# ON TERNARY MIXTURES. III.

By Wilder D. Bancroft.

IN addition to the results given in Tables XIX.–XXXI.[1], Pfeiffer made a few measurements on amylalcohol, monochlor-, dichlor-, and trichloracetic ester in the presence of alcohol and water. The solubility of amylalcohol in water is given by Roscoe and Schorlemmer as two parts in a hundred, and I have used this value. I could find no data whatsoever in regard to the chloracetic esters, so I have calculated the values on the false assumption that they are nonmiscible with water. The effect of this error is seen very markedly in the case of the monochloraceticester, which is undoubtedly the most soluble of the three. I give these tables in spite of the known inaccuracy, because the absolute values of the constants are, for the time being, of little value, whereas it is essential to show that the same general law covers all substances and that the substitution of chlorine for hydrogen does not affect the action of the Mass Law. The coincidence of the three chloraceticesters having the same exponential factor is probably only superficial, as the correction for the solubilities would alter the exponential factor somewhat.

Table XXXII.

$y = 3$ c.c. Amylalcohol; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x(y = 0.02\,x)^{0.4}/z^{1.4} = C$; $\log C = 0.100$. Temp. 9.1°.

| | $x$. | | |
|---|---|---|---|
| $z$. | **Calc.** | **Found.** | **log $C$.** |
| 3 | 3.81 | 3.21 | — |
| 6 | 10.26 | 10.35 | 0.104 |
| 9 | 18.53 | 18.34 | 0.095 |
| 12 | 28.45 | 27.47 | 0.085 |
| 15 | 40.85 | 41.25 | 0.104 |
| | | | 0.097 |

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[1] Tables XXIII.–XXXI. are given at the close of this article.

## Table XXXI.I.

$y = 3$ c.c. Amylalcohol ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.
Formula $x\,(y - 0.02\,x)^{0.4}/z^{1.4} = C$ ; $\log C = 0.112$. Temp. 19.2°.

| | *x*. | | |
|---|---|---|---|
| *z*. | Calc. | Found. | log *C*. |
| 3 | 3.93 | 3.50 | — |
| 6 | 10.55 | 10.80 | 0.122 |
| 9 | 19.10 | 19.10 | 0.112 |
| 12 | 30.05 | 29.15 | 0.099 |
| 15 | 42.30 | 43.15 | 0.121 |
| | | | 0.114 |

## Table XXXIV.

$y = 3$ c.c. Monochloraceticester ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.
Formula $xy^{0.43}/z^{1.43} = C$ ; $\log C = \bar{1}.700$.

| | *x*. | | |
|---|---|---|---|
| *z*. | Calc. | Found. | log *C*. |
| 3 | 1.54 | 1.32 | $\bar{1}.644$ |
| 6 | 4.05 | 4.01 | $\bar{1}.695$ |
| 9 | 7.23 | 7.30 | $\bar{1}.705$ |
| 12 | 10.91 | 10.78 | $\bar{1}.695$ |
| 15 | 15.04 | 16.16 | $\bar{1}.731$ |
| 18 | 19.50 | 22.16 | $\bar{1}.756$ |
| 21 | 24.33 | 28.74 | $\bar{1}.772$ |
| | | | $\bar{1}.714$ |

## Table XXXV.

$y = 3$ c.c. Dichloraceticester ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.
Formula $xy^{0.43}/z^{1.43} = C$ ; $\log C = \bar{1}.479$.

| | *x*. | | |
|---|---|---|---|
| *z*. | Calc. | Found. | log *C*. |
| 3 | 0.90 | 0.90 | $\bar{1}.477$ |
| 6 | 2.44 | 2.45 | $\bar{1}.481$ |
| 9 | 4.35 | 4.33 | $\bar{1}.477$ |
| 12 | 6.54 | 6.60 | $\bar{1}.482$ |
| 15 | 9.04 | 9.20 | $\bar{1}.487$ |
| | | | $\bar{1}.481$ |

## TABLE XXXVI.

$y = 3$ c.c. Trichloraceticester; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $xy^{0.43}/z^{1.43} = C$; $\log C = \bar{1}.336$.

| | $x$. | | |
|---|---|---|---|
| $z$. | Calc. | Found. | log $C$. |
| 3 | 0.65 | 0.65 | $\bar{1}.336$ |
| 6 | 1.76 | 1.80 | $\bar{1}.347$ |
| 9 | 3.13 | 3.02 | $\bar{1}.321$ |
| 12 | 4.72 | 4.50 | $\bar{1}.315$ |
| 15 | 6.50 | 6.50 | $\bar{1}.336$ |
| | | | $\bar{1}.331$ |

Tables XIX.-XXXI. furnish a striking confirmation of the way in which the Mass Law applies to this class of phenomena; while some of the results are not as satisfactory, perhaps, as I should like, there are some, notably those with propylbutyrate, where the agreement between the observed and the calculated values is something marvelous, though it is unfortunate that the solubility of propylbutyrate in water has never been determined experimentally.

