

TERNARY MIXTURES, IV

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Practically the only extended study of conjugate solutions is that made by Wright, alone and in collaboration with others.¹ This work consisted in a determination of isotherms for systems composed of two partially miscible metals and a third metal consolute with each of the others. It is easy to pick flaws in the experimental work. Wright, himself, has pointed out its shortcomings with great clearness and his statement is recapitulated here solely to show that the conclusions to be deduced in this paper from that work cannot be accepted as final until the measurements have been repeated under more favorable circumstances. The metals used were not always pure, the aluminum containing over four percent of iron and silicon.² These impurities were allowed for in the analyses so that the tabulated data give the gram percentages of each of the three metals forming the ternary mixture; but we are not able in any way to foretell the effect of the impurities upon the distribution ratios. The temperatures were not constant during the experiments, fluctuations of one hundred degrees not being excluded. From some experiments that were made it appears that the error due to the actual temperature difference between two measurements was probably not so serious as those due to changes of temperature in a single experiment, the convection currents thus generated preventing the reaching of equilibrium. The most serious source of error, however, occurred in the method adopted for separating the two phases. The two liquid layers were not drawn off at the temperature of the experiment and then analyzed. Instead of this,

¹ Wright and Thompson. *Proc. Roy. Soc.* **45**, 461 (1889); **48**, 25 (1890); **49**, 156 (1891); Wright, Thompson and Leon. *Ibid.* **49**, 174 (1891); Wright. *Ibid.* **50**, 372 (1891); **52**, 11 (1892); **52**, 530 (1893); **55**, 130 (1894).

² Wright. *Ibid.* **52**, 12 (1892).

the whole mass was cooled as rapidly as possible, the upper and lower portions of the ingot being then analyzed. When one recalls the difficulties to be overcome in making a homogeneous casting with only two metals, one can easily see that this method of analysis can be justified only on the ground taken by Wright—that he could find no better method. As a matter of fact, attempts to draw off the molten solutions proved unsatisfactory.¹ That the method of rapid cooling cannot give accurate results is shown by two facts. We know from the phase rule that all mixtures corresponding to points on a given tie-line must separate into the same two liquid phases provided the system is allowed to reach equilibrium. This was apparently not the case in the experiments of Wright and Thompson.² The second point is that with mixtures that did not separate into two liquid phases and which should therefore have been homogeneous, differences in composition between the upper and the lower portions of the ingot were found, amounting in one case to over two percent.³

In view of the numerous sources of error it is not surprising to find that increasing the amount of the consolute metal does not always produce an increase in the solubility of the partially miscible metals. Instead of this there are annoying fluctuations which, though evidently due to experimental error, are still sufficient to make the application of the mass law formulas to the isotherm an extremely unsatisfactory proceeding. On the other hand these variations produce relatively less effect on the distribution ratio. For this reason I shall limit myself, in this paper, to a discussion of the equilibrium between the solution phases. It has been shown⁴ that, for two non-miscible liquids, A and B, and a third, C, consolute with the other two, the distribution of the third liquid between the other two can normally be represented by the formula

$$\left(\frac{C_1}{A_1}\right)^n \div \frac{C_2}{B_2} = \text{constant}.$$

Wright and Thompson. *Proc. Roy. Soc.* **45**, 470 (1889).

² *Ibid.* **49**, 192 (1891).

³ Wright and Thompson. *Ibid.* **45**, 463 (1889).

⁴ S. F. Taylor. *Jour. Phys. Chem.* **1**, 471 (1897).

In this equation C_1 and C_2 refer to the amounts of the consolute liquid in the two phases while A_1 is the amount of the component A in the phase in which it is the solvent and B_2 is the amount of the component B in the phase in which it is solvent, these amounts being expressed in any units whatsoever. The exponential factor n is not necessarily an integer. So far, no hypothesis has yet been advanced enabling us to predict the value of this exponential factor in any one case. If the logarithm of C_1/A_1 be measured along one axis and the logarithm of C_2/B_2 along the other, the resulting curve is a straight line provided the above equation describes the facts. This graphical method is the easiest and quickest method of determining whether or not a given set of data conforms to the mass law, and the direct measurement of the pitch of the curve is by far the simplest method of getting at the value of the exponential factor.

