of the results of several investigators, the deviations between the observed and calculated values can be taken as an approximate estimate of the accuracy of the available data.

Summary

The new equation of state has been applied to the compressibility measurements on helium, neon, argon, hydrogen, oxygen, nitrogen, air and methane, and the values of the constants are given for these gases and for carbon dioxide and ethyl ether. A method is outlined for transforming the experimental pressure–volume–temperature data into isometric form, and a brief description of the procedure for evaluating the constants of the equation of state is given. Comparison of the observed pressures and those calculated from the equation have been made at 1777 points for these ten gases, the average deviation being 0.08 atmosphere or 0.18% over the entire temperature and density range considered. The average deviation is 0.06 atmosphere or 0.16% over the experimental temperature range and to a density of 5 moles per liter (an Amagat density of approximately 110).

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY OF VALIO, HELSINKI, FINLAND]

THE VOLATILITY WITH STEAM OF WATER-SOLUBLE ORGANIC SUBSTANCES

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Investigations on the determination of volatile fatty acids by means of steam (which from an analytical point of view is a very important mode of procedure) have in many ways explained our opinion as to the quantitative course of distillation by steam and have rendered it possible to express quantitatively in a simple manner the volatility of water-soluble substances with steam. When boiling the diluted solutions of fatty acids a certain percentage of acid is always distilled into a certain quantity of water, this percentage being different in the case of different acids. If there are several acids in the same diluted solution of acid, each acid is distilled independently of the others. Duclaux's[1] well known and purely empiric mode of procedure for the determination of volatile fatty acids is based on these facts. This procedure is, however, complicated and requires definite tables; it also applies only to fatty acids.

Among the investigations, the purpose of which has been to derive simple mathematical formulas in order to follow the course of distillation, should be mentioned Barrel, Thomas and Sidney Young's[2] differential equations,

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[1] Duclaux, *Traité de Microbiologie*, **3,** 384 (1900); **4,** 685 (1901).

[2] Barrel, Thomas and Young, *Phil. Mag. and J. of Science*, (V) **37,** 8 (1894).

which are based upon Brown's[3] work and of a later time upon Richmond's[4] and Wiegner's[5] logarithmical equations, which have evidently been derived independently.

From Brown's equation $dy/dx = ky/x$, where y is the weight of the volatile substance in the liquid and x is the weight of the water in the liquid, Wiegner has derived a simple logarithmical equation

$$\log y = k \log x + 2 - 2k$$

which is very well applicable in practice. If the quantity of water at the beginning of the distillation is denoted by x_1 and at the end by x_2, and the substance to be distilled at the beginning by y_1, and when completed by y_2, we get the following equation

$$\frac{\log y_1 - \log y_2}{\log x_1 - \log x_2} = k$$

k is a constant which according to the above equation is easily calculable from the observations.

k, which we may call the constant of distillation, is a very practical means of indicating the volatility of the substance. If the solution is diluted with regard to the volatile substance to be investigated and if the distillation is made so that the condensation of steam is completely prevented, the value of k is constant for each volatile substance. Now it is impossible in practice completely to prevent the condensation of steam on the walls of the retort, but it may, however, be reduced so much that practically constant values may be obtained for k.

An ordinary steam distillation by blowing steam through the solution is not applicable to quantitative analyses since it is difficult to keep the volume of the solution perfectly constant during the time of distillation and the steam bubbles may be too large in passing through the solution, in which case an exact state of equilibrium between the composition of the steam and the composition of the solution is not obtainable. In practical laboratory work it is in many respects very important to know the volatility of different substances.

First, it is in many cases possible by means of fractional distillation to decide whether the substance is chemically pure or a mixture and thus the purity of the substance can be determined. If many fractions are distilled, k will have the same value in each fraction if the substance under investigation is pure.

Second, it is possible by means of steam distillation to obtain a quantitative analysis of volatile substances, as shown by the determinations mentioned below.

Third, it is possible on the basis of the value of k to decide in advance

[3] Brown, *Trans. Chem. Soc.*, **1879**, 550; **49**, 304 (1880); 517 (1881).

[4] Richmond, *Analyst*, **33**, 209, 305 (1907).

[5] Wiegner, *Mitt. Gebiete Lebensmitteluntersuchung Hygiene*, **10**, Fasc. 3/6 (1919).

whether a substance can be separated from non-volatile substances by means of distillation, whether in such cases neutral salts must be added or whether it is necessary to use altogether different methods.

