05\ b = 1.378$
$x = 1.252 \times 13.359 = 16.72$ cc. acetic acid
$y = 1.068 \times 10.313 = 11.02$ cc. propionic acid
$z = 1.022 \times 1.378 = 2.02$ cc. butyric acid

We have found that a number of analyses may be conveniently calculated together, with a great saving of time. Quadrille-ruled notebooks are very convenient for the calculations.

Mixtures of Four or More Volatile Acids.

For mixtures of four or more volatile acids the ten equations are similar in form and differ only in having an extra term for each extra acid, and reduce by a like process to nine similar equations with the elimination of one unknown. The normal equations are best solved by the Gaussian method of substitution because of the convenient controls which it permits. This method has been explained in full for the case of three unknowns,[12] and we need not give the scheme, as we have obtained unreliable results with mixtures of four acids.

Graphic Methods for Calculating the Results of Analyses: Mixtures of Two Volatile Acids.

For mixtures of two acids we make use of coördinate paper $7^1/_2 \times 10$ inches with 10 lines to the half-inch. Let L_{10}, L_{20}, etc., be the distillation constants (Table II) of the less volatile acid, and M_{10}, M_{20}, etc., be those of the more volatile acid, and let l be the fraction of less volatile acid in 100 cc. of distillate. Choose the l-axis vertical. On the horizontal line where $l = 1.00$ mark off to the right the value of $M_{10} - L_{10}$, $M_{20} - L_{20}$ .... $M_{90} - L_{90}$, and draw a line through the origin through each mark. This gives nine lines, Nos. 10, 20, ... 90 representing the relation between l and $M_{10} - R_{10}$, $M_{20} - R_{20}$, etc., respectively, where R represents as usual the distillation percentage, according to Table II, of the mixture to be analyzed. A graph is shown in Fig. 2 for mixtures of acetic and propionic acids. For each analysis find the differences $M_{10} - R_{10}$, etc., and from each difference read off on the corresponding line of the graph the value of l. Very small values of M — R, which lie too near the origin to be easily found, may be multiplied by 10 and the result for l subsequently divided by 10. Another method is possible, using a graph between l and R, but it requires larger coördinate paper for the same degree of accuracy. Having found the nine values of l, the rest of the calculation is the same as for the algebraic method described above.

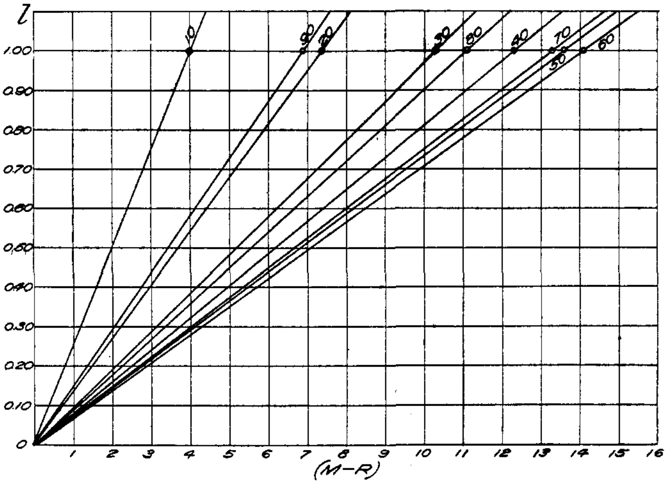

Fig. 2.—Graph for the analysis of all mixtures of acetic and propionic acids.

For any particular acids, appropriate letters will naturally be used in place of l, L, and M.

Mixtures of Three Volatile Acids.*

Let L_{10}, L_{20}, etc., be the distillation constants of the *least* volatile acid; I_{10}, I_{20}, etc., those of the *intermediate* acid; and M_{10}, M_{20}, etc., those of the *most* volatile acid. Let l be the fraction of the *least* volatile; i, that of the *intermediate*; and m, that of the *most* volatile acid in 100 cc. of distillate.

On a sheet of cross section paper (we use the size mentioned above), select two vertical axes a convenient distance apart (say 14 large divisions) and a horizontal axis *GH* (see Fig. 3). From G lay off the distance $M_{10} - I_{10}$ downward and from H the distance $M_{10} - L_{10}$ upward. Connect the extremities of the two distances thus located to find a point of intersection C_{10} on the horizontal axis. In practice, no line should be drawn,

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*This graphic method is an adaptation of one given by H. G. Deming (*Science, N. S.,* 43, 576 (1916)) and was suggested to us by him after our manuscript had been submitted to the editor. It is less cumbersome than the one we had been using and is preferable for that reason.

but the point C_{10} located with a pin-prick and its location recorded for later reference.