As it might be thought a mere assumption that the first measurements in several series were determinations of another equilibrium, namely, of a saturated solution from which water or ester precipitated water, I have made a few measurements with the few esters I had on hand. The object of these measurements was to show that the change from one equilibrium to another did come at the point shown by Pfeiffer's results, and to make sure that the variations in Pfeiffer's data were due to experimental error. On this account I have made no measurements on the end curves, where water and where ester are part solvents, and in the case of ethylisovalerate I have measured only one series. The results are given in Tables XXXVII.-XXXIX.

## TABLE XXXVII.

$x$ = c.c. $H_2O$; $y$ = c.c. Ethylisovalerate; 5 c.c. Alcohol. Temp. 20°.

Formula $(x - 0.004\,y)^n\,(y - 0.002\,x)/z^{n+1} = C$; $n = 2.45$; $\log C = \bar{1}.149$.

| Water. | | Et. Val. | | |
|---|---|---|---|---|
| **Calc.** | **Found.** | **Calc.** | **Found.** | **log $C$.** |
| 9.98 | 10.00 | 0.15 | 0.15 | $\bar{1}.152$ |
| 8.05 | 8.00 | 0.24 | 0.23 | $\bar{1}.142$ |
| 6.01 | 6.00 | 0.46 | 0.46 | $\bar{1}.147$ |
| 4.99 | 5.00 | 0.72 | 0.72 | $\bar{1}.152$ |
| 4.00 | 4.00 | 1.23 | 1.23 | $\bar{1}.149$ |
| | | | | $\bar{1}.148$ |

## TABLE XXXVIII.

$x$ = c.c. $H_2O$; $y$ = c.c. Ethylbutyrate; 5 c.c. Alcohol. Temp. 20°.

Formula $(x - 0.005\,y)^{n_1}\,(y - 0.008\,x)/z^{n_1+1} = C_1$; $n_1 = 2.44$; $\log C_1 = \bar{1}.449$.

| $x$. | | $y$. | | |
|---|---|---|---|---|
| **Calc.** | **Found.** | **Calc.** | **Found.** | **log $C_1$.** |
| 9.99 | 10.00 | 0.34 | 0.34 | $\bar{1}.450$ |
| 8.01 | 8.00 | 0.51 | 0.51 | $\bar{1}.447$ |
| 5.97 | 6.00 | 0.95 | 0.96 | $\bar{1}.453$ |
| 5.01 | 5.00 | 1.45 | 1.44 | $\bar{1}.447$ |
| 3.99 | 4.00 | 2.46 | 2.47 | $\bar{1}.451$ |
| | | | | $\bar{1}.449$ |

Formula $(x - 0.005\,y)^{n_2}.(y - 0.008\,x)/z^{n_2+1} = C_2$; $n_2 = 1.20$; $\log C_2 = \bar{1}.623$.

| | | | | **log $C_2$.** |
|---|---|---|---|---|
| 2.96 | 2.96 | 3.99 | 4.00 | $\bar{1}.624$ |
| 2.46 | 2.48 | 4.94 | 5.00 | $\bar{1}.628$ |
| 2.12 | 2.10 | 6.07 | 6.00 | $\bar{1}.618$ |
| | | | | $\bar{1}.623$ |

## TABLE XXXIX.

$x$ = c.c. Water; $y$ = c.c. Isoamylacetate; 5 c.c. Alcohol. Temp. 20°.