Taking all of the above-mentioned circumstances into consideration, it is important that the values of k should be found for all substances volatile with steam and that these values should be stated in the handbooks.

Volatility could be expressed not only by distillation constants but also simply by using the number which indicates the percentage of each substance distilled, when a certain volume (half, for instance) is distilled. By means of these values of semi- or quarter-distillations, it is easy to calculate k and *vice versa.*

In this investigation we have determined the value of k for numerous compounds which represent different groups of substances. For quantitative determinations it is important to know how different circumstances influence the value of k and therefore we have investigated by using certain fatty acids, the influence of some factors on the course of the distillation. At the same time we have made minute distillations with mixtures containing two or three different substances.

The influence of salts upon the distillation of substances by steam has been previously investigated by one of us.[6] With a view to theoretically explaining this question we have made additional investigations, which we shall present in this article.

Methods

In the quantitative distillation by steam the only exact procedure is by the method of boiling. For this purpose the solution of the substance in water to be investigated is distilled without leading steam through the solution, the volume of the solution thus steadily diminishing. While employing the method of boiling it is important that attention be paid to the size of the vessel used in order to prevent the steam from becoming condensed uselessly. For the same reason the tube which unites the retort with the condenser must be sufficiently large and as low as possible. In our experiments we have used a 300cc. Erlenmeyer flask, the volume of the solution being 200 cc. The dimensions of our apparatus are shown in Fig. 1. It is necessary to be certain that the volume of the flask really is precisely 300 cc.

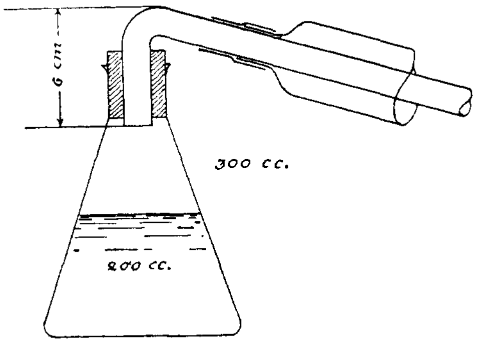

Fig. 1.

The flask was placed upon a network of asbestos and heated by means of an or-

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[6] Virtanen, *Suomen Kemistiseuran Tiedonantoja* (*Publications from the Chemical Society of Finland*), **1921**, 9.

dinary Bunsen burner. Calibrated volumetric flasks were used as receivers. The acids were determined by titration with $N/20$ sodium hydroxide, with phenolphthalein as indicator; the amines were determined by $N/10$ sulfuric acid with Congo red as indicator. The determination of other substances will be mentioned separately.

There are several circumstances which influence the course of the distillations of these substances in cases where the constant is very great or on the contrary very small. The concentration of the solution is of great importance even if the solution is very much diluted. (Table I.) According to Duclaux, his method of distillation is applicable up to solutions of 2%. Our determinations show that the differences of concentration in solutions with this dilution have a remarkable influence upon the value of k for a number of substances. The time of distillation, upon which the condensation of steam depends, must also be taken into consideration. Below are given a few examples which show the effects of these factors. (Table II.)

TABLE I

THE EFFECT OF CONCENTRATION UPON THE VALUE OF k

60-minute distillations in all experiments

Concentration %	Concentration N	k	Semi-dist. value, %
Formic Acid (Kahlbaum)			
0.02	0.0049	0.364	22.3
.07	.0151	.370	22.6
.24	.0521	.388	23.5
.42	.0920	.390	23.7
.53	.1154	.398	24.1
Acetic Acid[a] (Kahlbaum)			
0.09	0.0150	0.657	36.6
.51	.0843	.657	36.6
Propionic Acid (Kahlbaum)			
0.07	0.0088	1.235	57.5
.09	.0115	1.239	57.6
.13	.0169	1.239	57.6
1.32	.1785	1.270	58.5
Butyric Acid (Kahlbaum)			
0.05	0.0058	1.92	73.5
.16	.0181	1.96	74.4
.29	.0332	1.99	74.8
.88	.1000	2.00	75.0
2.29	.2600	2.02	75.3

The effect of the concentration of acetic acid is very small. For solutions of 2% and for more concentrated solutions, the value of k is almost the same as in the above distillations.

TABLE II

THE INFLUENCE OF THE TIME OF DISTILLATION UPON THE VALUE OF k

The time is that which elapsed in distilling from 200 to 100 cc.