Laying off the distances $M_{20} - I_{20}$ and $M_{20} - L_{20}$ in the same way, locate on the horizontal axis another point C_{20} and continue, obtaining the rest of the nine points of intersection. It will often be more convenient to lay off distances proportional to any given M — I and M — L. Prepare a table of the successive values of $2M_{10} - I_{10} - L_{10}$, $2M_{20} - I_{20} - L_{20}$, etc.

Now for the analysis of any given mixture the distillation figures according to Table II must first be calculated; these are R_{10}, etc. A ten-inch slide rule is not precise enough for this: five-place logarithms are suitable. Calculate the ratio $(M_{10} - R_{10}) \div (2M_{10} - I_{10} - L_{10})$ (a slide rule will do for this) and the other similar ratios. Lay off the first ratio vertically over C_{10}, locating a point 10. Lay off the second ratio vertically over C_{20}, obtaining a point 20, etc. A straight line passing as nearly as possible through all these points, 10, 20..........90, will intercept on the left-hand vertical axis the best value of l and on the other vertical axis the value of i. In practice, a thread is stretched through the points and the intersections read off without drawing the line. The sum of l and i, subtracted from unity, gives m; and x, y and z are finally found as described above for the algebraic method.

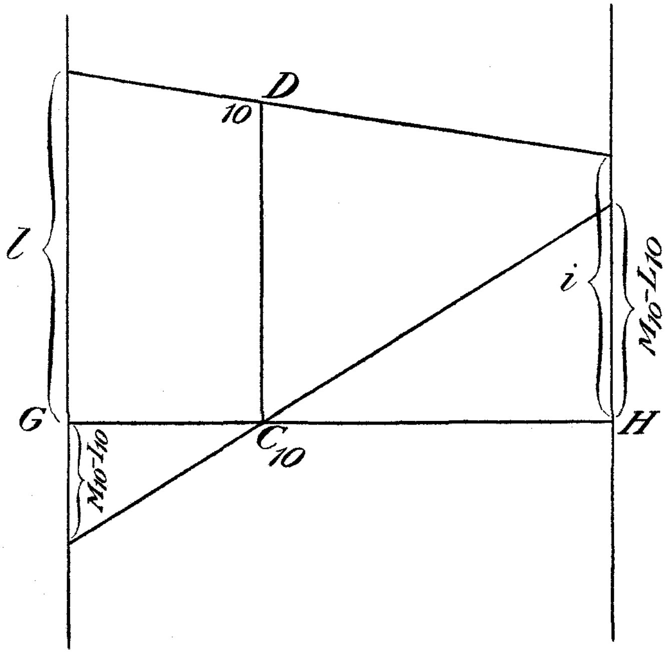

Fig. 3.

For any three particular acids, appropriate letters will naturally be used in place of l, i, m, L, I, and M.

Proof of the Construction.—Suppose the line finally found passes exactly through the point 10, or D. Then, dropping subscripts,

$$\frac{l - CD}{GC} = \frac{CD - i}{CH},$$

$$\left(l - \frac{\mathrm{M} - \mathrm{R}}{\mathrm{M} - \mathrm{I} + \mathrm{M} - \mathrm{L}}\right) \div \frac{(\mathrm{M} - \mathrm{I})GH}{\mathrm{M} - \mathrm{I} + \mathrm{M} - \mathrm{L}} = \left(\frac{\mathrm{M} - \mathrm{R}}{\mathrm{M} - \mathrm{I} + \mathrm{M} - \mathrm{L}} - i\right) \div \frac{(\mathrm{M} - \mathrm{L})GH}{\mathrm{M} - \mathrm{I} + \mathrm{M} - \mathrm{L}};$$

this reduces to $(\mathrm{M} - \mathrm{L})l + (\mathrm{M} - \mathrm{I})i = \mathrm{M} - \mathrm{R}$, which is the equation to be satisfied.

In graphs constructed by this method the desired points lie very close together and there is a considerable extrapolation involved. For this reason we present later some results obtained in this way. The more exact the experimental data, the more closely can we draw a line through the points. The distribution of the points about the line does not indicate whether or not the qualitative composition was correctly assumed.

General Applicability of the Algebraic and Graphic Methods.

The methods of calculation do not depend on the form of the law governing the rate of distillation of a pure acid in aqueous solution, and therefore do not necessarily depend on the *mode* of distillation. The distillations might in fact be conducted throughout in an entirely different manner, for instance, at constant volume, the volume lost by evaporation being restored by a properly regulated flow of water or of steam. If experience should show that in this way the actual amounts of acid distilling from a mixture could be as accurately calculated from the distillation figures of the single acids, this procedure might possess at least one advantage; for the titrations need not be limited to ten but could be extended to a greater number, and in this way more accurate analysis might possibly be attainable.