The data of Wright and Thompson are reproduced graphically in Fig. 1. The coordinates are the logarithms of the concentrations, these latter being expressed in grams of the consolute metal per gram of the solvent metal. In order to prevent overlapping, the origin is in a different place for each curve; but the scale is the same for all, each division being equal to 0.2. The curves are so labelled that the middle metal is the consolute one. The concentrations of the consolute metal in the first metal are measured along the ordinates and the concentrations in the last metal of the three along the abscissas. Curves are given for lead, silver and zinc¹; bismuth, tin and zinc²; zinc, cadmium and bismuth³; cadmium, tin and aluminium⁴; aluminium, tin and bismuth⁵; aluminium, silver and lead⁶; aluminium, silver and bismuth⁷; aluminium, tin and lead⁸; zinc, silver and

¹ Proc. Roy. Soc. 50, 391 (1891).

² Ibid. 50, 388 (1891).

³ Ibid. 52, 536 (1892).

⁴ Ibid. 55, 132 (1894).

⁵ Ibid. 52, 19 (1892).

⁶ Ibid. 52, 22 (1892).

⁷ Ibid. 52, 24 (1892).

⁸ Ibid. 52, 16 (1892).

bismuth.¹ It must be remembered in considering this diagram

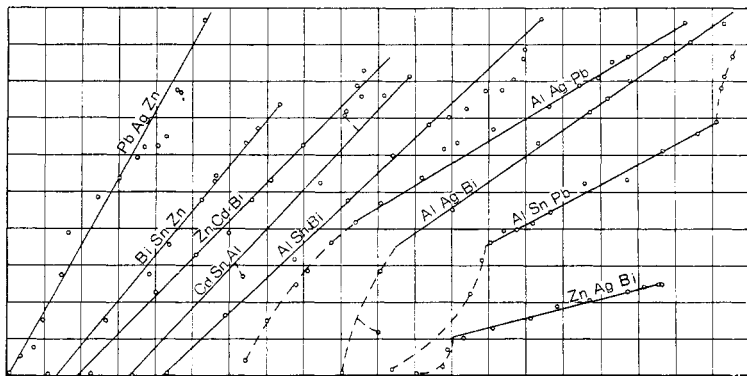


Fig. 1

that a very slight error causes a large displacement at the lower ends of the curves. For instance an error of less than one-half of one percent would make the aluminum, silver and lead curve a straight line. It is evident at once that all these systems are normal though there are some curious variations to which attention must be called. With lead, silver and tin and with aluminum, tin and bismuth, the curves sweep out and back just before the crest-point² is reached. It is probable that from such disturbances conclusions might be drawn as to the relative positions of the boundary curves; but I have not yet succeeded in getting any satisfactory results in this way. The sudden apparent change of direction at the upper end of the aluminum, tin and lead curve is quite unintelligible.

The same data are tabulated in Tables I-XII. The figures are given for only two of the metals in each phase, for the solvent metal and the consolute metal. Since the values given are grams per hundred grams of the alloy the amounts of the third metal can readily be determined by subtraction. The subscripts one and two refer to the denser and the less dense phase respectively. In the sixth column are the values of the constant as calculated from the formula at the head of each table. No cor-

¹ Proc. Roy. Soc. 50, 393 (1891).

² Snell. Jour. Phys. Chem. 2, 470 (1898).

rections have been made for the partial miscibility of the two hypothetically non-miscible metals even though bismuth is soluble up to fifteen percent or thereabouts in zinc. No formulas are given in the last three tables because it was evident that the data were so abnormal that it was useless to try to apply the theory. The bracketed figures are the data for the crest-points. They were not observed directly; but were obtained by extrapolation.