Concn., %	Minutes	k	Semi-dist. value, %
Formic Acid			
0.39	59	0.389	23.7
.39	125	.325	20.2
Acetic Acid			
0.12	41	0.668	37.0
.12	51	.659	36.7
.12	58	.658	36.6
.12	78	.641	35.9
.12	135	.608	34.4
Propionic Acid			
0.12	60	1.239	57.6
.12	75	1.245	57.9
Butyric Acid			
0.15	36	1.940	73.9
.15	60	1.964	74.4
.15	88	2.035	75.6

From the above values of distillation it is evident that the time used for distillation has a remarkable effect upon k, especially with formic and butyric acids. A rapidity of distillation is, in our opinion, most conveniently used when half of 200 cc. is distilled in sixty minutes. In order to obtain identical values the same rate of distillation should always be used.

The Use of Method of Distillation in Analyzing Mixtures of Volatile Substances

The aforesaid experiences concerning the course of distillation as influenced by the concentration and the time used for distillation are facts to be noted in the quantitative analysis of volatile substances. Previous investigators have not paid attention to these facts but have generalized their method for solutions of fatty acids of 2% at most. In all analyses the differences in concentration may in most cases be passed over, but the results in such cases may be comparatively inexact. By taking the conditions of concentration into consideration it is possible to determine the volatile substances with surprising accuracy by using the method of distillation, as is evident from the determinations mentioned below.

Wiegner has suggested, in his valuable investigation in which fractional steam distillation is theoretically treated, a method to be put into use according to which the solution to be investigated, if containing two volatile fatty acids, is first half distilled; an equal quantity of water is then added to the remainder and the solution is again distilled to a semi-volume. For safety's sake this treatment is repeated for the third time. From the first and second distillations equations will be obtained by which the quantities of acids in the solution may be determined. The third equation may be used as control.

As the conditions of concentration always exercise, according to our determinations, a great influence upon the values of k, it is evident that by using this method the first distillation gives values which are different from those of the second. The third distillation can by no means be compared to the first. One of the authors[7] has previously presented a much simpler method for analyzing a solution containing two volatile acids.

Exactly half of the solution, the total quantity of acid in which is known, is distilled and the quantity of acid in the distillate is determined by titration. If the wanted quantities of acids in the solution are A and B and the value of A's semi-distillation is marked with a and that of B's semi-distillation with b, it is possible to determine the quantities of acids by means of one single distillation. The total quantity of acid may be z and the quantity of acid distilled in the semi-volume Z_1. Thus we obtain the following equations

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[7] Virtanen, *Soc. Scient. Fennica, Comm. Physico-Mathemat.*, 1, 36 (1923).

$$A + B = z$$

$$\frac{a}{100} A + \frac{b}{100} B = z_1$$

The accuracy of this method is evident from the following example.

Experiment 1.—In 200 cc. there was acetic acid corresponding to 47.4 cc. of $N/20$ acid and propionic acid corresponding to 17.6 cc. of $N/20$ acid. The whole solution thus corresponded to 65.0 cc. of $N/20$ sodium hydroxide. The distillate of 100 cc. used 27.55 cc. of $N/20$ sodium hydroxide. The value of the semi-distillation of acetic acid (A) being 36.6% and that of the propionic acid (P) 57.7%, we obtain the equations $A + P = 65.0$ and $0.366\ A + 0.577\ P = 27.55$, which give $A = 47.2$ cc. of $N/20$ acid and $P = 17.8$ cc. of $N/20$ acid. The error in the acetic acid is −0.4% and that for the propionic acid, +1.1%.

Experiment 2.—In 200 cc. there was 23.6 cc. of $N/20$ acetic acid, 13.7 cc. of $N/20$ propionic acid and 24.0 cc. of $N/20$ butyric acid. Two fractions of 50 cc. were distilled, one of which consumed 18.5 cc. and the other 15.7 cc. of $N/20$ sodium hydroxide. The values of the semi-distillation being 36.6% for acetic acid, 57.7% for propionic acid and 74.0% for butyric acid, and the values of the quarter-distillation being 17.2% for acetic acid, 30.0% for propionic acid and 43.0% for butyric acid, we find the equations $A + P + B = 61.3$, $0.172\ A + 0.3\ P + 0.43\ B = 18.5$ and $0.366\ A + 0.577\ P + 0.74\ B = 34.2$, of which $A = 23.2$ cc. of $N/20$ acid, $P = 14.4$ cc. of $N/20$ acid, and $B = 23.7$ cc. of $N/20$ acid. The error as to the acetic acid is −1.7%; propionic acid, +5.1%; and butyric acid, −1.3%.