Formula $(x - 0.012y)^{n_1}(y - 0.002x)/z^{n_1+1} = C_1$; $n_1 = 3.50$; $\log C_1 = \bar{1}.414$.

| $x$. | | $y$. | | $\log C_1$. |
|---|---|---|---|---|
| Calc. | Found. | Calc. | Found. | |
| 7.00 | 7.00 | 0.41 | 0.41 | $\bar{1}.414$ |
| 6.00 | 6.00 | 0.70 | 0.70 | $\bar{1}.414$ |
| 5.01 | 5.00 | 1.32 | 1.31 | $\bar{1}.411$ |
| | | | | $\bar{1}.413$ |

Formula $(x - 0.012y)^{n_2}(y - 0.002x)/z^{n_2+1} = C_2$; $n_2 = 1.50$; $\log C_2 = \bar{1}.559$.

| | | | | $\log C_2$. |
|---|---|---|---|---|
| 3.62 | 3.61 | 3.00 | 3.00 | $\bar{1}.558$ |
| 3.00 | 3.01 | 3.99 | 4.00 | $\bar{1}.560$ |
| 2.60 | 2.60 | 5.00 | 5.00 | $\bar{1}.559$ |
| | | | | $\bar{1}.559$ |

Although Pfeiffer does not say so, his amylacetate and ethylvalerate are unquestionably iso- and not the normal compounds. We can now take up the results given in Tables XXXVII.–XXXIX. and see how satisfactorily they fulfil their object. Ethylbutyrate and amylacetate show the change from one equilibrium to the other at the same point that Pfeiffer found. The ethylbutyrate and ethylisovalerate mixtures are perfectly regular at concentrations beyond those used by Pfeiffer, and the isoamylacetate is normal throughout both in Pfeiffer's work and in mine, so that the variations in Tables XXIX.–XXXI. are due to experimental error. The agreement in results between the two sets is shown in Table XL., where I give in the first column the value of the exponential factor $n+1$ from the formula

$$(x - s_1 y)(y - s_2 x)^n / z^{n+1} = C,$$

and in the second column the values for the simplified integration constant log $K$.

### Table XL.

| Ester. | | $n+1$. | log $K$. |
|---|---|---|---|
| Ethylisovalerate | Pfeiffer | 1.40 | $\bar{1}.773$ |
| Ethylisovalerate | W. D. B. | 1.41 | $\bar{1}.754$ |
| Ethylbutyrate | Pfeiffer | 1.41 | $\bar{1}.847$ |
| Ethylbutyrate | W. D. B. | 1.41 | $\bar{1}.840$ |
| Isoamylacetate | Pfeiffer | 1.294 | $\bar{1}.893$ |
| Isoamylacetate | W. D. B. | 1.286 | $\bar{1}.870$ |

As will be seen, the values of $n+1$ are identical, the values for log $K$, though very close, are not quite the same. This may be due to inaccuracies in the work, but I am more inclined to attribute it to differences in temperature. It is not known at what temperature Pfeiffer worked, and it would take only a slight difference to account for the variation. In Table XLI. I have tabulated the $n+1$ values from Pfeiffer's results, together with log $C$ and log $K$.

### Table XLI.

| Ester. | $n+1$. | log $C$. | log $K$. |
|---|---|---|---|
| Methylisovalerate | 1.37 | $\bar{1}.807$ | $\bar{1}.859$ |
| Ethylisovalerate | 1.40 | $\bar{1}.682$ | $\bar{1}.773$ |
| Ethylisovalerate[1] | 1.41 | $\bar{1}.653$ | $\bar{1}.754$ |
| Methylbutyrate | 1.52 | $\bar{1}.888$ | $\bar{1}.926$ |
| Ethylbutyrate | 1.41 | $\bar{1}.785$ | $\bar{1}.847$ |
| Ethylbutyrate[1] | 1.41 | $\bar{1}.774$ | $\bar{1}.840$ |
| Propylbutyrate | 1.378 | $\bar{1}.651$ | $\bar{1}.747$ |
| Ethylpropionate | 1.39 | $\bar{1}.931$ | $\bar{1}.878$ |
| Propylpropionate | 1.45 | $\bar{1}.733$ | $\bar{1}.816$ |
| Ethylacetate[1] | 1.555 | — | — |
| Propylacetate | 1.23 | 0.166 | 0.135 |
| Butylacetate | 1.30 | $\bar{1}.912$ | $\bar{1}.932$ |
| Isoamylacetate | 1.294 | $\bar{1}.861$ | $\bar{1}.893$ |
| Isoamylacetate[1] | 1.286 | $\bar{1}.832$ | $\bar{1}.870$ |
| Propylformiate | 1.38 | $\bar{1}.967$ | $\bar{1}.976$ |
| Butylformiate | 1.333 | 0.057 | 0.043 |
| Isoamylformiate | 1.35 | $\bar{1}.808$ | $\bar{1}.858$ |

[1] My own measurements.

