ON TERNARY MIXTURES.

FIRST PAPER.[1]

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FOLLOWING out the analogy between dissolved substances and gases, Nernst deduces the law that, when two dissolved substances have no common ion and do not react chemically, the influence of each on the solubility of the other is zero, within certain undefined limits. He says:[2] "Die Analogie zwischen der Auflösung und Sublimation bezw. Dissociation fester Stoffe zeigt sich nun auch deutlich ausgesprochen, was den Einfluss fremden Zusatzes betrifft. Ebenso wenig wie die Sublimationsspannung bei Gegenwart fremder indifferenter Gase sich ändert, wird die Löslichkeit eines festen Stoffes durch Zusatz eines zweiten (in nicht zu grosser Menge) beeinflusst, wofern der hinzugefügte fremde Stoff nicht chemisch auf jenen einwirkt; und ebenso wie die Dissociationsspannung im höchsten Maasse durch Zusatz eines der gasförmigen Zersetzungsproducte beeinflusst wird, so variirt entsprechend auch die Löslichkeit derjenigen Stoffe, bei welchen die Auflösung mit einem mehr oder weniger vollständigen Zerfall verbunden ist, die also bei ihrer Auflösung mehrere Molekülgattungen liefern, wenn eine dieser letzteren der Lösung hinzugefügt wird." There are several things in this statement which are open to criticism. If taken literally, the author implies a fundamental difference between solutions of liquids in liquids, and solids in liquids, a distinction which is not in accordance with the view that in dilute solutions the solute,[3] whether liquid or solid in the pure state, behaves like a gas at that temperature.

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[1] A paper presented to the American Academy of Arts and Sciences, May 9, 1894.

[2] Theor. Chemie, p. 383.

[3] There seems to me a need for a word denoting the dissolved substance. In future I shall use the word "solute," meaning the substance dissolved in the solvent. Instead of the phrase "infinitely miscible liquids," I propose "consolute" liquids.

If applied to any dissolved substance, the statement just quoted is too inaccurate to need any comment. The precipitation of salts by alcohol is a well known instance where it does not apply, and, in general, adding to a solution a substance in which the solute is practically insoluble diminishes the solubility of the latter. This is recognized by Nernst, for he has based a method for determining reacting weights upon it.[1] Even if limited to solids, the proposition cannot be admitted. We have the precipitation of lactones by potassium carbonate as an intermediate step, and the precipitation of salts by phenol as a definite case of diminished solubility without the presence of a common ion. Other cases could be cited, if necessary, and there are also examples where an increase of solubility takes place when a solid substance is added to a solution containing another solid as solute. The explanation usually offered under these circumstances is, that "double molecules" are formed, a mode of getting round the facts which is not always entirely satisfactory.

Since in the application of the gas laws to solutions there has been observed no difference between a solid and a liquid when dissolved, I am inclined to think that the general statement should be, that in all cases where a third substance, B, is added to a solution of A in S, the solubility of A undergoes a change. This variation may be large or small, positive or negative, depending on the nature of the three substances, A, B, and S. When both A and B are liquids, or even when only one of them is, the effect is so marked as to be familiar to all; when both are solids, the effect is not yet recognized by so competent an authority as Nernst.

The work of the last few years on solutions has been devoted to bringing out the analogy between the dissolved substance and gases. In the cases of changed solubility, no common ion being present, the analogy is no longer with gases, but with liquids. The added substance acts as a liquid, precipitating the solute more or less in proportion as the dissolved substance happens to be more or less soluble in it. The laws governing these displacements are entirely unknown, with the exception of Nernst's Dis-

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[1] Zeitschr. f. ph. Chem., VI. 16. 1890.

tribution Law,[1] which is only a first approximation, in that it takes no account of the changing mutual solubilities of the hypothetically non-miscible liquids. Under these circumstances it seemed to me desirable to investigate the laws governing systems composed of three substances, and the experiments which I communicate in this paper have been made on the simplest form of ternary mixtures, — that where all three substances are liquids. The subject has been very little studied, the only researches known to me being by Tuchschmidt and Follenius,[2] Berthelot and Jungfleisch,[3] Duclaux,[4] Nernst,[5] and Pfeiffer.[6] Of these, all except the first and last deal with the equilibrium between two liquid phases; the paper of Tuchschmidt and Follenius contains but one series of measurements, while Pfeiffer remarks, apropos of his own extended investigations, that "there is very little to be made out of them." In this he does himself an injustice, for, as I shall show, his results are very satisfactory and astonishingly accurate when one remembers how they were made.