The above experiments show that by using the method of distillation it is possible to determine with great accuracy two volatile substances in the same solution when the time of distillation and the effect of the concentrations upon the value of the semi-distillation are taken into consideration. From our determinations it is evident that the best results will be obtained when each component has a value of semi-distillation which corresponds to the total concentration of acids in the solution. Thus, if there are in the solution, for example, 70 cc. of $N/20$ acetic acid and 30 cc. of $N/20$ butyric acid, for each acid the value of semi-distillation which corresponds to the concentration of 100 cc. $N/20$ must be used.

If the solution contains, at the same time, three volatile substances, it is possible to determine them with a comparatively great accuracy as is evident from Experiment 2. If four different substances have to be determined in the same solution, the errors will be very great.

The method of distillation is applicable in general to the determination of volatile substances of which the constant of distillation is not very great. If the value of k exceeds 5, the errors become so great as to render quantitative determinations out of the question.

The volatile acids can be determined according to the method suggested above only in solutions which contain no other substances. Therefore, in analyzing the results of reactions the volatile substances must first be distilled over quantitatively by passing steam through the solution. In the case of a volatile substance which has a low constant of distillation it is advisable to add sodium chloride to the solution so as to promote the distillation (see last section). On the other hand, one must take into account that if there is present in the solution lactic acid, for instance, this also passes over to some extent with steam. In studying cultures of bacteria and similar solutions, it is most advantageous to proceed as follows.

The alcohols, aldehydes, etc., which may be present in the neutral solution are removed by evaporating to half the original volume. The solution is then rendered acid with sulfuric acid and the volatile acids are removed by a current of steam, measured quantities of distillate (200 cc. for example) being collected. If the solution contains such a substance as lactic acid, it, too, passes over after the volatile acids have been removed. The process is stopped when the last two or three distillates contain a constant small quantity of acid. In order to eliminate carbon dioxide, it is necessary to boil the first fraction under an upright reflux condenser. All of the distillates are titrated with barium hydroxide of known strength. The solutions are then united, concentrated in an evaporating dish to small volume and quantitatively transferred to a 250-cc. volumetric flask. The calculated amount of sulfuric acid to react with the barium is added and the flask is filled up to the mark with distilled water. After standing for some time to allow the barium sulfate to settle, 200 cc. of the clear liquid is taken for the analysis. If it is known in advance which acids are present in the solution it is possible to make the quantitative determination as explained above. In order to eliminate the lactic acid which may have distilled together with the others the volatile acids must be expelled quantitatively, by means of steam, from the residue left after 100 cc. has been distilled from the 200 cc. The concentration of the lactic acid is now so low that it does not distil over any more. In this way we determine the amount of volatile acids present in the residue and the calculations can be made according to the method explained above. In order to hasten the volatilization, an excess of sodium chloride must be added to the residue before steam distillation. This addition is absolutely necessary especially when formic acid is present in the solution, since it distils rather poorly from very dilute solutions.

If we do not know what volatile acids are present in the solution, then several fractions, for instance of 10 or 25 cc., must be distilled. From the constants of distillation calculated on a basis of different fractions it is usually possible to judge which acids are present in the solution. Depending on the solution and the acids present we can, of course, use other methods for the qualitative determination of the acids.

Some Constants of Different Organic Substances

In all of the determinations the above-mentioned apparatus was used. From 200 cc. either two fractions of 50 cc. or four fractions of 25 cc. were distilled. In this manner it has been possible to ascertain whether k has the same value in different fractions and, consequently, the substances to be investigated are pure. At the same time the influence of the concentration can be determined.

Organic Acids.—

Acid	Concn., N	k	Semi-dist. value, %	Acid	Concn., N	k	Semi-dist. value, %
Diethylacetic	0.018	4.57	95.4	*o*-Toluic	0.010	0.508	29.7
Chloro-acetic	.036	0.047	3.2	*m*-Toluic	.013	.420	25.2
Phenylacetic	.017	.070	4.8	*p*-Toluic	.009	.378	23.1
Pyruvic	.033	.074	5.0	Anisic	.006	.050	3.4

Acid	Concn., N	k	Semi-dist. value, %	Acid	Concn., N	k	Semi-dist. value, %
α-Crotonic	.012	.760	41.0	Cinnamic	.010	.102	7.4
Benzoic	.024	.270	17.1	*o*-Aminobenzoic	.020	.019	1.3
Salicylic	.020	.088	5.9				

Meta and *p*-aminobenzoic acids and *o*-, *m*- and *p*-nitrobenzoic acids are not volatile with steam. Levulinic, glycolic and lactic acids are distillable in small quantities but have no constants of distillation. The quantity of distilled acid does not increase in proportion to the concentration. This proves that the said acids are not, in the proper sense of the word, volatile acids. It is possible that anhydrides which are volatile are formed in the distillation.