Dyer[8] has recently reported steam distillations of volatile fatty acids at constant volume but has not developed this possible advantage; the titration of only one fraction is used in calculating the results of each of the analyses. We admit that it may be arbitrary to give, as we do, every titration equal weight; yet is seems still more arbitrary to attempt to give the various titrations different weights, or to give all but one no weight at all. Four analyses are reported, each analyzed mixture containing two acids. The results seem to indicate that the Duclaux method can be carried out at constant volume, if desired, but sufficient data are not yet at hand to decide which process is better.

If the experimental data given in the paper of Dyer for pure normal butyric acid are plotted on the logarithmic chart,* it will be found that the line so obtained is not identical with the theoretically straight line for *n*-butyric acid on the chart, but it curves persistently and to a very large extent away from the straight line after the volume of distillate exceeds 100 cc., and apparently becomes parallel to the acetic or formic acid line. So also the actual lines for propionic and iso-valeric acid depart from the straight lines, apparently becoming parallel to the formic or acetic acid lines. We therefore doubt whether the logarithmic chart can be used in the manner described to identify the lower acid of a mixture except when this acid is formic or possibly acetic acid, unless it should be shown that the lines for the individual acids are really straight for acids of highest purity. It can be shown that if this is true the line for a mixture, whether of two or more acids, would ultimately approach a course parallel to the straight line representing the lowest constituent. However, in the line representing such a mixture there should not exist any such break in the curve as that implied in the statement: "The point at which the line begins its parallel course is the exact point at which the other, and higher, acid of the mixture has run out." It would therefore appear impossible to ascertain with a fair degree of probability the nature of the higher acid in the way suggested.

Analyses by a Single Duclaux Distillation of Mixtures of Known Qualitative Composition.

Any of the methods of calculation described above, if applied on totally erroneous assumptions as to the kinds and numbers of acids present in the mixture analyzed, will nevertheless yield a result for every constituent assumed present. The results in such a case may, however, be interpretable only on the hypothesis that the assumptions are incorrect, thus negative quantities of some acids may appear. Such a finding of course does not point to the absence of those acids found negative, unless the negative quantities are all within the usual numerical limits of error; the finding of larger negative quantities is evidence that the assumptions are in error and the calculations meaningless. If the distillation figures for a mixture calculated in the form of Table II be compared with Table II such very erroneous assumptions would often be excluded at a glance.

Before trying the Duclaux method as a means of qualitative analysis it is necessary to examine the success of the method when the assumptions are known to be perfectly correct. In Table V we summarize the results of the quantitative analysis of 18 mixtures of acids, some mixtures con-

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*The same result can be obtained without logarithmic paper by plotting on ordinary (linear) coördinate paper the logarithms of the percentage of acid *remaining in the flask* against the volumes of the distillate. Since the percentage of acid remaining in the flask equals 100% minus the percentage of acid distilled over, it will readily be seen that this procedure is exactly equivalent to plotting the line as was done on the logarithmic chart, because the divisions of the logarithmic scale are numbered, left to right, with numbers obtained by subtracting the usual number from 100.

TABLE V.—THE RESULTS OF ANALYSES OF VARIOUS MIXTURES OF FORMIC, ACETIC, PROPIONIC AND BUTYRIC ACIDS, CALCULATED BY ALGEBRAIC METHODS UNDER PERFECTLY CORRECT ASSUMPTIONS AS TO QUALITATIVE COMPOSITION, AND EXPRESSED IN CC. 0.1 *N* ACID.