The simplest case of three-liquid systems is when one has two practically non-miscible liquids, and a third with which each of the others is miscible in all proportions; for then any complication due to the mutual solubility of the two dissolved liquids is avoided. It is possible to say something *a priori* about the law which governs these saturated solutions. Let A and B be two non-miscible liquids, S the common solvent with which A and B are miscible in all proportions when taken singly, and let the quantity of S remain constant, so that we are considering the amounts of A and B, namely x and y, which will dissolve simultaneously in a fixed amount of S. It is known, experimentally, that the presence of A decreases the solubility of B, and *vice versa;* it is required to find the law governing this change of solubility. This, being a case of equilibrium, must come under the general equation of equilibrium.

$$(1)\qquad \frac{\delta F(x, y)}{\delta x}dx+\frac{\delta F(x, y)}{\delta y}dy=0,$$

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[1] Teilungssatz.

[2] B. B., IV. 583. 1871.

[3] Ann. chim. phys., [4.], XXVI. 396. 1872.

[4] Ibid., [5.], p. 264. 1876.

[5] Zeitschr. f. ph. Chem., VI. 16. 1890.

[6] Ibid., IX. 469. 1892.

where dx and dy denote the changes in the concentrations of A and B, respectively.

This equation, though absolutely accurate, is of no value practically so long as the differential coefficients are unknown functions. In regard to them we may make two assumptions. The decrease in the solubility of A may be proportional to the amount of B added, and independent of the amounts of A and B already present in the solution. The differential equation expressing this is:—

$$(2) \qquad adx+bdy=0,$$

where a and b are proportionality factors and constants. This equation may be rejected on *a priori* grounds, because it does not show that when B is absent, the miscibility of A with S is infinite, and also because it has no similarity with the other equations representing chemical equilibrium. The second assumption is that the change in solubility may be a function of the amounts of A and B already present. This is the usual condition of chemical equilibrium, and is known as the Mass Law. Its mathematical expression is:—

$$\frac{\alpha dx}{x}+\frac{\beta dy}{y}=0, \text{ or}$$

$$(3) \qquad \alpha d\log x+\beta d\log y=0,$$

where x and y denote the amounts of A and B in a constant quantity of S, α and β are proportionality factors, and the logarithms are natural logarithms.

If α and β are constants, this equation is integrable, and gives, when cleared of logarithms:—

$$(4) \qquad x^{\alpha}y^{\beta}=\text{Constant}.$$

If we make $\frac{\alpha}{\beta}=n$, we shall have:—

$$(5) \qquad x^{n}y=C,$$

where C is of course different in value from the constant in equation (4).

Before we proceed to test equation (5) experimentally, it remains to be seen in what unit x and y should be expressed. It is obvious that the nature of the unit has no effect on the general form of the equation, nor upon the exponential factor n. The only change will be in the value of the integration constant log C, so that the measurements may be expressed in any form that is convenient, as chemical units,[1] for example, grams per liter, volumes, reacting volumes, or anything else. It is not even necessary that x and y be expressed in the same unit, though it would probably always be more practical. In my own experiments, x and y are expressed in cubic centimeters because they were measured directly as such, and in this way it was not necessary to make determinations of the densities of the liquids used, nor any assumptions in regard to their reacting weights. Equation (5) will not remain unchanged if the reacting weight of A or B varies, that is, if the ratio of the active mass to the actual mass changes as x or y changes. The converse of this is also true, that if the system follows the law $x^n y = C$, the common solvent remaining constant, the reacting weights of the substances A and B cannot have varied with the concentration.

I have found that the equation, $x^\alpha y^\beta =$ Constant, is the expression representing the saturated solutions of two non-miscible liquids in a constant quantity of a consolute liquid. I find, however, that in most cases the concentrations cannot be given by one curve, but involve two, so that for one set of concentrations I have the relation $x^{n_1} y = C_1$, for the other set $x^{n_2} y = C_2$. This cannot be true unless the two sets of saturated solutions correspond to different conditions. This is the case. Duclaux[2] found that a saturated solution of amylalcohol and water in ethylalcohol became turbid on adding a drop either of amylalcohol or of water. In other words, the solution was sensitive to an excess of either liquid.[3] I have confirmed this result, and it is perfectly general. It is not proper,

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[1] I have adopted the following nomenclature for molecular and atomic weights, viz. reacting and combining weights. As the reacting weight is proportional to the chemical unit experimentally, I propose that the gram molecule in the unit of volume (reacting weight in grams per liter) be called the chemical unit, or simply the unit. The object of these arbitrary changes in our chemical terms is to do away with everything involving or implying the assumption of the existence of molecules and atoms.

[2] Ann. chim. phys, [5.], VII. 264. 1876.