According as the carbonic chain is prolonged and the solubility diminished, k increases in homologous series notwithstanding the rise of the boiling point. In the aromatic series the *o*-compounds distil best, then the meta. The *p*-compounds do not distil as well as the others.

Amines.—Many amines are so easily volatile as to be completely distilled by the removal of a half-volume. In these cases out of 200 cc. only 10 cc. was distilled and k was determined accordingly. In these cases an exact value for the constant could not be obtained. The amines were determined by titration with $N/10$ sulfuric acid with Congo Red as indicator.

Amine	Ammonia	Methyl	Ethyl	Propyl	Butyl	Diethyl
B. p., °C.	−34	−6	+19	+50	+77	+56
Concn., N	0.02	0.02	0.03	0.02	0.02	0.02
k, approx.	13	11	20	30	40	43

An increase of one carbon atom in the homologous series of monovalent aliphatic amines raises the value of k by about 10 units.

Amine	Ethylene di-	Aniline	Methylaniline	Benzyl	Benzyl	α-Naphthyl
Concn., N	0.03	0.05	0.03	0.02	0.20	0.01
k	.02	5.51	16	3.27	3.25	1.05
Semi-dist., %	1.4	98.6	...	89.6	89.5	51.7

β-Naphthylamine evaporates copiously but solidifies in the condenser. The value of k could not be determined. In some of the experiments aniline was determined by titration with a solution of $N/10$ sodium nitrite (0°); in other experiments by determining nitrogen by the Kjeldahl method. Methylamine also was determined by the latter method.

Phenols.—

Compound	Phenol	*p*-Chloro-	*p*-Nitro-	*m*-Nitro-	Thymol
Concn., N	0.10	0.01	0.07	0.06	0.06
k	1.94	1.30	.005	.01	12
Semi-dist., %	74.1	59.5	.35	.85	...

Phenol, *p*-chlorophenol and thymol were determined by titration with a solution of bromine. The nitrophenols could be titrated with $N/20$ sodium hydroxide by using phenolphthalein as indicator.

It is evident from the values given above that chlorine in replacing hydrogen in the benzene ring does not exert a noteworthy influence upon the volatility. On the contrary the nitro-group diminishes the volatility enormously. Of the nitro compounds the *m*-derivative is distilled better than the para. The influence of the position of the substituent has been proved to be the same in the cases of other substances.

Aldehydes.—The aldehydes were determined by titration with potassium bisulfite and a solution of iodine.

Compound	Formaldehyde	Acetaldehyde	Benzaldehyde	Anisaldehyde
Concn., *N*	0.03	0.01	0.01	0.01
k	2.6	Above 40	18	3.1
Semi-dist., %	83.0	...	...	88.5

Alcohols.—

Alcohol	Methyl	Ethyl
Concn., % by weight	0.05	0.10
k	8.9	12.5

Methyl and ethyl alcohols were determined according to Kuriloff by oxidation with a solution of sulfuric acid and bichromate of potash, which oxidizes ethyl alcohol quantitatively to acetic acid and methyl alcohol to carbon dioxide. The solution to be investigated was heated for three hours at 100° together with an oxidizing solution in a closed pressure flask. The quantity of alcohol was calculated according to the quantity of bichromate used. The precision of the method is 1%.

From these investigations the conclusion is reached that volatility with steam of water-soluble substances depends to a large extent upon the degree of hydration of these substances in solution. The lower members of an homologous series (for example formic acid in the series of fatty acids) are distilled much less easily than the higher members, although from the boiling points the reverse would be expected to be true. Since the value of *k* in an homologous series shows a regular increment with each added carbon atom (0.6 for fatty acids, 10 for amines), this evidently depends upon the fact that the degree of hydration regularly decreases as the carbon chain is lengthened. This is verified by the diminution in solubility. It is evident then that the effect of neutral salts upon the steam distillation is one of diminution of hydration of the volatile substance. The subject is treated more fully in the following section.