TABLE I

$$\left(\frac{\text{Sn}_1}{\text{Bi}_1}\right) \div \left(\frac{\text{Sn}_2}{\text{Zn}_2}\right)^{1.25} = K$$

Temperature about 650°

Sn ₁	Bi ₁	Sn ₂	Zn ₂	Sn ₁ /Sn ₂	K
0.00	85.72	0.00	97.68		
3.23	80.27	1.98	94.57	1.63	5.05
6.35	75.82	3.97	91.82	1.60	4.25
10.38	70.52	6.35	88.12	1.63	3.94
13.53	66.33	7.95	85.54	1.70	3.97
19.09	51.35	11.19	80.13	1.71	4.33
20.80	46.01	12.72	77.56	1.64	4.33
20.44	42.43	12.98	77.32	1.57	4.48
21.89	30.33	17.25	70.83	1.27	4.21
22.37	25.94	19.16	67.80	1.17	4.19
[21.5	18.5	21.5	60.0]	1.00	4.20

TABLE II

$$\left(\frac{\text{Ag}_2}{\text{Zn}_2}\right)^{1.5} \div \left(\frac{\text{Ag}_1}{\text{Pb}_1}\right) = K$$

Temperature 750°-850°

Ag ₁	Pb ₁	Ag ₂	Zn ₂	Ag ₂ /Ag ₁	K
1.25	96.69	38.91	57.97	31.1	34.8
1.54	96.28	40.89	55.73	26.6	36.0
1.71	96.43	45.01	51.62	26.3	44.0
2.39	95.78	47.68	48.58	20.0	38.8
4.18	94.43	52.80	43.11	12.7	28.1
5.55	93.16	54.93	40.86	9.9	28.8
10.22	88.02	60.14	30.86	5.9	28.6
12.62	85.38	63.70	25.00	5.1	36.2
15.69	81.88	65.34	20.79	4.2	40.9
17.43	80.15	65.94	19.27	3.8	42.1
17.65	79.78	67.03	16.49	3.8	44.8
19.51	78.54	63.79	13.92	3.3	61.2
29.53	68.03	60.35	11.23	2.1	47.8
29.90	67.21	59.32	11.53	2.0	38.1
[45.5	48.2	45.5	6.3]	1.0	32.6

TABLE III

$$\left(\frac{\text{Cd}_1}{\text{Bi}_1} \right) \div \left(\frac{\text{Cd}_2}{\text{Zn}_2} \right)^{0.96} = K$$

Temperature about 600°

Cd ₁	Bi ₁	Cd ₂	Zn ₂	Cd ₁ Cd ₂	K
0.00	85.72	0.00	97.68		
6.98	78.84	3.77	92.91	1.85	1.92
14.27	71.34	9.80	85.74	1.46	1.64
21.19	64.38	14.37	80.09	1.48	1.71
28.24	56.75	18.04	75.94	1.57	1.98
33.67	50.34	24.48	69.18	1.37	1.81
38.06	46.02	29.32	63.78	1.30	1.74
46.20	37.08	37.42	55.57	1.24	1.82
53.88	24.93	46.73	44.20	1.15	1.62
54.48	21.21	49.73	37.97	1.09	1.96
53.08	21.55	50.93	33.82	1.04	1.66
[52.0	19.5	52.0	28.5]	1.00	1.50

TABLE IV

$$\left(\frac{\text{Sn}_1}{\text{Cd}_1} \right)^{0.92} \div \left(\frac{\text{Sn}_2}{\text{Al}_2} \right) = K$$

Temperature 700°-750°

Sn ₁	Cd ₁	Sn ₂	Al ₂	Sn ₂ Sn ₁	K
0.00	99.78	0.00	96.61		
4.75	94.84	2.75	92.80	1.73	2.15
14.78	84.70	9.98	85.09	1.48	1.71
35.98	61.49	22.28	71.94	1.61	1.97
53.15	40.79	27.88	66.04	1.91	3.02
57.28	34.26	37.07	54.75	1.55	2.37
59.18	27.77	43.17	46.18	1.37	2.14

TABLE V

$$\left(\frac{\text{Sn}_1}{\text{Bi}_1}\right) \div \left(\frac{\text{Sn}_2}{\text{Al}_2}\right)^{1.05} = K$$