The first thing that strikes one about this table is the way in which so many of the $n+1$ values approximate to 1.40. Why this should be so is entirely unknown. In the log $K$ values we notice that, for the same acid, increasing the carbon atoms in the alcohol radical diminishes the constant. There is only one exception to this, butylformiate, and here the possible error is very large. It looks also as if the constants might be additive, being made up of one factor for the alcohol and another for the acid radical; but the experimental data are too insufficient to justify this hypothesis. It is very much to be hoped that some one will make a careful series of experiments to settle this point.

Formula II. was deduced for the case when the reacting weights of the substances in equilibrium are not functions of the concentration. The measurements of Pfeiffer and myself show that, with the possible exception of the chloroform-water-acetone series, this condition has been satisfied in all the cases studied, though the experiments extended over a wide range of concentrations. This is in flat contradiction with the determinations of the reacting weights by the boiling-point and freezing-point methods. These methods give accurate results only for very dilute solutions, and even then only for certain solutes in certain solvents. To explain the variations, we are forced to assume "double molecules" in some cases, polymerization with increasing concentration in practically all cases, and "variations from the gas laws." I have brought together a large series of measurements in which there is no sign of any of these things. I see only two possible hypotheses to account for this discrepancy: first, to enunciate a new and most interesting law, to wit, presence of a third substance prevents "polymerization" and "variations from the gas laws"; second, the formula for the change of vapor pressure with the concentration is incorrect. The first hypothesis seems to me out of the question, and there remains only the second. It is a bold thing to question so universally accepted a formula, but I feel convinced that it is not right, and that equal reacting weights of different substances do not produce the same change of vapor pressure. I think that the mistake in the past lay in assuming that the work done in compressing a dissolved substance from the volume $V_1$ to the volume $V_2$ by means of a semipermeable piston is equal to $\int p\,dv$ between those limits, irrespective of the nature of solute and solvent. I have already collected some experimental evidence in favor of this view, and I hope before long to be able to establish my point.

The facts brought out in this paper throw light on a research by Abegg[1] carried out under the direction of Arrhenius. Abegg let alcohol diffuse into a salt solution and found, to his surprise, that the salt, instead of remaining equally divided throughout the liquid, diffused somewhat into the part not yet reached by the alcohol. He concludes that this extraordinary behavior can only be accounted for on the assumption that alcohol increases the osmotic pressure of a dissolved salt. What happens is very simple. When the alcohol has diffused only a little way, one may consider the solution as composed of two parts, one containing a large amount of alcohol, the other very little. The dissolved substance, being in this case less soluble in the first layer than in the second, diffuses into the second only to go back again as the alcohol becomes more evenly divided throughout the liquid. Except that the part containing much alcohol and little water merges insensibly into the part containing much water and little alcohol, and is not in equilibrium with it, the case does not differ from two layers formed by ether and water, where it is well known that the concentration of a third substance is not the same in the two layers. The effect of the alcohol is not, as Abegg assumes, to increase the osmotic pressure of the solute, but to diminish its solubility in that portion of the liquid. If, instead of taking salts which were only slightly soluble in alcohol, Abegg had let water diffuse into water containing in solution some substance very soluble in alcohol, slightly soluble in water, he would have observed the opposite effect, and the dissolved substance would have diffused partially into the layer rich in alcohol.

Another line of reasoning which is not quite defensible is that taken by Wildermann,[2] in his paper, "Ueber cyclische Gleichgewichte." His train of thought is something as follows: Suppose he has a system of three phases, bromine, a solution of bromine

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[1] Zeitschr. f. ph. Chem., XI. 248. 1893.