The Effect of Salts upon the Volatility of Substances with Steam

Neutral salts have in general a stimulating effect upon the constant of distillation, the influence of each salt having a different force. The investigations previously made by Virtanen show that the effect of the anions is most important, while that of the cations is much weaker. The influence of the different salts upon the distillation of acetic acid in dilute solution is shown by the curves in Fig. 2. In distilling acetic acid in a saturated sodium chloride solution a value of $k = 2.3$ is obtained and, consequently, in distilling the semi-volume of the solution a quantity of 80% is distilled (of a pure water solution 36.6%). In the aforesaid investigation it has already been shown that the influence of salts upon the distillation of different acids is different. Fig. 3 indicates the distillation of different acids from a sodium chloride solution. The curves of formic acid and of acetic acid (both entirely soluble in water) are fairly straight lines, while the curves of less soluble acids the solubilities of which are appreciably diminished by the salts, rise more or less.

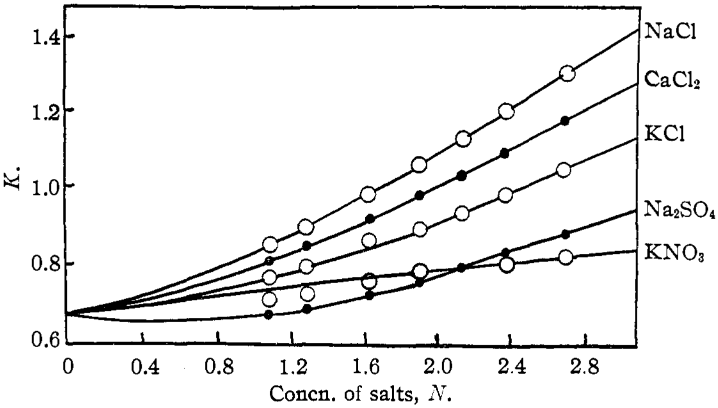

Fig. 2.—The curves indicate the influence of different salts upon the distillation of acetic acid.

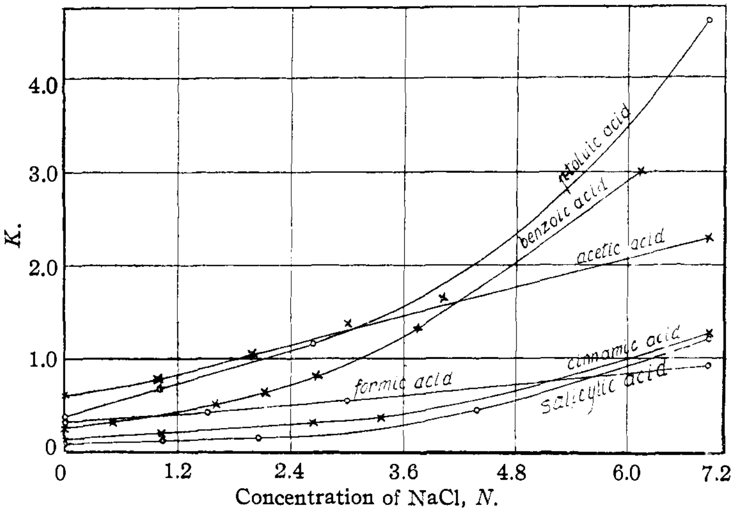

Fig. 3.—Influence of NaCl upon the distillation of some organic acids.

The question as to the real influence of the salts upon the distillation with steam has already been treated by Virtanen in a publication mentioned above. The rise in boiling point produced by the salt does not considerably alter the distillation. This is evident from the fact that several substances which are apt to raise the boiling point as much and even more than sodium chloride do not in a noteworthy degree raise the value of *k*. For example, the sodium acetate facilitates very little the distillation of acetic acid and glycerin does not in a noteworthy degree change the value of *k*, not even in a solution of 25%.

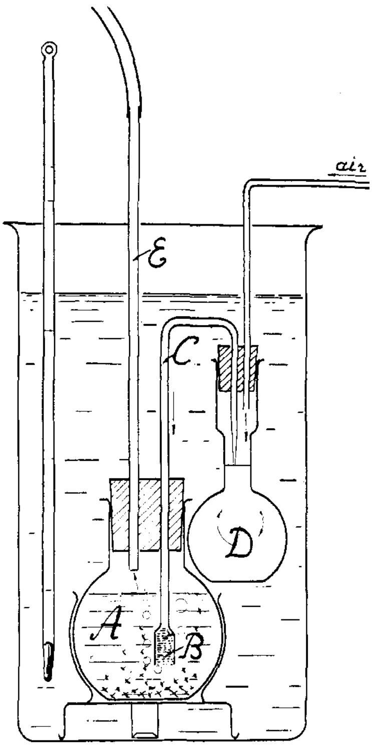

Fig. 4.