Temperature 750°–850°

Sn ₁	Bi ₁	Sn ₂	Al ₂	Sn ₁ Sn ₂	K
0.00	99.72	0.00	97.98		
2.79	96.64	2.45	95.15	1.14	1.35
5.57	93.58	4.90	92.35	1.14	1.30
12.26	86.03	9.43	87.51	1.30	1.47
21.02	76.90	17.56	78.94	1.20	1.33
31.37	65.19	26.40	68.33	1.19	1.31
40.76	54.37	34.18	58.83	1.19	1.33
45.13	47.60	35.63	56.28	1.29	1.56
50.09	41.64	38.12	53.51	1.32	1.72
54.22	35.82	42.80	48.11	1.27	1.71
56.91	30.73	42.97	47.54	1.32	2.06
57.61	27.10	45.76	44.71	1.26	2.08
58.17	24.01	49.48	37.44	1.18	1.84
57.23	23.20	51.32	34.31	1.12	1.61
[55.75]	18.60	55.75	25.65]	1.00	1.32

TABLE VI

$$\left(\frac{\text{Ag}_2}{\text{Al}_2}\right)^{1.65} \div \left(\frac{\text{Ag}_1}{\text{Pb}_1}\right) = K$$

Temperature 830°–900°

Ag ₁	Pb ₁	Ag ₂	Al ₂	Al ₂ Al ₁	K
0.00	99.93	0.00	98.09		
0.30	99.61	15.05	83.35	50.2	20
0.61	99.24	31.98	66.05	51.3	49
0.80	99.01	43.15	54.58	54.0	84
1.13	98.59	53.85	44.03	47.8	122
1.31	98.40	58.43	39.69	44.7	142
1.74	98.10	66.40	31.50	38.1	193
2.32	97.47	71.07	26.10	29.3	220
3.16	96.53	75.33	22.04	23.8	232
5.19	94.61	80.37	16.78	15.1	242
6.69	93.18	84.34	12.38	12.6	330
7.87	91.99	84.63	11.54	10.8	313
11.75	88.14	84.91	9.69	7.2	270
20.99	78.87	83.10	7.17	4.0	215
28.15	71.55	81.17	5.36	2.9	225
32.82	66.77	77.64	4.61	2.4	215
36.40	62.85	74.65	3.70	2.3	246
40.73	58.31	72.88	3.36	1.8	232
[58.25]	40.00	58.25	1.75]	1.0	223

TABLE VII

$$\left(\frac{Ag_2}{Zn_2} \right)^{3.8} \div \left(\frac{Ag_1}{Bi_1} \right) = K$$

Temperature 700°-800°

Ag ₁	Bi ₁	Ag ₂	Zn ₂	Ag ₂ /Ag ₁	K
5.08	79.28	37.06	57.60	7.3	3.7
6.84	77.24	38.80	55.27	5.8	3.0
7.58	78.58	43.16	48.85	5.7	6.5
8.98	77.99	46.31	45.02	5.1	9.7
12.71	76.19	47.94	42.01	3.8	10.0
18.68	68.97	49.92	37.66	2.7	10.8
22.96	62.72	51.34	34.32	2.2	12.4
29.26	53.10	51.16	31.63	1.8	11.3
37.33	43.27	49.73	27.49	1.3	11.1
41.22	38.52	47.15	24.09	1.14	11.9
43.74	33.82	45.25	22.64	1.04	10.7
[44.63	33.12	44.63	22.25]	1.00	10.5

Table VIII

$$\left(\frac{Ag_2}{Al_2} \right)^{1.43} \div \left(\frac{Ag_1}{Bi_1} \right) = K$$

Temperature 830°-900°

Ag ₁	Bi ₁	Ag ₂	Al ₂	Ag ₂ /Ag ₁	K
0.00	99.72	0.00	97.98		
0.74	98.39	12.30	85.04	16.6	8.4
1.59	97.43	24.20	72.31	15.2	8.1
1.95	97.31	33.95	62.55	17.4	20.8
2.01	97.49	51.80	44.81	25.8	61.1
4.81	94.72	68.63	27.43	14.3	75.0
11.51	88.09	81.29	14.00	7.2	75.3
21.56	77.72	83.75	9.80	3.8	77.6
25.41	74.07	83.88	8.14	3.3	81.8
31.05	68.28	82.60	7.44	3.0	83.6
40.92	57.97	75.64	5.66	1.8	57.7
48.53	49.62	68.16	3.34	1.4	76.4
[58.25	39.50	58.25	2.25]	1.0	71.8