[2] Ibid., XI. 407.

in water, and the vapor of bromine and water, it being assumed that the amount of water which dissolves in the bromine can be neglected. He adds to the aqueous solution some substance which does not dissolve in bromine perceptibly, such as potassium bromide or sulphuric acid. The three phases, when in equilibrium, have still the same concentration of liquid bromine and of bromine vapor. Therefore the solubility of the bromine in the liquid cannot have changed. It does change experimentally; therefore, in order to reconcile the reasoning with the facts, he concludes that the apparent change, decrease or increase, is due to chemical action, and that the amount of bromine dissolved as such remains unchanged. This may be true in the special examples studied by Wildermann.[1] That I cannot say; but it is not true that it is a necessary theoretical conclusion, and there is no proof that it is correct in any case. If, instead of adding potassium bromide, we add to the water some liquid in which bromine is readily soluble, the amount of bromine dissolved will increase without there being any reason to assume chemical action in order to account for it. Bromine is not a good substance to consider, because there are so few liquids soluble in water in which it dissolves without decomposition, and also because we cannot ignore the solubility of the added substance in it. Let us rather treat the case when we have iodine instead of bromine. Suppose we have the system, solid iodine, a solution of iodine in water, and vapor of iodine and water; we add alcohol to the solution. The concentrations of the solid iodine and the iodine vapor will remain practically unchanged; therefore the solubility of iodine in the water and alcohol should remain unchanged according to Wildermann. As a matter of fact it does change, and I do not see how this variation can be attributed to chemical action unless all solution is defined as chemical action, which begs the question, though very possibly true. There may be a radical difference between the action of the alcohol and the action of potassium iodide; but that difference has not been shown. As far as I can see, Wildermann's conclusions require that adding alcohol to a saturated salt solution should have no effect on the concentration of the salt, because the equi-

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[1] See Jakovkin, Zeitschr. f. ph. Chem., XIII. 539. 1894.

librium between the solid salt and its own vapor would remain unchanged.

Early in this paper I proposed the word "solute" as something distinct from "solvent," and it is necessary for me to justify that distinction. The usual way of looking at binary solutions is to consider them as mixtures, and that it is purely arbitrary which of the two substances we consider as solvent and which as dissolved substance. The following citations will show what the prevailing opinion at the present moment is.

Lothar Meyer, after pointing out that in alcohol-water mixtures it depends on the nature of the semipermeable membrane which substance exerts the osmotic pressure, says:[1] "Mit der Beschaffenheit der Membran tauschen beide Stoffe die Rollen; es ist daher eine Willkür wenn wir den einen als gelöst, den anderen als das Lösungsmittel bezeichnen." Ostwald is consistent to the bitter end, saying:[2] "Lösungsmittel ist derjenige Stoff des Gemenges, welcher bei dem betrachteten Vorgange ausgeschieden wird." This view is heroically logical, for it means that when a salt crystallizes from a saturated solution, the mother liquor consists of water dissolved in the salt.

Nernst's position on the subject is doubtful. He puts solutions under the head of physical mixtures and remarks:[3] "Die verdünnten Lösungen sind Gemische welche eine Komponente in grossem Ueberschuss zu den übrigen enthalten; erstere bezeichnen wir in diesem Falle als das Lösungsmittel, letztere als gelöste Stoffe." On the other hand, he draws a distinction between freezing out the solvent and crystallizing out the solute.[4] He does not accept the view that the salt is the solvent in a saturated solution; but he does not suggest in any way that there may be different laws for the solute and the solvent. Planck is very clear and precise; he defines dilute solutions in almost the same words as Nernst, and goes on:[5] "Bei einer beliebigen Lösung kann jeder Bestandtheil derselben als Lösungsmittel oder als gelöster Stoff aufgefasst werden." This means that in a mixture of two liquids

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[1] Zeitschr. f. ph. Chem., V. 24. 1890.

[2] Ibid., XII. 394. 1893.

[3] Theoretische Chemie, p. 115.

[4] Ibid., p. 393.

[5] Grundriss der Thermochemie, p. 131.

either may be considered as the dissolved substance, and will therefore decrease the partial vapor pressure of the other, and this decrease of the vapor pressure will be greater the greater the concentration of the dissolved substance. This is not in agreement with the facts. A saturated solution of ether in water has the same partial vapor pressures as a solution of water in ether saturated at the same temperature.[1] For the moment we will consider ether as the dissolved substance. In the first solution, the volume concentration is roughly 10 per cent; in the second, about 99 per cent at 20°; and yet this enormous change of concentration has no effect on the partial vapor pressures. The figures are still more remarkable if we consider solutions of chloroform in water and water in chloroform, when one of the components is present in infinitesimal quantities. We must assume one of two things: either that our present formula for the change of the vapor pressure with the concentration is all wrong, since it does not admit of the vapor pressure of one of the components passing through a minimum; or that there is a difference between solvent and solute, and that each has its own law expressing the change of its vapor pressure with the concentration. This time I prefer the second assumption, with all that it implies. The equations of van 't Hoff and Raoult are the rough statements of the laws for the solvent. The corresponding expressions for the solute have not yet been worked out. The distinction between solvent and solute is very clear in solid solutions of metals in metals. Starting from either of two pure metals a depression of the freezing point is noted when the other is added, the two curves thus formed meeting at the melting point of the eutectic alloy. Here there can be no question that along one curve the first metal is solvent, while on the other it plays the role of solute. In the case of two partially miscible liquids there is also no difficulty in determining which is solvent and which solute. When ether and water are shaken together, the upper layer contains water as dissolved substance, the lower ether. With completely miscible liquids having a maximum (or minimum) vapor pressure at some concentration, such as propylalcohol and water (formic acid and water), it is probable