The volume mechanically taken up by the salts and the diminution of the quantity of water due thereto are not sufficient to explain the great influence of numerous salts. In 200 cc. of a solution of 1 *N* sodium chloride there are about 196.3 cc. of water at 20°. This small change in the volume of water cannot have much influence upon the value of *k*.

The only plausible explanation as to the influence of salts is that the salts in being hydrated or, in other words, in uniting themselves more or less firmly with the water molecules, diminish the hydration of the organic substances so that these substances detach themselves from the water molecules. Should this be the case, it is probable that the influence of the salts upon the solubility of volatile substances is, at least to some extent, to be compared to the influence of these salts in the distillation by steam. This appears, in general, to be the case, though unexpected exceptions are to be found, through the parallel determinations of the influence of some salts upon the solubility and upon the distillation of benzoic acid and salicylic acid. Fig. 5 shows the influence of the salts upon the volatility and upon the solubility of benzoic acid.

The distillation was determined so that out of 200 cc. one fraction of 25 cc. was always distilled. The determinations of solubility were made by using the apparatus shown in Fig. 4. The whole apparatus is submerged in boiling water (100°). The substance to be examined is dissolved in bottle A. From this the saturated solution is blown through the glass filter B and pipe C into the 25cc. volumetric flask (D), from which the solution can be taken for titration. Stirring is effected by means of air flowing in the opposite direction, being forewarmed to 100° in the flask D. The pipe E leads to the vertical condenser, which prevents the water evaporating from the solution in the bottle A.

Of the salts investigated, sodium chloride most diminishes the solubility of benzoic acid. The influence of this salt upon the distillation of benzoic acid is also most effective. Sodium nitrate diminishes the solubility of benzoic acid to a less extent and correspondingly its effect upon the constant of distillation is also small. Sodium sulfate decreases the solubility more than sodium nitrate. In a weaker concentration, up to a normality of 2.5, sodium sulfate diminishes, strangely enough, the distillation of benzoic acid as well as that of other acids. To what this is due is, at present, inexplicable. Fig. 5 shows graphically the effect of sodium chloride, sodium sulfate and sodium nitrate upon the solubility and distillation of benzoic acid.

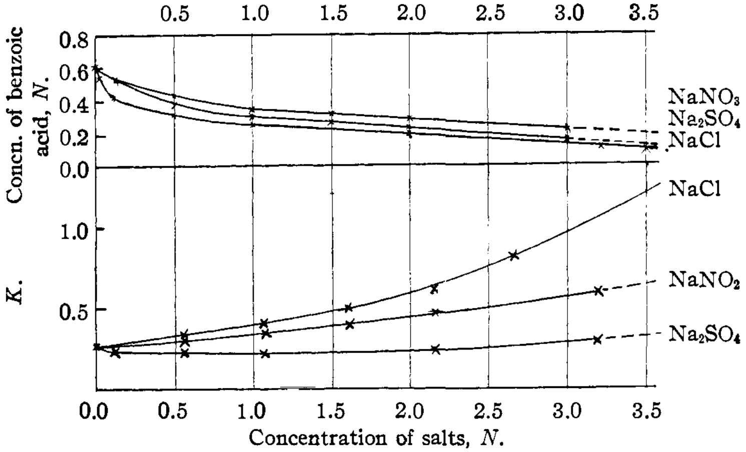

Fig. 5.—The curves in the upper figure indicate graphically the solubility of benzoic acid in NaCl, $NaNO_3$ and Na_2SO_4 solutions of different concentrations. The lower figure shows correspondingly the effect of the same salts upon the values of the distillation constant, *k*.