TABLE IX

$$\left(\frac{\text{Sn}_1}{\text{Pb}_1} \right) \div \left(\frac{\text{Sn}_2}{\text{Al}_2} \right)^{1.85} = K$$

Temperature 750°-850°

Sn ₁	Pb ₁	Sn ₂	Al ₂	Sn ₂ /Sn ₁	K
0.00	99.93	0.00	98.09		
4.60	95.33	6.25	91.89	1.36	6.97
11.17	88.77	14.50	83.17	1.30	3.19
12.51	87.43	20.26	77.52	1.62	1.71
14.01	85.75	24.50	72.95	1.75	1.23
15.97	83.61	27.00	70.01	1.69	1.11
18.25	81.42	27.47	69.64	1.51	1.25
21.13	78.40	28.98	67.63	1.37	1.32
25.10	74.17	31.83	64.79	1.27	1.25
33.64	65.35	39.37	55.61	1.17	0.98
45.41	51.89	45.34	49.08	1.00	1.02
55.16	39.73	48.11	46.11	0.87	1.29
61.52	29.14	52.27	40.57	0.85	1.32
64.21	24.52	54.62	36.00	0.83	1.21
65.07	23.06	59.14	25.86	0.91	0.60
63.92	21.78	60.27	22.69	0.94	0.48
[62.6	19.4	62.6	18.0]	1.00	0.32

TABLE X

Temperature about 650°

Sn ₁	Pb ₁	Sn ₂	Zn ₂	Sn ₂ /Sn ₁
0.00	98.76	0.00	98.86	
4.45	93.79	6.64	90.75	1.49
6.94	91.01	9.91	86.71	1.43
9.60	87.91	13.47	82.18	1.40
12.60	83.74	16.68	78.48	1.32
14.76	81.02	19.27	75.36	1.31
16.11	79.16	20.35	73.51	1.27
18.71	75.67	22.51	70.04	1.20
21.95	70.48	25.07	66.72	1.14
26.28	60.48	27.49	62.33	1.04
29.43	53.81	28.64	59.94	0.97
31.63	48.64	29.58	57.87	0.94
33.88	43.76	30.33	56.25	0.90
35.03	39.59	30.24	55.33	0.87
35.65	29.10	32.85	48.51	0.92
[35.0	22.5	35.0	42.5]	1.00

TABLE XI
Temperature 550°-650°

Cd ₁	Pb ₁	Cd ₂	Zn ₂	Cd ₂ /Cd ₁
0.00	98.76	0.00	98.86	
5.17	92.85	10.12	88.34	1.91
13.45	83.89	24.91	72.65	1.85
17.57	80.18	31.48	65.67	1.79
19.14	78.73	36.50	60.01	1.91
21.44	76.34	46.42	47.62	2.17
22.68	75.13	55.72	34.12	2.46
22.23	76.32	59.20	27.36	2.66
22.37	76.31	70.78	11.05	3.17
23.70	74.85	72.76	8.44	3.07
33.80	64.35	72.06	6.72	2.13
46.93	50.82	69.50	4.64	1.48
50.30	47.45	67.67	4.04	1.34
[60.6	36.5	60.6	2.9]	1.00

TABLE XII
Temperature 600°-700°

Sb ₁	Pb ₁	Sb ₂	Zn ₂	Sb ₂ /Sb ₁
0.00	98.79	0.00	98.86	
2.69	93.87	4.60	93.13	1.71
7.11	87.02	11.41	81.06	1.60
8.37	85.22	16.75	69.73	2.00
9.77	80.81	22.33	60.21	2.29
15.45	67.17	26.68	48.98	1.73
21.00	53.65	27.11	43.34	1.29
[26.5	38.1	26.5	35.4]	1.00