[3] Ostwald, Lehrbuch, I. 819.

however, to draw the conclusion that the solution is saturated in respect to both liquids. If to a given saturated solution of chloroform, water, and alcohol, for instance, one adds a drop of water or of chloroform, the solution becomes turbid; but what separates out is the same in both cases. It is analogous to a saturated solution of salt in a mixture of alcohol and water. It is indifferent whether one adds alcohol or salt to the solution. In either case, there is a precipitate; but in both cases the precipitate is salt, and the solution is saturated in respect to salt, not in respect to alcohol. It is not so easy to see what takes place in a system composed of liquids because the precipitate, being itself a liquid, dissolves part of the solution, and the new phase is not composed of pure substance. This need not trouble us, for, theoretically at any rate, the precipitate may be treated as pure liquid, and the final equilibrium looked upon as due to a subsequent reaction. One of the two curves represents, then, the set of solutions which is saturated in respect to chloroform, and not in respect to water. Whether one adds water or chloroform to these solutions, the precipitate is chloroform. The other curve represents the mixtures which are saturated in respect to water, and not in respect to chloroform. Either water or chloroform, when added to these solutions, produces a precipitate of water. These two sets of solutions are easily distinguishable qualitatively, because in the first case the new phase, containing a large percentage of chloroform, is denser than the mixture from which it separates, while in the second case the new phase, containing chiefly water, is lighter than the original solution. The point where the new phase changes from being denser to being lighter than the first phase is the point of intersection of the two curves. At this point only is the nature of the precipitate determined by the nature of the infinitely small excess added. The intersecting point represents the concentration at which, were chloroform and water solids at that temperature, both could be in equilibrium with the solution and its saturated vapor. It corresponds to the concentration of a solution containing two salts with a common ion which is in equilibrium with the two solid salts, formation of a double salt being excluded. In one respect the analogy between a system having three liquid components and one composed of two solids and a liquid does not hold. If to a saturated solution of silver bromate silver acetate is added, the precipitate is silver bromate, and, conversely, the precipitate is silver acetate if silver bromate be added to a saturated solution of silver acetate. The salt with the less concentration precipitates the one with the greater, up to a certain point. In a chloroform-water-alcohol mixture in which chloroform is present in large quantities, the precipitate is water, or the substance with the greater precipitates the one with the lesser concentration. This difference of behavior is due to the new phase being a solid in the one case and a liquid in the other. By a suitable choice of the three components, and by varying the temperature, the substance in respect to which the solution was saturated could be made to separate either as a liquid or a solid phase, and this difference could be made zero. The transition point would come when the equilibrium was between four phases, one solid, two liquid, and one gaseous.

There is no apparent theoretical reason why the two curves should not be prolonged beyond their intersection; but there is a very good practical one. Beyond the point of intersection the curves denote saturated but labile solutions, and a supersaturated system composed of liquids is almost impossible to realize. When I come to the study of ternary mixtures having one or more solid components, I hope to be able to follow one of the curves at least beyond the intersecting point; but in the present work I have made no such attempt.

I will now describe the method used in my work, and then take up the experimental data obtained. As pairs of non-miscible liquids, I have taken chloroform and water, benzol and water; and as consolute liquids, ethylalcohol, methylalcohol, and acetone. The next point was how to determine the composition of the saturated solutions. The methods of quantitative analysis are useless in this case; but the problem is solved without difficulty by quantitative synthesis. Instead of making a saturated solution and analyzing it, I measured the quantities required to make a saturated solution at the required temperature. Definite amounts of the consolute liquids were put in test tubes by means of a carefully graduated pipette; varying quantities of one of the non-miscible liquids were run in from a burette, and the second non-miscible liquid added from another burette to saturation. The test tubes were corked, warmed just above the temperature at which the final readings were made, so that there should be a single homogeneous liquid layer, and placed in a constant temperature bath. If the tube clouds, it is beyond the saturation point; if it remains clear, it is not up to it, the required value lying between the two. By making a series of experiments one can bring the limiting values very close together, and thus determine the saturation point with great accuracy. The constant temperature bath was at 20° C. No correction was made for the amounts of the three liquids evaporating off into the vapor space in the upper part of the test tubes; but by using different sized test tubes this space did not vary much, being about five cubic centimeters, so that the error due to this may be neglected.