Mixture No.	Taken.					Found.					Errors.				
	F.	A.	P.	B.	Total.	F.	A.	P.	B.	Total.	F.	A.	P.	B.	Total.
1	...	3.50	39.20	...	42.70	...	2.90	40.19	...	43.09	....	—0.60	0.99	....	0.39
2	...	17.30	19.60	...	36.90	...	16.72	19.96	...	36.68	....	—0.58	0.36	....	—0.22
3	...	30.80	1.20	...	32.00	...	31.19	1.14	...	32.33	....	0.39	—0.06	....	0.33
4	...	10.00	...	10.20	20.20	...	9.77	...	10.37	20.14	....	—0.23	....	0.17	—0.06
5	11.30	...	...	16.20	27.50	10.74	...	...	16.34	27.08	—0.56	....	....	0.14	—0.42
6	...	15.00	16.20	17.90	49.10	...	13.78	18.02	17.00	48.80	....	—1.22	1.82	—0.90	—0.30
7	...	34.60	19.60	4.05	58.25	...	36.90	16.33	5.61	58.84	....	2.30	—3.27	1.56	0.59
8	...	34.60	19.60	4.05	58.25	...	36.00	17.85	4.78	58.63	....	1.40	—1.75	0.73	0.38
9	...	17.30	9.80	2.02	29.12	...	16.72	11.02	1.41	29.15	....	—0.58	1.22	—0.61	0.03
10	...	10.00	19.60	10.20	39.80	...	9.01	20.92	9.53	39.46	....	—0.99	1.32	—0.67	—0.34
11	...	19.20	10.20	2.20	31.60	...	17.45	14.33	0.04	31.82	....	—1.75	4.13	—2.16	0.22
12	...	2.90	10.20	22.00	35.10	...	1.52	12.04	21.28	34.84	....	—1.38	1.84	—0.72	—0.26
13	...	19.20	2.05	22.00	43.25	...	18.28	3.14	22.04	43.46	....	—0.92	1.09	0.04	0.21
14	...	17.30	19.60	4.05	40.95	...	16.04	21.57	2.85	40.46	....	—1.26	1.97	—1.20	—0.49
15	2.20	7.70	15.30	22.00	47.20	6.52	—1.69	17.78	16.29	38.90	4.32	—9.39	2.48	—5.71	—8.30
16	2.20	15.35	25.50	11.00	54.05	9.27	4.67	32.03	8.86	54.83	7.07	—10.68	6.53	—2.14	0.78
17	2.20	14.40	5.10	22.00	43.70	16.64	—8.86	19.33	17.58	44.69	14.44	—23.26	14.23	—4.42	0.99
18	21.95	14.40	8.15	2.20	46.70	27.07	5.33	14.45	0.04	46.89	5.12	—9.07	6.30	—2.16	0.19
19	11.30	17.30	19.60	16.20	64.40	12.51	10.73	21.85	13.22	58.31	1.21	—6.57	2.25	—2.98	—6.09

taining two, others three, and others four acids. For the calculations perfectly correct assumptions were made as to the number of acids present and their identity, and algebraic methods were used. The distillations were not done in duplicate except in the case of mixture No. 19.

It will be seen from Table V that mixtures of two or of three acids can be quantitatively analyzed with success when the qualitative analysis is known. The errors for mixtures of three is greater than for those of two acids but is as a rule only about 2 cc. or less. In only two cases was the error for a constituent in a mixture of three considerably larger: In mixture No. 11 it was 4.13 cc. for propionic acid, and in No. 7 it was 3.27 cc., also for propionic acid, but the errors for No. 8, which had the same composition as No. 7, were small. The large error in No. 11 is not to be explained as due to unusual properties of the mixture, but rather to experimental errors. It would evidently be advisable to distil in duplicate for the best results.

It will be observed that the errors are not proportional to the quantities taken for analysis, but are to a high degree independent of these quantities; so that the errors are more intelligibly expressed in cc. than in percentage of the quantities taken.

The errors in analyses of mixtures of four acids are so large as to make the method useless for the direct calculation of four constituents. The distillation of No. 19 was done in duplicate. Although it is probable that somewhat better results for mixtures of four acids could be obtained by determining the constants in duplicate and also distilling each mixture in duplicate, it will become evident to anyone who carries out the actual calculation that even very small experimental errors will cause large errors in the calculated results for mixtures of four acids. In order to make this clear we give in Table VI the observed and calculated titration figures for mixture No. 16, together with the compositions of various theoretical mixtures with their calculated titration figures.

Mixture No. T1 is that found as the result of calculating for four acids; T2 that found by calculating for acetic, propionic, and butyric acids; T3, that found by calculating for formic, propionic, and butyric acids; and T4, that found by assuming present only acetic and propionic acids. It will be noted that the observed titration figures agree better with those calculated for the first three theoretical mixtures than with those calculated for the actual mixture taken. Now the compositions of the five mixtures for which the titration figures were calculated differ very widely. One perceives therefore that a high degree of precision will be demanded if mixtures of four acids are to be analyzed for all constituents by a single Duclaux distillation. Assumption of the presence of three acids permits the observations to be "fitted" as well as they deserve, even if four acids are present, and although the assumption of four acids will permit better

TABLE VI.—THE OBSERVED TITRATION FIGURES FOR MIXTURE NO. 16, COMPARED WITH THE TITRATION FIGURES CALCULATED FOR THIS MIXTURE AND WITH THOSE FOR FOUR THEORETICAL MIXTURES: T1, T2, T3 AND T4.