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[1] Wied. Ann., XIV. 219, 1881; Ostwald, Lehrbuch, I. 644.

that the change of solvent occurs at the concentration corresponding to the maximum (or minimum) vapor pressure. With such things as ethylalcohol and water, which are infinitely miscible and which show no maximum or minimum vapor pressure, it is impossible at present to say at what concentration alcohol ceases to be the solvent and water assumes that duty. As soon as we have worked out the relation between the concentrations in the solution and in the vapor, I feel certain that we shall find that it requires two curves to express the relation, and not one. The intersection of these curves will be the point where the solvent changes. I look upon my own results with ternary mixtures as very significant in this respect, the change from one curve to another coming at the point where the precipitate or the solvent changed. It is interesting to note that at the point, for instance, where an excess of one of the partially miscible liquids first has no effect, the solubility curve of the dissolved substance has a "break." The possibility of such a case has always been denied except by the upholders of the "hydrate theory."

The effect of temperature on the various equilibria will form the subject of a special paper, and I shall reserve for it the discussion of changes of temperature coefficient at the intersections of two curves, one or two very striking instances of which I have come upon incidentally in my work so far. I hope also to be able to present a paper on equilibrium in two liquid layers, a subject which is of especial interest because the theoretical treatment based on the experimental work in this paper gives results which are not in accordance with the assumptions on which Nernst bases his Distribution Law. Besides, there is the application of the Mass Law to the case where one or more of the components is solid, and to the instances where there is an increase instead of a decrease of solubility.

The results of this paper may be summarized briefly as follows:

1. The equilibria between two partially miscible liquids and a consolute liquid follow the Mass Law.

2. There are four sets of equilibria corresponding to four different series of solutions.

3. If the two liquids are practically non-miscible, there are only two sets of equilibria.

4. The reacting weights of the liquids studied were not functions of the concentration, — possibly with one exception.

5. There is a fundamental difference between the solute and the solvent.

6. The solubility curve of a substance in a varying mixture of two liquids at constant temperature has a break.

### Table XXIII.

$y = 3$ c.c. Propylbutyrate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.002\,x)^{0.378}/z^{1.378} = C$; $\log C = \bar{1}.651$.

| | $x$. | | |
|---|---|---|---|
| $z$. | Calc. | Found. | log $C$. |
| 3 | — | 1.19 | — |
| 6 | 3.49 | 3.55 | $\bar{1}.658$ |
| 9 | 6.11 | 6.13 | $\bar{1}.652$ |
| 12 | 9.05 | 9.05 | $\bar{1}.651$ |
| 15 | 12.31 | 12.31 | $\bar{1}.651$ |
| 18 | 15.92 | 15.90 | $\bar{1}.650$ |
| 21 | 19.68 | 19.68 | $\bar{1}.651$ |
| 24 | 23.72 | 23.72 | $\bar{1}.651$ |
| 27 | 27.92 | 27.84 | $\bar{1}.650$ |
| 30 | 32.20 | 32.10 | $\bar{1}.649$ |
| 33 | 36.71 | 36.71 | $\bar{1}.651$ |
| 36 | 41.66 | 41.55 | $\bar{1}.650$ |
| 39 | 46.64 | 46.49 | $\bar{1}.649$ |
| 42 | 51.56 | 51.60 | $\bar{1}.652$ |
| 45 | 56.80 | 56.90 | $\bar{1}.652$ |
| 48 | 62.64 | 62.40 | $\bar{1}.649$ |
| 51 | 67.84 | 68.00 | $\bar{1}.652$ |
| 54 | 73.93 | 73.85 | $\bar{1}.650$ |
| | | | $\bar{1}.651$ |

