5. A definite quantity of Form B, that produced by cooling about 0.55 g. of high grade gelatin in ice-water for 8 hours (or longer), is necessary to form a jelly of the degree of viscosity selected as a standard in this work. The presence of this quantity, slightly increased as concentrations increase, produces the standard jelly in much higher concentration of gelatin. Maximum gelation temperatures, or melting points, approach 33 to 35° as a limit as the concentration of gelatin increases. At these maximum gelation temperatures gelation is produced by the presence of the minimum quantity of Form B, 0.60 to 1.00 g., required for the formation of a jelly. Above 35° gelation does not take place in any concentration.

6. Additional evidence of the existence of two forms of gelatin, upon which gelation, in the case of gelatin solutions, is dependent, is found in observations made by the author on the behavior of such solutions when treated with alcohol, and in measurements of osmotic pressure, viscosity and of gold numbers, to which references have been given.

7. Gelatin sols dried above 35° and gels dried below 15° give different solid forms and while the gelatin in the solid state, so prepared, might or might not be in the same form in which it exists in the material from which it was prepared, there is some indication that the solid gelatin prepared by drying sols above 35° is the form existing in the sols.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

RELATIONS BETWEEN DISTRIBUTION RATIO, TEMPERATURE AND CONCENTRATION IN SYSTEM: WATER, ETHER, SUCCINIC ACID.

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When a substance is distributed between two pure solvents or two solvents, each of which dissolves a constant percentage of the other, the distributed substance being identical in both phases, the ratio of its concentrations in the two phases at any given temperature is usually assumed to be constant. The case of succinic acid in water and ether[1] has been much used as an example in elementary instruction. In this case, however, the ratio is found to be by no means constant, but varies by 7% more or less, when expressed in volume concentrations. This is hardly surprising when one considers that neither of the fundamental conditions is more than approximately fulfilled. The solvents are not pure, but each dissolves the other. If the composition of the solvents in the two layers were constant, there would be no reason to suppose that the constancy of the distribution ratio would be disturbed. But this is not the

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[1] Berthelot and Jungfleisch, *Ann. chim. phys.*, [4] 26, 396, 408 (1872).

case, for the composition of the solvents varies with the concentration of dissolved acid. In addition, the acid in the water layer at least, is electrolytically dissociated to an appreciable extent. Finally, if the temperature is not constant, the mutual solubilities vary in a complicated fashion.

All these complexities have been recognized, qualitatively at least, by previous investigators.[1] Thus Berthelot and Jungfleisch[2] showed the distribution ratio in the system under consideration, the concentration of the acid in the aqueous layer being in the numerator, to increase with temperature and dilution of acid. Klobbie[3] represented graphically the mutual solubilities of water, ether, and malonic acid throughout a wide range of temperature, and studied the distribution ratios. Schreinemakers[4] worked out a complete general scheme for equilibrium in such three-component systems. Nernst,[5] also Küster[6] and Tolloczko[7] investigated the lowering of solubility of one solvent in another resulting from the addition of a third substance soluble in only one of these. Rothmund and Wilsmore[8] showed that the solubility of the third substance also was lowered, and pointed out the relation between this fact and distribution ratios. Bödtker[9] concluded that the increased solubility of water in ether containing oxalic acid could best be explained by the formation of a compound of oxalic acid and water in ethereal solution. A similar compound of succinic acid and water seems to us less probable. Hantzsch and Sebaldt[10] demonstrated anew the importance of temperature changes, and concluded that the variation of the distribution ratio was a measure of the change suffered by the distributed substance. Hantzsch and Vagt[11] discussed and rejected the hypothesis that such fluctuations result from changes in the degree of polymerization of water with temperature. Herz and Kurzer[12] showed the distribution law applicable to mixed solvents, recognizing the importance of constancy in the composition of such mixed solvents, a consideration which will be again emphasized below. The actual value of the distribution ratio could not be calculated from the composition of the mixed solvents. Herz and Rathmann[13] attributed

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[1] Berthelot and Jungfleisch, *Ann. chim. phys.*, [4] **26**, 396, 408 (1872).

[2] Nernst, *Z. physik. Chem.*, **8**, 110 (1891); Herz and Fischer, *Ber.*, **37**, 4746 (1904); see the monograph, with bibliography, by W. Herz, *Ahrens Sammlung*, **15**, 1 (1910).

[3] Klobbie, *Z. physik. Chem.*, **24**, 615 (1897).

[4] Schreinemakers, *Ibid.*, **22**, 93, 515 (1897).

[5] Nernst, *Ibid.*, **6**, 16 (1890).

[6] Küster, *Ber.*, **27**, 328 (1894).

[7] Tolloczko, *Z. physik. Chem.*, **20**, 389 (1896).

[8] Rothmund and Wilsmore, *Ibid.*, **40**, 611 (1902).

[9] Bödtker, *Ibid.*, **22**, 505 (1897).

[10] Hantzsch and Sebaldt, *Ibid.*, **30**, 258 (1899).

[11] Hantzsch and Vagt, *Ibid.*, **38**, 710 (1901).