The chloroform used (Squibb's) was treated with sodium bisulphite solution to free it from acetone, washed thoroughly with water, dried over calcium chloride and fractionated, twelve hundred grams going over within one quarter of a degree. Kahlbaum's crystallized benzol was recrystallized twice and fractionated to constant boiling point. The ethylalcohol was dried over lime and copper sulphate and fractionated. The lot used distilled within half a degree. Part of the acetone (from Eimer and Amend) was converted into the bisulphite compound, back again, dried over potassium carbonate and calcium chloride, and fractionated. Another portion was treated direct with calcium chloride and fractionated. I could detect no difference between the two lots. I tried to purify a sample of acetone from Cutler Brothers, purporting to be manufactured by Merck in Darmstadt; but it was so bad that I used none of it in my experiments. The methylalcohol (from Kahlbaum) was dried over anhydrous copper sulphate and fractionated.

The measurements in the tables are the mean of at least four determinations, and the error is probably not more than 5 per cent, except in the cases where the quantity of one component is less than 0.20 c.c., when it may easily rise to 10 per cent. The values for n are accurate to within 2 per cent without much question.

The values for log C are more untrustworthy, being much affected by a slight variation in n, while the term C is liable to even greater fluctuations, and is not given, as being too uncertain. Under the headings "Calc." are the values required by the formula to correspond with the experimental data for the other component. The figures in the column marked log C are Briggsian logarithms. As will be noticed, I have not always taken the mathematical mean of this column as the value of log C in the formula. It seemed better to take the value which best satisfied the experimental data, and to ignore numbers which were obviously faulty.

Table I.

x c.c. H_2O; y c.c. $CHCl_3$; 5 c.c. Alcohol. Temp. 20°.
Formula $x^{n_1}y=C_1$; $n_1=1.90$; log $C_1=1.190$.

Water.		**CHCl$_3$.**		
Calc.	**Found.**	**Calc.**	**Found.**	**log C_1.**
9.94	10.00	0.195	0.20-	1.195
8.99	9.00	0.24	0.24	1.192
7.98	8.00	0.30	0.30	1.193
7.14	7.00	0.385	0.37	1.174
6.00	6.00	0.515	0.515	1.190
5.97	5.00	0.73	0.73	1.191
3.97	4.00	1.12	1.13	1.197
	Average, ...			1.190

Formula $xy^{n_2}=C_2$; $n_2=1.111$; log $C_2=0.742$.

				log C_2.
3.00	3.00	1.73	1.73	0.741
1.99	2.00	2.49	2.51	0.745
1.01	1.00	4.66	4.60	0.737
0.92	0.91	5.07	5.00	0.736
0.755	0.76	5.96	6.00	0.745
0.635	0.63	7.06	7.00	0.738
0.55	0.55	8.00	8.00	0.743
0.48	0.49	8.86	9.00	0.750
0.43-	0.425	10.06	10.00	0.739
0.20	0.20-	20.00	20.00	0.742
0.127	0.125	30.24	30.00	0.738
	Average, ...			0.741

TABLE II.

x c.c. Water; y c.c. $CHCl_3$; 5 c.c. Methyl Alcohol. Temp. 20°.
Formula $x^{n_1}y = C_1$; $n_1 = 2.30$; $\log C_1 = 1.291$.

Water. Calc.	Water. Found.	$CHCl_3$. Calc.	$CHCl_3$. Found.	$\log C_1$.
9.91	10.00	0.10	0.10	1.300
5.01	5.00	0.48	0.48	1.288
4.03	4.00	0.81	0.80	1.283
1.99	2.00	3.97	4.00	1.294
	Average,			1.291

Formula $x^{n_2}y = C_2$; $n_2 = 1.25$; $\log C_2 = 1.061$.

				$\log C_2$.
1.49	1.49	7.00	7.00	1.061
1.34	1.35	7.93	8.00	1.065
1.12	1.12	10.00	10.00	1.061
	Average,			1.062

TABLE III.

x c.c. Water; y c.c. Chloroform; 5 c.c. Acetone. Temp. 20°.
Formula $x^{n_1}y = C_1$; $n_1 = 1.415$; $\log C_1 = 0.194$.

Water. Calc.	Water. Found.	Chloroform. Calc.	Chloroform. Found.	$\log C$.
5.01	5.00	0.16	0.16	0.193
4.00	4.00	0.22	0.22	0.194
3.47	3.50	0.266	0.27	0.201
3.00	3.00	0.33	0.33	0.193
2.49	2.50	0.43	0.43	0.196
2.01	2.00	0.586	0.58	0.189
	Average,			0.194
	1.50		0.74	
	1.20		0.83	
	1.00		0.955	
	0.93		1.00	
	0.79		1.12	
	0.71		1.20	
	0.58		1.40	
	0.53		1.50	
	0.505		1.60	
	0.38		2.00	
	0.30-		2.50	
	0.25		3.00	
	0.21		3.50	
	0.19		4.00	
	0.16		5.00	
	0.12		10.00	