	Composition of mixture in cc. 0.1 *N* acid.				Total number of cc. 0.1 *N* acid collected, in various volumes of the distillate in cc.										
Mixture No.	F.	A.	P.	B.	Volume of distillate.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100.
16	2.20	15.35	25.50	11.00	Observed	5.70	11.30	16.55	21.70	26.60	31.30	35.80	40.10	44.30	48.45
16	2.20	15.35	25.50	11.00	Calculated	5.74	11.27	16.58	21.66	26.59	31.22	35.77	40.05	44.22	48.33
					Difference	−0.04	0.03	−0.03	0.04	0.01	0.08	0.03	0.05	0.08	0.12
T1	9.27	4.67	32.03	8.86	Calculated	5.73	11.27	16.59	21.69	26.60	31.27	35.82	40.10	44.28	48.43
					Difference	−0.03	0.03	−0.04	0.01	0.00	0.03	−0.02	0.00	0.02	0.02
T2	0	18.77	23.83	11.39	Calculated	5.74	11.28	16.59	21.68	26.62	31.26	35.83	40.13	44.32	48.44
					Difference	−0.04	0.02	−0.04	0.02	−0.02	0.04	−0.03	−0.03	−0.02	0.01
T3	12.31	0	34.77	8.02	Calculated	5.73	11.27	16.59	21.70	26.60	31.28	35.82	40.10	44.27	48.43
					Difference	−0.03	0.03	−0.04	0.00	0.00	0.02	−0.02	0.00	0.03	0.02
T4	0	6.24	46.42	0	Calculated	5.60	11.12	16.41	21.58	26.59	31.38	36.03	40.38	44.52	48.43
					Difference	0.10	0.18	0.14	0.12	0.01	−0.08	−0.23	−0.28	−0.22	0.0

fitting such accurate fitting is unjustifiable. It must also be concluded that those results calculated by the indirect method by previous investigators on the assumption that four or more acids were present may be enormously in error.

It might be incautiously assumed, since mixture No. T4 succeeds fairly well in accounting for the observed titration figures, that this same line of thought could be extended to prove calculations of mixtures of three acids valueless. Discussion below of Tables VII, VIII and IX will show, however, that this is not true. Table IX will show clearly that the titration figures observed for mixture No. 16 contradict the assumption that the only acids are acetic and propionic.

Analyses by a Single Duclaux Distillation of Mixtures of Partially Known Qualitative Composition.

The analytical results of some of the mixtures containing only two acids were calculated on the assumption that three adjacent* acids were present and are summarized in Table VII.

From the fact that the errors, when the correct assumptions are made, are not proportional to the quantities taken for analysis we might expect that the errors would be no larger when an acid is not really present than when it is. This is borne out by Table VII. The quantities found, though not present, are italicized. In one case, to be sure, 4.3 cc. of formic acid are falsely found present, but one exceptional error of 4.13 cc. was mentioned above in an analysis of three constituents when the correct assumptions were made, and the error of 4.3 cc. was probably also exceptional. It appears therefore, that if two adjacent acids are known and a third is suspected to be present, it is safe to assume the third acid, recollecting of course the magnitude of the error to be expected. This procedure would fail miserably if a fourth acid, not adjacent to the third, were present in considerable quantity. The procedure should not fail, however, if a fourth acid adjacent to the third were present in reasonably small quantity, as will appear from the discussion of Table VIII.

We studied the effect of neglecting the presence of some acids which we knew to be present, in calculating the results of analyses, and the results are shown in Table VIII.

Among the results summarized in Table VIII the last one (No. 18), is exceptional, as in this case neglect of 2.2 cc. of butyric acid caused rather large errors in the calculated results. With this exception the following remarks hold: The largest error in each calculated result is in the quantity of acid found for the acid adjacent to the neglected acid, and indeed the quantity found for this adjacent acid is nearly equal to the sum of the quantities taken of this acid and of the neglected acid. In other words, the amount of the neglected acid is included in the result found for the

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*We mean by adjacent acid an acid next in order of volatility.

TABLE VII.—RESULTS OF SOME ANALYSES OF MIXTURES OF TWO ACIDS, CALCULATED BY THE ALGEBRAIC METHOD ON THE ASSUMPTION THAT THREE ACIDS WERE PRESENT. THE QUANTITIES FALSELY FOUND PRESENT ARE ITALICIZED.