[12] Herz and Kurzer, *Z. Elektrochem.*, **16**, 240, 869 (1910).

[13] Herz and Rathmann, *Ibid.*, **19**, 552 (1913).

irregularities in the distribution of halogen, acetone and phenol between water and chlorinated aliphatic hydrocarbons to polymerization and solvation in the non-aqueous layer. A further advance was made by Lewis and Burrows,[1] who, to evaluate the activity of urea in equilibrium with water, ammonia, and carbon dioxide, distributed these solutes between the aqueous system and ethyl acetate. The solubility of urea in ethyl acetate containing various percentages of water was determined, and its solubility in the particular mixture of solvents formed in the experiment was found by extrapolation. Recently Georgievics[2] denies that only undissociated molecules are distributed—indeed he concludes that the distribution law is without value. Less radical hypotheses, however, may yet account for the complexities which he describes.

The puzzling irregularities in distribution ratios are clearly due to a complicated superposition of many conflicting tendencies. In view of the frequency and importance of distribution phenomena, these irregularities deserve further analysis, based on precise experimental data, and more thorough mathematical treatment.

The aim of this research is to derive and verify equations showing, in terms of less complex temperature and solubility coefficients, the variation of a distribution ratio with (1) temperature and (2) concentration of solute. Other variables, such as pressure, appear negligible under the conditions prevailing.

The published data on the solubilities and distribution ratios in question are not sufficiently numerous for present purposes. Nor are they sufficiently concordant for the evaluation of differentials. Consequently a complete set of new determinations was undertaken.

Materials.—Commercial succinic acid was twice recrystallized, and possessed the same solubility as a sample prepared several years before. The water was distilled from a block tin condenser. To make pure ether, several commercial samples were worked up—Squibb's anaesthetic, Kahlbaum's distilled over sodium, and Baker and Adamson's of the same grade. All were carefully purified by many washings, first with water, then with alkaline permanganate, then with water until free from alkali. The ether was then dried over calcium chloride followed by phosphoric anhydride, or in one case by sodium, and finally distilled, only the middle portion being used. Fresh ether was prepared every month, and stored in the dark. No inconsistency was ever found which could be traced to a difference between samples of ether from different sources. A very delicate test for alcohol is the green coloration of strong sodium hydroxide containing a little permanganate. If a drop of alcohol is added to 50 cc. of water in a test-tube, the whole poured out, and pure water added, the

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[1] Lewis and Burrows, THIS JOURNAL, 34, 1524 (1912).

[2] Georgievics, *C. A.*, 8, 7 (1914); 9, 2171, 2340 (1915).

resulting mixture will turn the reagent green almost immediately. The ether used was washed until this reaction did not occur when shaken 5 minutes with the reagent. Some stress is laid on this point, since our results on the solubility of ether in water are higher than those in the literature,[1] and we wished to feel certain that this did not proceed from insufficient purification. Rough preliminary experiments indicated that the presence of 1% of alcohol increased the solubility of ether in water by 2% of itself, and that of acid in ether by 20% of itself. The effect on the solubility of acid in water was much less.

The method of analysis adopted after discarding several others was as follows: A mixture of the desired composition was placed in a Pyrex vessel shaped like a submarine boat, Fig. 1, and shaken in a thermostat for a period previously determined to be sufficient to establish equilibrium. This shape had several advantages. The ground stopper was in contact neither with the contents of the vessel nor with the water of the thermostat. There was therefore no need to grease it, with the attending danger of contamination. The submarine could be rocked in the bath at such a speed that the air contained had time to go all the length of the tube and back, which gave thorough mixing. The rocking was stopped for 10 minutes to allow complete settling. By suitably inclining the tube, is was possible to extract either layer conveniently.

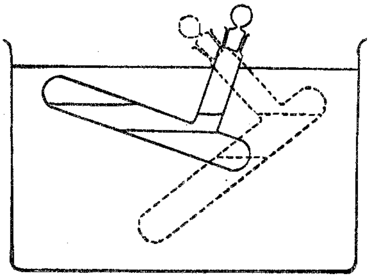

Fig. 1.—Vessel for attaining equilibria.

The pipets used for this purpose (Fig. 2) were made to fulfil the following requirements:

There must be little air space when the liquid has been introduced, as this is filled with ether vapor at the second weighing, involving an error proportional to its size. The pipet must be capable of being filled and emptied at will, without the use of greased stopcocks, or possibility of loss. The evaporation should be conducted in the vessel used for extraction of the sample, as each transference means loss of ether, especially by evaporation. To secure rapid evaporation, the air should pass over considera-

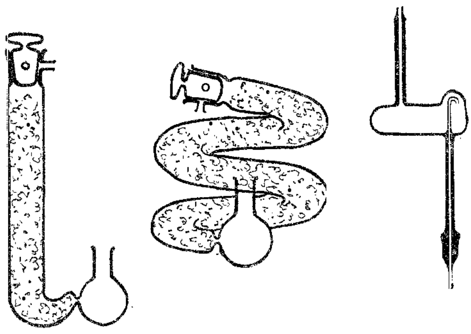

Fig. 2.—Pipets for analysis.