The hydration of acids has been shown to diminish at the same time that the degree of dissociation diminishes,[8] and it is to be concluded, accordingly, that the ions hydrate themselves. Since in the series of fatty acids the dissociation of acids diminishes at the same time that the molecular weight augments, it might be supposed that the weaker distillation of the first fatty acids would be due to their greater ionization in the diluted solutions. This opinion is, however, contradicted by the observation that if in the diluted solutions of acetic and formic acids alkaline salts of the same acids are added while the dissociation of acids diminishes to a minimum, the distillation of acids augments much less than through

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[8] Kendall, Booge and Andrews, This Journal, **39**, 2303 (1917).

many other salts. On the contrary, the constant of the distillation of formic acid diminishes somewhat. As the great reduction in the dissociation of acetic and formic acids by no means essentially affects the distillation of these acids by steam, it is evident that it is chiefly through the hydration of the non-dissociated molecules of acids that the acids attach themselves to water.

The tendency of the electrolytes to unite molecules of water to themselves causes changes in the solutions which occur in many different ways. Especially have those changes been investigated which are caused by the neutral salts in the dissolution of the different substances.[9]

Wiegner, Magasanik and Virtanen[10] have investigated the influence of salts upon the adsorption of fatty acid by bone-charcoal and have found that the absorption becomes more effective, for example, through the influence of sodium chloride. We can in general find a great analogy in the influence of salts upon the distillation and adsorption of fatty acids. This is quite natural, for the detachment of acids from water through the influence of salts is the reason why acids escape more easily in steam and why they attach themselves more easily to adsorbent substances.

We will later on enlarge upon the question as to the distillation by steam of substances soluble in water and on the influence of salts.

Summary

The steam distillation of substances soluble in water and passing over with steam gives a possibility of determining whether the substance to be examined is pure or contains other substances belonging to the same group, for instance homologs. As a quantitative means of expression for the distillation of a substance with steam, either the distillation constant, k, or half-distillation, or one-fourth distillation value, respectively, can be employed.

By means of steam distillation volatile substances can be determined according to a very simple method. This mode of determination has been developed very accurately in this study. If there are in the same solution two substances belonging to the same group (for example, organic acids), they can be determined by means of a single fraction with considerable accuracy. If there are three substances, then the determination may be made by means of two fractions. The time of distillation and the variations of concentration in solutions have an appreciable effect on the course of distillation. If the volatility of the substance is so great that the value of the distillation constant k is above 5, the steam distillation cannot easily be used for the quantitative determination of the substance.

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[9] Geffken, *Z. physik. Chem.*, **49**, 257 (1904); Euler, *ibid.*, **49**, 303 (1909); Rothmund, *ibid.*, **40**, 611 (1902).

[10] Wiegner, Magasanik and Virtanen, *Kolloid-Z.*, **28**, 51 (1921).

Distillation constants have been determined for many organic substances belonging to different groups. In homologous series the value of *k* increases with the lengthening of the carbon chain. This is obviously due to the decline in hydration as the molecular weight increases.

The effect of salts upon the steam distillation is powerful. Among the salts studied sodium chloride has in the greatest degree raised the value of *k*. The influence of anions is obviously much more intense than that of cations.

The effect of the salts upon the distillation of different substances is variable (Fig. 3). The curves indicating the dependency of *k* on salt concentration rise rather rectilinearly for those substances which dissolve indefinitely in salt solutions, while for those substances which do not dissolve indefinitely in water and which in part separate from water through the effect of salts, *k* rises with the increase in salt concentration so powerfully that the curve arches strongly upward.

The promoting effect of salts upon distillation is obviously due to the fact that they diminish the hydration of the substance, especially of undissociated molecules. The promoting effect of salts upon distillation can to a great extent be turned to advantage in distinguishing volatile from non-volatile compounds.

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A NEW EQUATION OF STATE FOR FLUIDS. III. THE NORMAL DENSITIES AND THE COMPRESSIBILITIES OF SEVERAL GASES AT 0°

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The compressibility of gases at 0° and at pressures up to one atmosphere is of great importance in the determination of the atomic weights of the inert gases from density measurements and for the calculation of the normal densities of those gases whose molecular weights can be determined by chemical analysis. The experimental evaluation of the ratio of the pressure–volume product at 0° and at one atmosphere, p_1V_1, to the product at zero pressure, p_0V_0, is difficult, and it is believed that this ratio can be obtained for any gas for which there are extensive p–V–T data with as great an accuracy from the equation of state.

The relations between these quantities are given by the equations

$$p_0V_0/p_1V_1 = 1 + \lambda \tag{1}$$

$$p_0V_0 = (m/M)\, RT_0 \tag{2}$$

$$d_n = \frac{m}{V_1} = \frac{M(1+\lambda)}{RT_0} \tag{3}$$

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