Mixture No.	Taken.					Found.					Errors.				
	F.	A.	P.	B.	Total.	F.	A.	P.	B.	Total.	F.	A.	P.	B.	Total.
1	....	3.5	39.2	....	42.7	...	3.1	40.0	*0.1*	43.2	...	—0.4	0.8	0.1	0.5
1	....	3.5	39.2	....	42.7	*—0.1*	3.1	40.1	...	43.1	—0.1	—0.4	0.9	...	0.4
2	....	17.3	19.6	....	36.9	...	18.4	16.7	*1.8*	36.9	...	1.1	—2.9	1.8	0.0
2	....	17.3	19.6	....	36.9	*4.3*	11.3	21.6	...	37.2	4.3	—6.0	2.0	...	0.3
3	....	30.8	1.2	....	32.0	...	29.9	3.6	*—1.3*	32.2	...	—0.9	2.4	—1.3	0.2
4	....	10.0	....	10.2	20.2	...	9.0	*1.2*	9.8	20.0	...	—1.0	1.2	—0.4	—0.2

TABLE VIII.—RESULTS OF SOME ANALYSES CALCULATED BY ALGEBRAIC METHODS, IGNORING THE PRESENCE OF SOME ACIDS. THE ITALICIZED QUANTITIES ARE THE ONES IGNORED. IN TWO STARRED CASES, ACIDS WERE MOREOVER ASSUMED PRESENT WHICH WERE ABSENT. ALL QUANTITIES ARE IN CC. 0.1 *N* ACID.

Mixture No.	Taken.					Acids assumed and quantities found.					Errors.				
	F.	A.	P.	B.	Total.	F.	A.	P.	B.	Total.	F.	A.	P.	B.	Total.
3*	....	30.8	*1.2*	....	32.0	....	31.8	....	0.6	32.4	...	1.0	...	0.6	0.4
8	....	34.6	19.6	*4.0*	58.2	....	30.8	27.3	....	58.1	...	—3.8	7.7	...	—0.1
11	....	19.2	10.2	*2.2*	31.6	....	17.4	14.4	....	31.8	...	—1.8	4.2	...	0.2
11*	....	19.2	10.2	*2.2*	31.6	0.7	16.5	14.7	....	31.9	0.7	—2.7	4.5	...	0.3
12	....	*2.9*	10.2	22.0	35.1	....	....	14.7	19.9	34.6	...	...	4.5	—2.1	—0.5
13	....	19.2	*2.0*	22.0	43.2	....	20.0	....	23.7	43.7	...	0.8	...	1.7	0.5
14	....	17.3	19.6	*4.0*	40.9	....	12.8	27.3	....	40.1	...	—4.5	7.7	...	—0.8
15	*2.2*	7.7	15.3	22.0	47.2	....	10.0	14.7	22.1	46.8	...	2.3	—0.6	0.1	—0.4
16	*2.2*	15.4	25.5	11.0	54.1	....	18.8	23.8	11.4	54.0	...	3.4	—1.7	0.4	—0.1
17	*2.2*	14.4	5.1	22.0	43.7	....	16.5	4.6	22.1	43.2	...	2.1	—0.5	0.1	—0.5
18	22.0	14.4	8.1	*2.2*	46.7	26.8	5.3	14.5	....	46.6	4.8	—9.1	6.4	...	—0.1

adjacent assumed acid. When the quantity of acid neglected does not exceed 2.9 cc., the remaining errors are not serious, when it reaches 4.0 cc. the error (for assumed mixtures of two acids), is greater, but hardly invalidates the analyses.

The four cases where 2.2 cc. of acid were neglected in mixtures of four acids merit especial attention. Comparing these results with the results obtained by assuming four acids present, as given in Table V above, one sees that mixture No. 18 gave almost identical results under either assumption, and that in the other three cases very much better results were obtained by neglecting the small quantity of fourth acid than by assuming the fourth acid present.

It may be interesting to note that when 2.2 cc. are neglected this quantity is never less than 4% of the total acid in the mixture taken for analysis.

Indications of a Third Acid Given by a Single Duclaux Distillation.

Duclaux, and others following him, have calculated the 10 values of a ratio between the quantities of the two acids assumed present, and have judged the correctness of the qualitative analyses by the constancy of this ratio. When the ratio has not seemed sufficiently constant, they have tried other combinations of two acids.

We have observed that when results are calculated on the assumption that only two acids are present the values found for the percentage of one acid (in every case the percentage of the less volatile acid, reckoned on the quantity in 100 cc. of distillate and expressed decimally), furnish sometimes evidence of the presence of other acids than those assumed. We give in Table IX these percentages for eight cases where the assumptions were either incomplete or actually wrong, together with those for three cases where the assumptions were correct.

At least one, and possibly two other of these incorrect assumptions would have been excluded by a hasty comparison of the distillation figures calculated according to Table II with Table II itself, but they illustrate the point to be noted as well as the others. It will be observed that the presence of considerable quantities of acids other than those assumed causes the percentage to undergo a persistent variation; in the cases given, a rise in value. Since the variation is generally irregular, we have checked our judgment as to the trend by drawing rough graphs. The principle illustrated here does not appear to be particularly useful, however, since it does not enable one to tell whether three or four acids are present, and if by other means it can be stated that not more than three are present, the presence of a third is as well or better determined by calculating for three.