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[1] Landolt and Börnstein, *Tabellen*, 1912, p. 588.

ble surface of liquid. In order to minimize evaporation during filling, the pipets were previously filled with air saturated with ether vapor. Entrance of acid crystals was prevented by making the lower orifice very small. The small quantity of ether which entered the pipet intended for the water layer was blown out by a very little air saturated with ether before the sample was taken. Gentle suction was then applied until the pipet was nearly full, after which it was removed, and the liquid in the stem allowed to drain out.

For the determination of ether, the pipet was first weighed together with an absorption tube containing calcium chloride and of special design as shown (Fig. 2) which prevents the saturated solution of calcium chloride formed from running ahead in the tube, and wetting subsequent layers of absorbent. In the first weighing, the tubes had to be separate, with the grease for the joint entirely on the opening of the absorption tube, as the pipet must be scrupulously clean. After filling, the pipet was fitted into the tube and again weighed to obtain the weight of the sample for analysis. Air purified and dried with calcium chloride was now blown into the top of the pipet and over the surface of the liquid therein, from which the ether rapidly evaporated, and was determined by loss in weight. In the earlier determinations the end of the tube was filled with phosphorus pentoxide, and the current of air was dried with the same material. But it was soon found that results equally accurate could be obtained in much less time by the use of calcium chloride alone, both in the tubes and in the preliminary drying. Constant weight was obtained by the slow passage of 20 liters of air through the water layer tube, and of 25 liters through the ether layer tube.

As has been pointed out, the results obtained for the solubility of ether in pure water were somewhat higher than those given in the literature. They were therefore checked at 25° by an independent method. Sections of burets were substituted for the necks of 3 flasks of widely differing sizes. Weighed amounts of water and ether were introduced, the ends sealed, and the flasks shaken to equilibrium in the thermostat, first from a higher, then from a lower temperature. Things were so contrived that most of the ether dissolved, but a few cc. remained in the neck. Knowing the density, it was easy to calculate the weight of this amount of water-saturated ether and thence the weight of pure ether dissolved. Any systematic error here would have led to differing results, as the amounts taken were so different in the different flasks.

The following data on the solubility of ether in water at 25° demonstrate that both of the above methods are sufficiently accurate:

	% ether in water.			
Flask method	5.99	6.00	6.02	
Absorption method	5.98	5.98	6.02	6.03

In the ether layer, whose water content is of the order of one per cent. the flask method was not sufficiently accurate. The water was here determined by subtracting the weight of the acid found by titration from the gain in weight noted after complete expulsion of ether. To determine the acid, the pipet was simply inverted, and the contents washed into a flask and titrated with barium hydroxide. Two concentrations of the latter were used, both standardized directly against succinic acid, and indirectly against sodium carbonate by the use of a hydrochloric acid standard. The titrations, in which phenolphthalein was used as an indicator, were made in water free from carbon dioxide.

Table I, which follows, gives the percentage composition of saturated solutions. The first-mentioned solvent is in excess; the substance determined is placed last, in italics. As the solubility of ether in water was discussed above, only the extreme values are given below. Rejected values are bracketed.

Table I.—Percentage Composition of Saturated Solutions.

	15°.	20°.	25°.		15°.	20°.	25°.
Water-*ether*............	7.82	6.88	5.98	Ether-*water*......	1.03	1.07	1.19
	7.84	6.90	6.03		1.04	1.10	1.20
Water-acid-*ether*........	8.19	7.10	6.55		(1.11)	1.13	...
	8.22	7.23	6.56	Ether-acid-*water*...	1.38	1.52	1.66
	8.24	7.24	..		1.38	1.53	1.66
Water-*acid*............	5.09	6.30	7.67		1.44	...	...
	5.10	6.30	7.67		1.49	...	...
Water-ether-*acid*.......	5.68	7.09	8.75		(1.50)	...	...
	5.68	7.10	8.76		(1.52)	...	...
				Ether-*acid*.......	0.353	0.418	0.487
					0.354	0.422	0.488
				Ether-water-*acid*..	1.288	1.474	1.689
					1.289	1.477	1.689
					1.302	...	...

Table II, which follows, contains average values for saturated solutions. The densities were determined by a pycnometer, with capped ends, at 25° and 20°, and extrapolated to 15°. They render possible a conversion of the data to volume units.

Table II.—Composition and Densities of Saturated Solutions.

	Weight. %.			Mol. % undissociated.			Density $t°/4°$.		
	15°.	20°.	25°.	15°.	20°.	25°.	15°.	20°.	25°.
Water-*ether*.........	7.83	6.89	6.00	2.027	1.772	1.528	0.985	0.986	0.987
Water-acid-*ether*.....	8.22	7.23	6.56	2.246	1.985	1.821	0.999	1.005	1.010
Water-*acid*..........	5.09	6.30	7.67	0.803	1.005	1.241	1.012	1.016	1.021
Water-ether-*acid*....	5.68	7.10	8.76	0.964	1.211	1.512	0.999	1.005	1.010
Ether-*water*.........	1.04	1.10	1.19	4.1	4.4	4.7	0.722	0.718	7.14
Ether-acid-*water*.....	1.405	1.53	1.66	5.55	6.0	6.5	0.730	0.726	0.722
Ether-*acid*..........	0.353	0.420	0.487	0.222	0.264	0.305	0.719[1]	0.714[1]	0.710[1]
Ether-water-*acid*....	1.289	1.475	1.689	0.777	0.889	1.014	0.730[1]	0.726	0.722

[1] By extrapolation.