Nernst's distribution law was deduced under the explicit proviso that there is no passage of either non-miscible liquid into the other phase on addition of the third component. This condition is not satisfied in any of these systems. Since the distribution ratio at the crest-point must be unity, it is obvious that the ratio can remain constant only in case the ratio at infinite dilution is also unity—a condition which is rarely fulfilled. From this it follows that when the third substance is a liquid no really accurate conclusion as to its reacting weight can be drawn from a study of the distribution ratio—in the pres-

ent state of our knowledge. In spite of these facts, the distribution ratio does remain remarkably constant in a number of cases over a surprising range of concentrations. For this and other reasons I have calculated the distribution ratio for the twelve systems considered and have given the results in the fifth column of the tables. It seemed best to take the concentrations expressed in grams per hundred grams of the phase because this was as near to volume concentrations as one could get and also because this gave better results than any other method available. To have expressed the concentrations in grams per hundred grams of the solvent metal would merely have made the results in the fifth column a bad imitation of those in the sixth, which certainly would not have helped the cause of science.

Surprisingly good constants are obtained with tin in bismuth and zinc; with cadmium in zinc and bismuth (Table III); with cadmium in tin and aluminum; with tin in aluminum and bismuth. With bismuth, tin and zinc (Table I), the rate remains practically constant until there is over twenty percent of tin in the bismuth phase and thirteen percent in the zinc phase, the mean value being 1.63. With cadmium, tin and aluminum (Table IV), the ratio varies irregularly until there is fifty-seven percent of tin in the cadmium phase and thirty-seven percent in the aluminum phase. In this particular system the solvent action of the tin is very slight, there being less than nine percent of cadmium in the aluminum phase and an equally small quantity of aluminum in the cadmium phase in the conjugate solutions just cited. This, however, seems not to be an essential feature because the distribution ratio of tin in bismuth and aluminum (Table V) remains practically constant until there is fifty-seven percent of tin in the bismuth phase and fifty-one percent in the aluminum phase while, at the same point, there is nearly twenty percent of aluminum in the bismuth phase and about fourteen percent of bismuth in the aluminum phase.

Very bad distribution ratios are obtained for silver in lead and zinc, in lead and aluminum, in bismuth and aluminum, and in bismuth and zinc (Table VII) if we consider any great range of

concentrations. For silver in lead and aluminum (Table VI) or bismuth and aluminum (Table VIII) the distribution ratio remains about constant for the first three concentrations and that is all. To bring silver in zinc and lead (Table II) even approximately into line would require the assumption of Ag_6 in zinc.

With tin in lead and aluminum (Table IX) and in lead and zinc (Table X), the distribution ratio changes its sign with increasing concentration, being first greater than unity, then less than unity, becoming unity again at the crest-point. It seems very probable that this is due to experimental error; but one cannot be certain of this until the experiments have been repeated by someone, especially since the variation appears to lie completely outside any experimental error. For the present, therefore, it is a case of possibly inexact theory against possibly inaccurate measurements.¹ With cadmium (Table XI) or antimony (Table XII) in zinc and lead we have the reverse phenomenon of a sharp increase in the value of the distribution ratio, the value of course falling to unity at the crest-point.

When the value of the distribution ratio remains constant, it is equal to the ratio of the solubilities provided the third substance is a solid. When the third component is a liquid we have no way even of guessing at the value of the distribution ratio at infinite dilution unless we make use of the van't Hoff-Raoult formula $nN = \log p/p_i$. No one would claim that this formula would hold accurately for extreme concentrations since it is limited explicitly to cases in which the component whose vapor-pressure does not enter into the formula may be treated as an ideal gas. On the other hand it was conceivable that the variations might be approximately the same for two different metals so that the ratios of the concentrations might remain constant. If this were the case the distribution ratio at infinite dilution would be equal to the inverse ratio of the reacting weights of the two non-miscible liquids. To see how far this might hold I have calculated these values and compared them

¹ Such a variation does take place in certain systems where polymerization and dissociation are possible. Cf. Jakowkin, *Zeit. phys. Chem.* **18**, 589 (1895).

with the distribution ratios as obtained from the most dilute solutions given in Tables I–XII. The results are tabulated in Table XIII, the values in parentheses being taken from data by Wright for systems in which the isotherm was obviously distorted by the separation of a compound on cooling. The ratios are given to the nearest tenth.