Use of the Duclaux Method for Unknown Mixtures.

A single Duclaux distillation, unsupported by the sense of smell or by color or other auxiliary tests, will not suffice to determine the number of

TABLE IX.—INDICATIONS OF THE PRESENCE OF MORE THAN TWO ACIDS OBTAINED ON CALCULATING FOR TWO ACIDS.

Mixture No.	1.	2.	3.	1.	4.	5.	8.	11.	12.	14.	16.
Remarks.	Only two acids present and correctly assumed.			More than two acids present, or the wrong two assumed.							
Acids present	A, P	A, P	A, P	A, P	A, B	F, B	A, P, B	A, P, B	A, P, B	A, P, B	F, A, P, B
Acids assumed	A, P	A, P	A, P	P, B	P, B	P, B	A, P	A, P	P, B	A, P	A, P
Acids neglected in cc.	....	....	....	3.5 A	10.0 A	11.3 F	4.0 B	2.2 B	2.9 A	4.0 B	2.2 F, 11.0 B
Fraction No.	Percentages found for the lower acid assumed, referred to 100 cc. of distillate and expressed decimally as fractions of unity.										
10	0.050	0.425	0.925	1.042	0.830	0.596	0.450	0.500	0.383	0.250	0.050
20	0.068	0.419	0.973	1.061	0.830	0.659	0.486	0.513	0.415	0.257	0.054
30	0.058	0.417	0.961	1.056	0.851	0.731	0.466	0.505	0.407	0.272	0.068
40	0.057	0.422	0.976	1.058	0.869	0.760	0.480	0.504	0.405	0.284	0.081
50	0.059	0.353	0.971	1.064	0.913	0.808	0.492	0.514	0.424	0.302	0.103
60	0.057	0.425	0.958	1.070	0.940	0.864	0.496	0.503	0.419	0.284	0.114
70	0.068	0.429	0.947	1.090	0.999	0.940	0.504	0.504	0.425	0.308	0.135
80	0.063	0.432	0.965	1.093	1.052	1.052	0.504	0.513	0.421	0.288	0.153
90	0.045	0.433	0.955	1.072	1.168	1.214	0.537	0.523	0.429	0.319	0.174
Variation in percentage found.	no persistent trend			slight rise	large rise	large rise	rise	very slight rise	slight rise	rise	large rise

acids present in an unknown mixture, unless the number is two. It should not be very difficult, however, to determine whether or not more than three acids are present. If necessary, the acids may be partially freed from their salts and distilled, as suggested by Liebig.[13]

If more than three acids are present it would appear likely to us, though we have no evidence to offer, that the application of Duclaux distillations after partial separation according to Liebig or by means of their quinine salts[14] will permit a fair estimation of the extreme acids, though possibly but a poor one of the middle acids.

If no more than three acids are found present in significant quantities, it seems best to assume present the three (adjacent) acids probably present for the calculation of the results of the Duclaux distillation, unless it is positively known that only two acids occur in the mixture. There seems to be no danger that any absent acid will falsely be concluded to be present.

Accuracy of the Graphic Methods.

The graphic method for mixtures of two acids is so easy to carry out that the three examples given in Table X are enough to show that it is sufficiently accurate.

TABLE X.—APPLICATION OF THE GRAPHIC METHOD TO MIXTURES OF TWO ACIDS; ACETIC AND PROPIONIC.

Mixture No.	1.			2.			3.		
	A.	P.	Total.	A.	P.	Total.	A.	P.	Total.
Taken	3.5	39.2	42.7	17.3	19.6	36.9	30.8	1.2	32.0
Found	2.8	40.2	43.0	16.6	20.0	36.6	31.4	1.2	32.6
Error	—0.7	1.0	0.3	—0.7	0.4	—0.3	0.6	0.0	0.6
Error by the algebraic method	—0.6	1.0	0.4	—0.6	0.4	—0.2	0.4	—0.1	0.3

In Table XI we give the results obtained by the graphic method for some of our mixtures containing acetic, propionic, and butyric acids, or two of them, all calculated under the assumption that all three of these acids were present. We also give for comparison the errors resulting from the application of the algebraic method to each case.

Examination of Table XI shows that when relatively large errors occur in the graphic results they also occur in the least square results, and the difference between the errors of the two methods is small, compared with the error of either.

Although some workers may prefer the least square procedure because of the elimination of the personal equation, the graphic method for three acids is in general sufficiently accurate and affords a control over unusual technical errors of analysis.

TABLE XI.—THE RESULTS OF SOME ANALYSES CALCULATED BY THE GRAPHIC METHOD, ASSUMING IN EACH CASE THE PRESENCE OF ACETIC, PROPIONIC, AND BUTYRIC ACIDS. ALL QUANTITIES ARE IN CC. 0.1 *N* ACID.