Tables III to V give the composition of solutions unsaturated with one of the three substances. Solutions in the first lines of each table are saturated with acid, but not with the second solvent; the solution saturated with both is in heavy type; the rest are saturated with the second solvent, but not with acid. The analyses of the solutions containing water as the principal solvent form the left half of each table. Moles of undissociated acid were figured assuming it to behave as a monobasic acid, $k = 0.000060$. Ionization in the ether layer was assumed to be negligible. Occasionally, in analyzing two layers in equilibrium, the determination of acid in one layer was lost, or the amount was too small to be determined accurately with the solutions at hand. In these cases,

TABLE III.—SOLUTIONS AT 15° UNSATURATED WITH ONE CONSTITUENT.

Water layer.					Ether layer.			
Ether.		Acid.		Undissociated.	Water.		Acid.	
%.	Mol. %.	%.	Mol. %.		%.	Mol. %.	%.	Mol. %.
0	0	5.05	0.813	0.803	0	0	0.353	0.222
0.34	0.087	5.11	0.817	0.807	0.03	0.1	0.39	0.244
1.60	0.242	5.18	0.838	0.828	0.41	1.7	0.61	0.376
4.22	1.112	5.36	0.887	0.877	0.51	2.0	0.68	0.423
5.37	1.430	5.44	0.907	0.897	0.76	3.0	0.86	0.528
5.86	1.567	5.49	0.922	0.912	1.27	5.0	1.186	0.720
8.22	**2.246**	**5.68**	**0.974**	**0.964**	1.33	5.3	1.236	0.748
8.22	2.222	(4.58)	0.778	0.768	1.34	5.3	1.254	0.759
8.20	2.218	4.11	0.698	0.689	**1.405**	**5.55**	**1.289**	**0.777**
8.25	2.209	3.47	0.584	0.576	1.36	5.4	1.03	0.62
8.07	2.153	3.22	0.536	0.528	1.21	4.8	0.77	0.46
8.06	2.140	2.69	0.448	0.441	1.17	4.6	0.59	0.36
8.06	2.131	2.28	0.378	0.371	1.16	4.6	0.50	0.30
7.94	2.090	1.73	0.286	0.280	1.07	4.2	(0.18)	0.11
7.91	2.063	0.82	0.134	0.131	1.04	4.1	0	0
7.83	2.027	0	0	0				

TABLE IV.—SOLUTIONS AT 20° UNSATURATED WITH ONE CONSTITUENT.

Water layer.					Ether layer.			
Ether.		Acid.		Undissociated.	Water.		Acid.	
%	Mol. %.	%.	Mol. %.		%.	Mol. %.	%.	Mol. %.
0.0	0.0	6.30	1.016	1.005	0	0	0.420	0.264
1.00	0.260	6.39	1.040	1.029	0.30	1.2	0.60	0.37
2.83	0.746	6.53	1.079	1.068	0.56	2.2	0.75	0.46
3.88	1.032	6.64	1.107	1.096	0.83	3.3	0.97	0.60
6.77	1.854	7.01	1.204	1.192	1.12	4.5	1.20	0.73
6.92	1.894	7.00	1.202	1.190	**1.53**	**6.0**	**1.475**	**0.889**
7.23	**1.985**	**7.10**	**1.223**	1.211	1.34	5.3	1.14	0.69
7.09	1.907	4.94	0.833	0.823	1.34	5.3	(1.00)	0.61
7.16	1.925	4.88	0.823	0.813	1.40	5.5	0.86	0.52
7.01	1.848	3.03	0.503	0.495	1.37	5.4	0.86	0.52
6.89	1.772	0	0	0	1.23	4.8	0.53	0.32
					1.10	4.4	0	0

TABLE V.—SOLUTIONS AT 25° UNSATURATED WITH ONE CONSTITUENT.