Table IV.

x c.c. Water; y c.c. Benzol; 5 c.c. Alcohol. Temp. 20°.
Formula $x^n y = C$; $n = 1.60$; $\log C = 0.554$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C.
19.87	20.00	0.03	0.03	0.557
10.65	10.00	0.09	0.08	0.503
7.94	8.00	0.13	0.13	0.559
4.97	5.00	0.273	0.275	0.557
4.00	4.00	0.39	0.39	0.554
3.02	3.00	0.61	0.61	0.558
2.01	2.00	1.18	1.17	0.550
1.72	1.72	1.50	1.50	0.553
1.50	1.50	1.87	1.87	0.554
1.44	1.45	1.98	2.00	0.559
1.00	1.00	3.58	3.57	0.553
0.605	0.605	8.00	8 00	0.554
0.526	0.525	10.04	10.00	0.552
0.34	0.34	20.14	20.00	0.551
	Average,			0.551

Table V.

x c.c. Water; y c.c. Benzol; 5 c.c. Methyl Alcohol. Temp. 20°.
Formula $x^{n_1} y = C_1$; $n_1 = 1.48$; $\log C_1 = 0.216$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C_1.
5.05	5.00	0.15	0.15	0.211
3.95	4.00	0.21	0.215	0.223
3.01	3.00	0.32	0.32	0.211
2.00	2.00	0.59	0.59	0.216
1.40	1.40	1.00	1.00	0.216
	Average,			0.215

Formula $x^{n_2} y = C_2$; $n_2 = 2.00$; $\log C_2 = 0.281$.

				log C_2.
1.13	1.13	1.50	1.50	0.282
1.00	1.00	1.91	1.90	0.279
0.80	0.80	2.99	3.00	0.283
0.69	0.69	4.01	4.00	0 280
0.49	0.49	7.96	8.00	0.283
	Average,			0.281

TABLE VI.

x c.c. Water; y c.c. Benzol; 5 c.c. Acetone. Temp. 20°.
Formula $x^{n_1}y = C_1$; $n_1 = 1.40$; log $C_1 = 0.262$.

Water.		Benzol.		
Calc.	**Found.**	**Calc.**	**Found.**	**log C_1.**
7.97	8.00	0.10	0.10	0.264
7.00	7.00	0.12	0.12	0.262
5.04	5.00	0.19	0.19	0.258
4.03	4.00	0.26	0.26	0.258
2.99	3.00	0.393	0.395	0.264
2.49	2.50	0.51	0.51	0.265
2.18	2.20	0.61	0.615	0.269
2.01	2.00	0.69	0.69	0.260
	Average, ...			0.2625

Formula $xy^{n_2} = C_2$; $n_2 = 1.35$; log $C_2 = 0.114$.

				log C_2.
1.67	1.67	0.833	0.833	0.114
1.50	1.50	0.90	0.90	0.114
1.30	1.30	1.00	1.00	0.114
1 005	1.00	1.215	1.21	0.112
0.65	0.65	1.67	1.67	0.114
0.51	0.51	2.00	2.00	0.114
0.38	0.38	2.49	2.50	0.116
0.295	0.295	3.00	3.00	0.114
0.20	0.20	4.00	4.00	0.114
0.15	0.15	4.96	5.00	0.119
	Average, ...			0.1145

There is but one exception, in the chloroform-water-acetone series. As chloroform and water behave normally with alcohol (Table I.), water and acetone with benzol (Table VI.), the disturbing effect must be due to chloroform and acetone in presence of each other. I have not yet had time to investigate mixtures of chloroform and acetone in the absence of water, to determine whether they are abnormal in respect to any other physical properties. In the other five cases the agreement between observed and calculated values is a remarkable one, well within the limits of experimental error, and this in spite of the wide range that the measurements cover. In the benzol-water-alcohol series the ratio of benzol to water varies as one to forty thousand; in the chloroform-water-alcohol series the ratio chloroform-water varies as one to twelve thousand. In the last measurement of Table I., the chloroform forms over 85 per cent by volume synthetically of the solution, so that in this instance we are well beyond the realms of the "dilute solutions," without noticing any disturbing effect due to "variations from the gas laws." The series benzol-water-alcohol is represented by a single curve; but it must not be thought that in this it forms a real exception to the other mixtures. Theoretically, there are two curves for this series; but the two happen to have the same direction, and therefore appear as one. The point where the precipitate ceases to be less dense than the original solution lies between the mixtures benzol 2.00 c.c., water 1.45 c.c., and benzol 3.57 c.c., water 1.00 c.c.

(*To be continued.*)