Mixture No.	Taken.				Found, graphic method				Errors, graphic method.				Errors, least square method. (Table V above.)			
	A.	P.	B.	Total.	A.	P.	B.	Total.	A.	P.	B.	Total.	A.	P.	B.	Total.
1	3.5	39.2	0	42.7	3.0	40.0	0.0	43.0	—0.5	0.8	0	0.3	—0.4	0.8	0.1	0.5
3	30.8	1.2	0	32.0	29.9	3.1	—0.8	32.2	—0.9	1.9	—0.8	0.2	—0.9	2.4	—1.3	0.2
4	10.0	0	10.2	20.2	9.2	1.2	9.5	19.9	—0.8	1.2	—0.7	—0.3	—1.0	1.2	—0.4	—0.2
6	15.0	16.2	17.9	49.1	14.3	17.4	17.4	49.1	0.7	—1.2	—0.5	0.0	—1.2	1.8	—0.9	—0.3
7	34.6	19.6	4.0	58.2	37.6	14.9	6.4	58.9	3.0	—4.7	2.4	0.7	2.3	—3.3	1.6	0.6
8	34.6	19.6	4.0	58.2	36.4	17.5	4.7	58.6	1.8	—2.1	0.7	0.4	1.4	—1.7	0.7	0.4
10	10.0	19.6	10.2	39.8	10.8	17.7	11.1	39.6	0.8	—1.9	0.9	—0.2	—1.0	1.3	—0.7	—0.3
11	19.2	10.2	2.2	31.6	18.2	12.9	0.8	31.9	—1.0	2.7	—1.4	0.3	—1.7	4.1	—2.2	0.2
14	17.3	19.6	4.0	40.9	17.1	19.2	4.2	40.5	—0.2	—0.4	0.2	—0.4	—1.3	2.0	—1.2	—0.5

Summary.

The laws which must be assumed in order to calculate the results of analyses by the Duclaux method have been stated and verified.

Both algebraic and graphic methods for the computation of the results for mixtures of two or of three acids have been described and the algebraic calculation for four or more acids has been indicated.

Application of the methods to known mixtures show that mixtures of two or of three acids may be quantitatively analyzed without too great error by either algebraic or graphic methods, but that the errors are too large in general for mixtures of four acids.

The errors of the Duclaux method are not proportional to the quantities of acid present.

If four or more acids are present in significant quantities the mixture must be fractionated before applying the Duclaux method, into mixtures containing only three acids in significant quantity.

In order to apply the Duclaux method to unknown mixtures it is necessary to establish that not more than three acids are present in significant quantities. This fact established, a distillation by the Duclaux method should suffice for both qualitative and quantitative analysis of the mixture.

The methods of calculation do not depend on the form of the laws governing the rates of distillation of pure acids in aqueous solution and therefore do not necessarily depend on the mode of distillation. The calculations may therefore be applied to distillations made in other ways, for instance, to steam distillations at constant volume. It is merely necessary to conduct all distillations both of pure acids and of mixtures in the same manner.

Addendum

We have lately found a still more convenient graphic method for three acids, which appears to be also slightly more accurate than the one given above.

Choose a vertical axis for values of $\frac{(M-R)}{(M-L)}$ and a horizontal axis for $\frac{(M-I)}{(M-L)}$. Lay off nine points representing the successive values of $\frac{(M-R)}{(M-L)}, \frac{(M-I)}{(M-L)}$. Stretch a thread as nearly as possible through the nine points, ignoring the first if this point alone deviates much from a straight line. Read off l along the vertical axis at the intersection of the thread, and read off $(l+i)$ where the thread crosses the vertical line where $\frac{(M-I)}{(M-L)}$ equals one. The stretched thread represents the line $\frac{(M-R)}{(M-L)} = i \frac{(M-I)}{(M-L)} + l$ in ordinary (Cartesian) coördinates, where the quotients are the variables. The extrapolation involved is much less than with the (alignment chart) method given in the body of the paper.

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Washington, D. C.

[Contribution from the Laboratories of the Office of Soil Fertility, Bureau of Plant Industry, U. S. Department of Agriculture.]

A SIMPLIFIED MICRO-COMBUSTION METHOD FOR THE DETERMINATION OF CARBON AND HYDROGEN.

By Louis Elsberg Wise.

Received June 25, 1917.

The micro-combustion method devised by Pregl[1] and successfully used by various European investigators, has apparently received scant atten-

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[1] F. Pregl, in "Abderhalden's Handbuch der Biochem. Arbeitsmethoden," [ii] **5**, 1307.