Water layer.					Ether layer.			
Ether.		Acid.			Water.		Acid.	
%.	Mol. %.	%.	Mol. %.	Undissociated.	%.	Mol. %.	%.	Mol. %.
0	0	7.67	1.253	1.241	0	0	0.487	0.305
0.49	0.128	7.73	1.267	1.255	0.22	0.9	0.66	0.41
1.85	0.490	7.91	1.315	1.303	0.60	2.4	0.90	0.55
2.10	0.556	7.95	1.323	1.311	0.62	2.5	0.91	0.56
3.53	...	7.99	...	...	0.68	2.7	0.95	0.58
3.26	0.875	8.12	1.367	1.355	1.07	4.3	1.27	0.77
4.02	1.085	8.21	1.393	1.381	1.24	4.9	1.34	0.81
3.89	1.051	8.23	1.395	1.383	1.39	5.5	1.49	0.90
4.28	1.164	8.31	1.416	1.403	**1.66**	**6.5**	**1.689**	**1.014**
5.49	1.507	8.49	1.463	1.450	1.53	6.0	1.21	0.73
6.14	1.696	8.62	1.494	1.481	1.51	5.9	1.21	0.73
6.03	1.665	8.67	1.502	1.489	1.42	5.6	0.80	0.48
6.56	**1.821**	**8.76**	**1.524**	**1.512**	1.41	5.5	0.79	0.48
6.39	1.732	6.44	1.094	1.083	1.32	(5.2)	...	...
6.24	1.658	4.38	0.730	0.721	1.29	(5.1)	0.41	0.25
6.09	1.585	2.27	0.370	0.365	1.19	4.7	0	0
6.00	1.528	0	0	0				

the amount of acid was calculated from the other layer, by means of the corresponding distribution ratio. Such results are given in parentheses.

Fig. 3 exhibits results for the water layer, Fig. 4 those for the ether layer. Curves starting from vertical axes represents the acid-saturated solutions recorded in the upper parts of Tables III to V. Curves starting from horizontal axes represent saturation with the secondary solvent, as recorded in the lower parts of these tables.

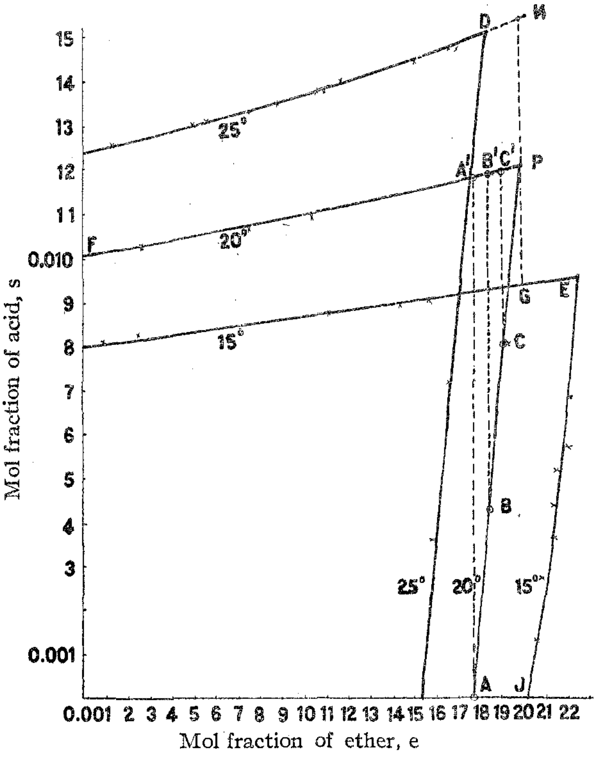

Fig. 3.—Saturation of water with succinic acid and with ether.

A series of measurements of the distribution ratio R was made at each of 3 temperatures, and at various concentrations of acid. The percentage accuracy of the results of course decreases as the dilution of acid titrated increases. The highest concentrations of acid, representing saturation, are identical with those given in Table I. The ratios are plotted in mols. per liter, also in mols. per hundred mols. of solution, corrected and uncorrected, in Figs. 5 and 6. The uncorrected results form the right-hand curve in each pair.

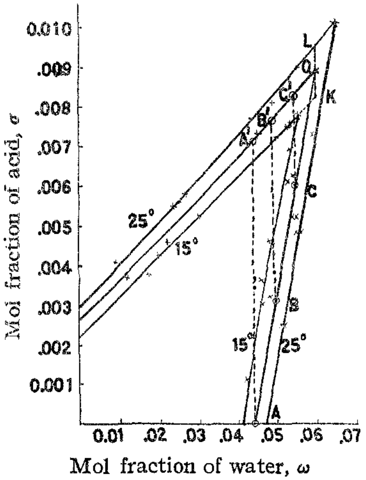

Fig. 4.—Saturation of ether with succinic acid and with water.

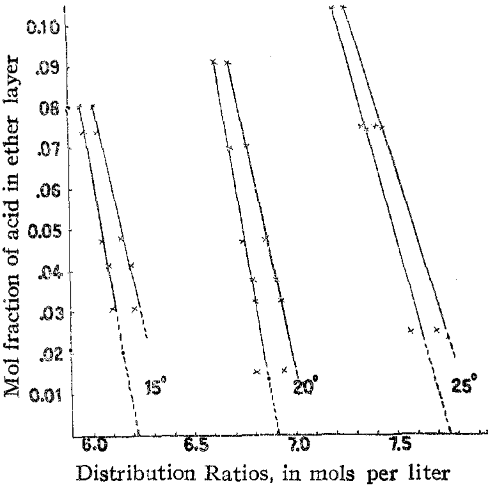

Fig. 5.—Changes in distribution ratio with concentration.