TABLE XIII

	Pb Zn	Bi Zn	Pb Al	Bi Al	Cd Al
Calculated	3.2	3.2	7.6	7.7	4.1
Sn found	1.5	0.6	1.4	0.9	1.7
Ag found	31.1	7.3	50.2	16.6	
Cd found	1.9	0.5			
Sb found	1.7	(0.3)	(3.3)	(2.6)	

Although the 'found' values are not those at infinite dilution, I have convinced myself that extrapolation would not help matters any. On the other hand, experimental error may play a relatively large part since a small percentage error in the composition of the phases would have a very large effect on the composition of the phases. For this reason as well as for others already mentioned, it is very much to be desired that these systems should be studied again under the most favorable instead of under the least favorable circumstances. Taking the data as they stand, it is obvious that in no case do the 'calculated' values agree with those found by direct experiment. For the present, therefore, we have no method even of approximating the initial value of the distribution ratio when the third component is a liquid. I have laid what may seem to be undue stress on this point because it has been ignored with surprising consistency in the past.¹

Ostwald's position in regard to the matter is distinctly unsatisfactory.² He first takes up the case where the third substance is a solid and answers Berthelot's claim that the distribution coefficient for a saturated solution is not the same as the ratio of the solubilities in the following manner: "It is easy to

¹ See, however, Tammann. *Zeit. phys. Chem.* **22**, 481 (1897).

² *Lehrbuch*, I, 811.

see, however, that as a matter of fact, the ratio of the solubilities and the distribution ratio must be identical. For let us imagine as much succinic acid added to a mixture of ether and water as this will dissolve, each of the two solutions will, after separation, be saturated with respect to succinic acid, and will at the same time be in equilibrium, since neither can take succinic acid from the other; the ratio of the two concentrations is therefore simultaneously that of solubility and of distribution." This is open to criticism. It is a fair answer to Berthelot; but is not quite a fair statement of the case because it ignores the fact that if two non-miscible liquids are saturated separately with a solid the solutions will not be in equilibrium (theoretically at any rate) if mixed. In the instance cited by Ostwald of ether, water and succinic acid, no reference is made to the fact that the ratio of ether to water in each of the phases cannot be the same after saturation with succinic acid as when no succinic acid is present. The difference may be very slight owing to the slight solvent action of succinic acid and its low solubility in water; but the fact that there is a change should not be ignored by anyone interested in exact theory. Ostwald then goes on: "Berthelot makes a further argument intended to prove *a priori* the impossibility of such an identity. With bromin in water and carbon bisulfid the distribution coefficient has at each moment a finite value, while the solubility of bromin in carbon bisulfid and therefore the ratio of its solubility to the solubility in water is unlimited. This difficulty disappears if we give up the definition of the distribution ratio, selected for convenience only, which refers this value to equal volumes of the solutions and substitute for it the more rational reference to equal quantities of the solvent. If one takes the distribution coefficient as the ratio of the amounts of the solute in equal quantities of the two solvents, then in the case that the dissolved substance is infinitely miscible with one of the solvents the distribution coefficient will also be infinite for a saturated solution, that is one containing an infinite amount of the dissolved substance." This leaves the really important point untouched and is not strictly accurate in

the part that is taken up. If an infinite amount of bromin be added there will be only one solution and not two, because the solubility of water in bromin, though slight, is not zero. The important point, however, is the question why the distribution ratio of bromin in carbon bisulfid and water should have such a relatively low value for dilute solutions of bromin. In regard to this we have, as yet, no theory whatsoever, chiefly because no one has studied the application of Henry's law to mixtures of liquids, nor the way in which the system passes from concentrations for which Henry's law holds more or less accurately to concentrations for which the van't Hoff-Raoult formula holds more or less accurately.

The general results of this paper are:

1. Within the limits of experimental error the formula $\left(\frac{C_1}{A_1}\right)^n \div \left(\frac{C_2}{B_2}\right) = \text{constant}$ describes the equilibrium between conjugate solutions for a number of systems consisting of three metals.
2. With the exception of cadmium or antimony in zinc and lead the distribution ratio does not exceed two for any system not containing silver when the concentrations are expressed in grams per hundred grams of the two phases.
3. The distribution ratio for dilute solutions stands in no obvious relation to the reacting weights of the partially miscible metals.

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