## TABLE XXIV.

$y = 3$ c.c. Ethylpropionate; $x =$ c.c. Water; $z =$ c.c. Alcohol.
Formula $x\ (y - 0.03\ x)^{0.39}/z^{1.39} = C$; $\log C = \bar{1}.931$.

| | *x*. | | |
|---|---|---|---|
| *z*. | Calc. | Found. | log *C*. |
| 3 | 2.36 | 2.32 | $\bar{1}.924$ |
| 6 | 6.89 | 6.87 | $\bar{1}.930$ |
| 9 | 12.38 | 12.35 | $\bar{1}.930$ |
| 12 | 19.10 | 19.17 | $\bar{1}.933$ |
| 15 | 27.12 | 27.12 | $\bar{1}.931$ |
| 18 | 36.84 | 36.84 | $\bar{1}.931$ |
| 21 | 50.35 | 50.42 | $\bar{1}.932$ |
| 24 | — | ∞ | |
| | | | $\bar{1}.930$ |

## TABLE XXV.

$y = 3$ c.c. Propylpropionate; $x =$ c.c. Water; $z =$ c.c. Alcohol.
Formula $x\ (y - 0.0065\ x)^{0.45}/z^{1.45} = C$; $\log C = \bar{1}.733$.

| | *x*. | | |
|---|---|---|---|
| *z*. | Calc. | Found. | log *C*. |
| 3 | — | 1.58 | — |
| 6 | 4.45 | 4.70 | $\bar{1}.757$ |
| 9 | 8.27 | 8.35 | $\bar{1}.738$ |
| 12 | 12.25 | 12.54 | $\bar{1}.743$ |
| 15 | 17.04 | 17.15 | $\bar{1}.736$ |
| 18 | 22.27 | 22.27 | $\bar{1}.733$ |
| 21 | 28.00 | 27.83 | $\bar{1}.731$ |
| 24 | 34.20 | 33.75 | $\bar{1}.727$ |
| 27 | 40.80 | 40.24 | $\bar{1}$·727 |
| 30 | 47.95 | 47.15 | $\bar{1}.725$ |
| 33 | 55.70 | 54.65 | $\bar{1}.725$ |
| 36 | 63.50 | 63.18 | $\bar{1}.731$ |
| 39 | 72.25 | 71.59 | $\bar{1}.729$ |
| 42 | 81.15 | 83.05 | $\bar{1}.743$ |
| 45 | 91.30 | 93.91 | $\bar{1}.746$ |
| 48 | 102.00 | 107.46 | $\bar{1}.756$ |
| | | | $\bar{1}.737$ |

## Table XXVI.

$y = 3$ c.c. Propylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.
Formula $x\ (y - 0.03\,x)^{0.23}/z^{1.23} = C$; log $C = 0.166$.

| | *x.* | | |
|---|---|---|---|
| *z.* | **Calc.** | **Found.** | **log *C*.** |
| 3 | 4.44 | 4.50 | 0.170 |
| 6 | 10.57 | 10.48 | 0.163 |
| 9 | 17.75 | 17.80 | 0.167 |
| 12 | 25.95 | 26.00 | 0.167 |
| 15 | 35.72 | 35.63 | 0.165 |
| 18 | 46.50 | 47.50 | 0.178 |
| 21 | 59.00 | 58.71 | 0.164 |
| 24 | — | ∞ | 0.168 |

## Table XXVII.

$y = 3$ c.c. Butylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.
Formula $x\ (y - 0.007\,x)^{0.3}/z^{1.8} = C$; log $C = \bar{1}.912$.

| | *x.* | | |
|---|---|---|---|
| *z.* | **Calc.** | **Found.** | **log *C*.** |
| 3 | — | 2.08 | — |
| 6 | 6.06 | 6.08 | $\bar{1}.914$ |
| 9 | 10.29 | 10.46 | $\bar{1}.920$ |
| 12 | 15.04 | 15.37 | $\bar{1}.922$ |
| 15 | 20.10 | 20.42 | $\bar{1}.918$ |
| 18 | 25.64 | 25.60 | $\bar{1}.911$ |
| 21 | 31.49 | 31.49 | $\bar{1}.912$ |
| 24 | 37.60 | 37.48 | $\bar{1}.911$ |
| 27 | 44.05 | 43.75 | $\bar{1}.909$ |
| 30 | 50.74 | 50.74 | $\bar{1}.912$ |
| 33 | 58.00 | 59.97 | $\bar{1}.927$ |
| | | | $\bar{1}.916$ |