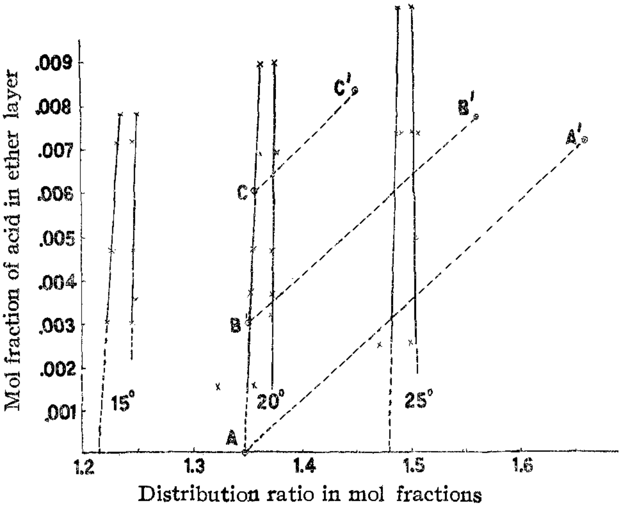

Fig. 6.—Changes in distribution ratio with concentration.

TABLE VI.—DISTRIBUTION RATIOS AT 15°.

Acid, % in water layer	2.285	2.689	3.475	5.22	5.68
Acid in mols. per liter	0.190	0.225	0.292	0.443	0.481
Same, undissociated	0.187	0.222	0.288	0.438	0.476
Acid, in mols. per hundred	0.3795	0.448	0.584	0.890	0.973
Same, undissociated	0.372	0.440	0.575	0.880	0.963
Acid, % in ether layer	0.5025	0.592	0.773	1.182	1.289
Acid in mols. per hundred	0.305	0.358	0.468	0.714	0.778
Distribution ratio in %	4.55	4.54	4.50	4.42	4.41
In mols. per liter	6.21	6.20	6.15	6.04	6.03
Same, undissociated	6.12	6.11	6.07	5.97	5.96
In mols. per hundred	1.245	1.249	1.247	1.246	1.250
Same, undissociated	1.223	1.229	1.228	1.233	1.237

TABLE VII.—DISTRIBUTION RATIOS AT 20°.

Acid, % in water layer	1.274	2.655	3.03	3.82	5.57	7.10
Acid, in mols. per liter	0.107	0.223	0.254	0.322	0.472	0.604
Same, undissociated	0.105	0.220	0.250	0.318	0.467	0.598
Acid, in mols. per hundred	0.2075	0.438	0.503	0.638	0.946	1.223
Same, undissociated	0.2025	0.431	0.495	0.629	0.936	1.211
Acid, % in ether layer	0.2525	0.528	0.605	0.768	1.137	1.475
Acid, in mols. per hundred	0.1535	0.319	0.366	0.465	0.686	0.889
Distribution ratio in %	5.04	5.03	5.01	4.97	4.90	4.82
In mols. per liter	6.94	6.93	6.90	6.85	6.77	6.68
Same, undissociated	6.80	6.80	6.79	6.75	6.69	6.61
In mols. per hundred	1.355	1.373	1.373	1.375	1.379	1.376
Same, undissociated	1.322	1.351	1.353	1.355	1.364	1.363

TABLE VIII.—DISTRIBUTION RATIOS AT 25°.

Acid, % in water layer	2.273	4.38	6.44	8.76	...
Acid, in mols. per liter	0.191	0.370	0.547	0.749	...
Same, undissociated	0.188	0.366	0.542	0.742	...
Acid, in mols. per hundred	0.371	0.730	1.098	1.525	...
Same, undissociated	0.364	0.720	1.088	1.513	...
Acid, % in ether layer	0.410	0.804	1.208	1.214	1.689
Acid, in mols. per hundred	0.248	0.485	0.727	0.731	1.014
Distribution ratios in %	5.54	5.45	5.33	5.31	5.19
In mols. per liter	7.69	7.58	7.43	7.40	7.26
Same, undissociated	7.56	7.49	7.36	7.33	7.20
In mols. per hundred	1.498	1.505	1.508	1.503	1.505
Same, undissociated	1.471	1.485	1.493	1.489	1.492

A rejected point was % in water 4.38, in ether 0.789, ratio 5.55.

Discussion.

An expression for the complete differential of the distribution ratio with respect to temperature was derived as follows:

s = mol. fraction of succinic acid (undissociated) in water layer.
e = mol. fraction of ether in water layer.
w = mol. fraction of water in water layer.
σ = mol. fraction of succinic acid in ether layer.
ω = mol. fraction of water in ether layer.
ϵ = mol. fraction of ether in ether layer.

The distribution ratio $R = s/\sigma$. Considering for the present only solutions mutually saturated at the various temperatures, $R = f(t)$.

$$dR/dt = (1/\sigma \,.\, ds/dt) - (s/\sigma^2 \,.\, d\sigma/dt). \qquad (1)$$

Let $a = [\delta s/\delta e]_t$, $b = [\delta s/\delta t]_e$, $m = [\delta e/\delta s]_t$, $n = [\delta e/\delta t]_s$.

Then
$$ds/dt = \delta s/\delta t + (\delta s/\delta e \,.\, de/dt) = b + a\, de/dt$$
$$de/dt = \delta e/\delta t + (\delta e/\delta s \,.\, ds/dt) = n + m\, ds/dt$$

Combining and eliminating de/dt,

$$ds/dt = (b + an)/(1 - am). \qquad (2)$$

Equation 2 shows how the 4 partial differentials a, b, m, and n together determine s as a function of t alone.

Similar reasoning applies to the ether layer, for which the corresponding Greek letters are used:

Let $\alpha = [\delta\sigma/\delta\omega]_t$, $\beta = [\delta\sigma/dt]_\omega$, $\mu = [\delta\omega/\delta\sigma]_t$, $\nu = [\delta\omega/\delta t]_\sigma$.

$$d\sigma/dt = (\beta + \alpha\nu)/(1 - \alpha\mu) \qquad (3)$$

Substituting (2) and (3) in (1)

$$dR/dt = (b + an)/\sigma(1 - am) - s(\beta + \alpha\nu)/\sigma^2(1 - \alpha\mu). \qquad (4)$$

This equation shows the complete differential of the distribution ratio with respect to temperature as a function of 8 partial differentials.

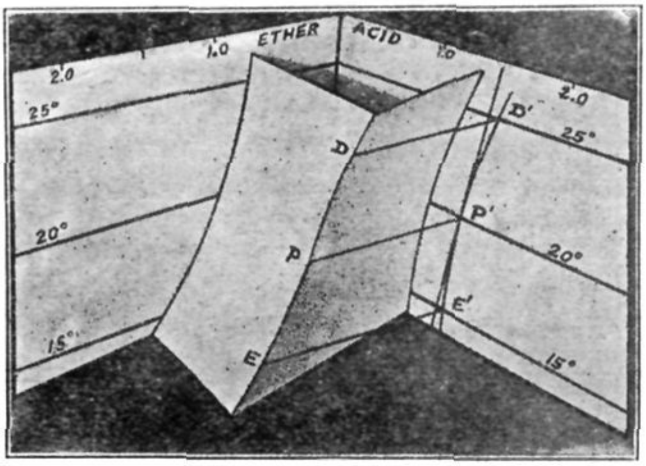

Fig. 7.—Relations between concentrations and temperature in the water layer.

This reasoning becomes clearer when followed out on a solid diagram, Fig. 7, representing the water layer. The curvatures are purposely exaggerated. We may take the acid and ether axes in the horizontal plane, and measure temperature vertically. Then there will be a curved surface representing all solutions saturated with acid, but containing any amount of ether, and at any temperature, while another surface will represent the amounts of ether which will dissolve in various acid solutions at various temperatures. These two surfaces will intersect in a twisted curve DE, which will represent the amounts of acid and of ether which will dissolve together at any temperature. This curve will need for its definition two equations between e, s, and t. But we can eliminate any one of these variables, say e, having left a single equation between the other two, which defines the projection D'E' of the original twisted curve upon the acid plane. The tangent to the twisted curve at P is defined by two linear equations, from which one variable can be eliminated, leaving the equation of the tangent to the projection on a principal plane. Finally, these equations can all be expressed in the differential form. This is precisely what we have done. We have conbined the differential equations of the tangent planes to the two surfaces, whose intersection is the tangent to the twisted curve. We have eliminated e from these equations, obtaining a single differential equation for the tangent to the projection upon the s, t plane, which shows s as a function of t alone.

The reason for dealing with tangent planes and lines, instead of with the original surfaces and curves, is that the tangents may be determined experimentally with much less work than would be necessary to show the form of the whole surface or curve.

The ether layer may be discussed in a similar fashion.

To verify Equation 4, at 20° the values of a and m are first found by drawing tangents to the curves at P in Fig. 3, and to the curves at Q in Fig. 4, in all cases at the intersections representing mutual saturation, according to the assumption underlying the formula. Reading the slopes,

$$a = 0.132 \qquad \alpha = 0.107$$
$$m = 0.176 \qquad \mu = 2.0$$

The temperature coefficients are obtained with the help of the assumption that they are the same at 20° as the average values from 15° to 25°, which is probably nearly true. Nevertheless, had time permitted, we should have made experiments at other temperatures to get more light on the exact form of the temperature curves. The values of $b\,\Delta t$ and $\beta\,\Delta t$ were laid off in Figs. 3 and 4 vertically (not GH and KL) between the curves for 15° and 25° (extrapolated) so as to pass through the mutual saturation points P and Q at 20°. Read from large scale curves $b = [\delta s/\delta t]_{e\,=\,0.01985} = 0.000602$; $\beta = [\delta\sigma/\delta t]_{\omega\,=\,0.060} = 0.000129$.