## TABLE XXVIII.

$y = 3$ c.c. Amylacetate ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.
Formula $x(y - 0.02x)^{0.294}/z^{1.294} = C$; log $C = \bar{1}.861$.

| | $x$. | | |
|---|---|---|---|
| $z$. | Calc. | Found. | log $C$. |
| 3 | — | 1.76 | — |
| 6 | — | 4.24 | — |
| 9 | 9.03 | 9.03 | $\bar{1}.861$ |
| 12 | 13.11 | 13.24 | $\bar{1}.866$ |
| 15 | 17.43 | 17.52 | $\bar{1}.864$ |
| 18 | 22.22 | 22.22 | $\bar{1}.861$ |
| 21 | 26.99 | 26.99 | $\bar{1}.861$ |
| 24 | 32.24 | 32.14 | $\bar{1}.860$ |
| 27 | 37.59 | 37.23 | $\bar{1}.856$ |
| 30 | 42.78 | 42.66 | $\bar{1}.859$ |
| 33 | 48.41 | 48.41 | $\bar{1}.861$ |
| | | | $\bar{1}.861$ |

## TABLE XXIX.

$y = 3$ c.c. Propylformiate ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.
Formula $x(y - 0.04x)^{0.38}/z^{1.38} = C$; log $C = \bar{1}.967$.

| | $x$. | | |
|---|---|---|---|
| $z$. | Calc. | Found. | log $C$. |
| 3 | 2.82 | 2.83 | $\bar{1}.969$ |
| 6 | 7.52 | 7.50 | $\bar{1}.966$ |
| 9 | 13.65 | 13.50 | $\bar{1}.962$ |
| 12 | 21.30 | 21.60 | $\bar{1}.973$ |
| 15 | 30.95 | 30.60 | $\bar{1}.962$ |
| 18 | 52.40 | 53.00 | $\bar{1}.972$ |
| 21 | — | $\infty$ | $\bar{1}.967$ |

## TABLE XXX.

$y = 3$ c.c. Butylformiate ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.01\,x)^{\frac{1}{3}}/z^{\frac{4}{3}} = C$; $\log C = 0.057$.

| | $x$. | | |
|---|---|---|---|
| $z$. | Calc. | Found. | log $C$. |
| 3 | 3.43 | 3.45 | 0.060 |
| 6 | 8.71 | 8.83 | 0.063 |
| 9 | 15.02 | 14.75 | 0.049 |
| 12 | 22.32 | 21.45 | 0.041 |
| 15 | 30.25 | 29.65 | 0.048 |
| 18 | 39.00 | 39.00 | 0.057 |
| 21 | 48.80 | 51.80 | 0.083 |
| 24 | — | $\infty$ | 0.057 |

## TABLE XXXI.

$y = 3$ c.c. Amylformiate ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.

Formula $x(y - 0.005\,x)^{0.35}/z^{1.35} = C$; $\log C = \bar{1}.808$.

| | $x$. | | |
|---|---|---|---|
| $z$. | Calc. | Found. | log $C$. |
| 3 | — | 1.80 | — |
| 6 | 4.92 | 5.17 | $\bar{1}.829$ |
| 9 | 8.54 | 8.77 | $\bar{1}.820$ |
| 12 | 12.63 | 12.64 | $\bar{1}.809$ |
| 15 | 17.10 | 17.01 | $\bar{1}.806$ |
| 18 | 21.90 | 21.86 | $\bar{1}.807$ |
| 21 | 27.06 | 27.06 | $\bar{1}.808$ |
| 24 | 32.50 | 32.31 | $\bar{1}.805$ |
| 27 | 38.31 | 38.31 | $\bar{1}.808$ |
| 30 | 44.40 | 44.50 | $\bar{1}.809$ |
| 33 | 50.71 | 50.71 | $\bar{1}.808$ |
| 36 | 57.20 | 57.82 | $\bar{1}.813$ |
| 39 | 62.70 | 65.21 | ($\bar{1}.830$) |
| 42 | 71.35 | 77.05 | ($\bar{1}.842$) |
| 45 | 78.75 | 85.10 | ($\bar{1}.842$) |
| 48 | 86.55 | 94.20 | ($\bar{1}.845$) |
| | | | $\bar{1}.811$ |