The values of n and ν were determined in a similar fashion, and the values of $n\,\Delta t$ and $\nu\,\Delta t$ were drawn horizontally through the mutual saturation points P and Q at 20°.

$$n = [\delta e/\delta t]_{s\,=\,0.01211} = -0.000530.$$
$$\nu = [\delta\omega/\delta t]_{s\,=\,0.00889} = 0.00050.$$

Finally, by direct experiment

$$s = 0.01211 \qquad \sigma = 0.00889$$
$$e = 0.01985 \qquad \omega = 0.060$$

Substituted in Equation 4, these values give

$$dR/dT = 0.0258.$$

Direct calculation from the distribution ratios at 15° and 25° gives

$$\Delta R/\Delta t = (1.492 - 1.237) \div 10 = 0.0255.$$

We have therefore succeeded in reducing the temperature coefficient of the distribution ratio into 8 much simpler coefficients—4 of temperature, and 4 of mutual solubility, effects. Of course, these effects themselves are by no means simple, but are determined, in the first case for example, by the separate effects of temperature upon the rates of diffusion of components in and out of the phases involved. But an attempt to analyze them further would be out of place in the present connection. It would be better to attack them singly than to complicate our formula further by expanding each of the 8 coefficients. We are content to have traced effects so familiar and easy of measurement as temperature and mutual solubility coefficients.

There is, however, a slight inconsistency in our formulation of the problem. We have measured concentrations throughout in mol. fractions of the solution—the ratio of the number of mols. of the substance present, to the total number of mols. present. This is correct with respect to the distributed substance, because the law of the constancy of the ratio of distribution rests on the proposition that the activity of the substance in both layers is proportional to its mol. fraction. But when dealing with the effect of temperature on single solubilities, we should maintain constant, not the proportion of the third component in the solution, but rather its proportion in the solvent. For example, if we are interested to find how much succinic acid will dissolve at various temperatures in a solvent composed of 19 parts of water and one of ether, we can easily investigate this by shaking acid with liquid of this composition. Of course, as acid dissolves, the proportion of both the other components to the whole will decrease. Either one, but not both, could be maintained constant by the addition of the pure substance, but that would be an arbitrary procedure, and the results would not yield a pure partial derivative. We ought to investigate the distribution ratio between solutions having constant composition of *solvent* (as Herz and Kurzer[1] have done empirically), and in investigating the effects of changing solvents at constant temperature, we should express the changes in the same system. This consideration is not very important in dilute solutions, but as it can easily be done, the calculations in these units seems worth while.

Let $s' = s/(w + s) = s/(w + e + s - e) = s/(1 - e)$, the proportion of acid in the water-acid solvent.

Likewise
$$e' = e/(1 - s)$$
$$\sigma' = \sigma/(1 - \omega)$$
$$\omega' = \omega/(1 - \sigma).$$

Further, let $a' = \delta s/\delta e'$ $b' = \delta s/\delta t_{[e' = \text{constant}]}$ $m' = \delta e/\delta s'$ $n' = \delta e/\delta t_{[s' = \text{constant}]}$ with corresponding Greek letters for the ether layer.

Then $ds/dt = \delta s de'/\delta e' dt + \delta s/\delta t_{[e']} = a' \, de'/dt + b'$.

But
$$de'/dt = \frac{(1 - s)de/dt + e\, ds/dt}{(1 - s)^2}.$$

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[1] Herz and Kurzer, *Loc. cit.*

Whence
$$ds/dt = \frac{b' + a'de/(1 - s)\,dt}{1 - a'e/(1 - s)^2}. \tag{5}$$

Likewise
$$de/dt = \frac{n' + m'ds/(1 - e)dt}{1 - m'\ s/(1 - e)^2}.$$

Eliminating *de/dt*,

$$ds/dt = \frac{b'(1 - m's/(1 - e)^2) + a'n'/(1 - s)}{(1 - m's/(1 - e)^2)(1 - a'e/(1 - s)^2)a'm'/(1 - s)(1 - e)}. \tag{6}$$

And finally

$$dR/dt = \frac{b'(1 - m's/(1 - e)^2) + a'n'/(1 - s)}{\sigma[(1 - m's/(1 - e)^2)(1 - a'e/(1 - s)^2) - a'm'/(1 - s)(1 - e)]} - \frac{s[\beta'(1 - \mu'\sigma/(1 - \omega)^2) + \alpha'v'/(1 - \sigma)]}{\sigma^2[(1 - \mu'\sigma/(1 - \omega)^2)(1 - \alpha'\omega/(1 - \sigma)^2) - \alpha'\mu'/(1 - \sigma)(1 - \omega)]}. \tag{7}$$

The evaluation of these constants may most easily be done graphically. If from every point on the principal axis of ether, for example, in the water layer, Fig. 3, a line is drawn so as to pass through the point $s = 1.000$, $e = 0$, then it will be found that all points on any one of these lines will represent solutions of ether in water (real or imaginary) in which the ratio of ether to water is constant. The line J H, passing through P, is such a line, for all points on which $e' = 0.002010$. Now at H, $s = 0.01542$, and at G, $s = 0.00943$; therefore $b'\Delta t = 0.00599$, and $b' = 0.000599$. Another set of lines drawn to meet $e = 1.000$, $s = 0$, allows the evaluation of n' in a similar way. These sets of lines may be designated the e' coördinates and the s' coördinates, the original vertical and horizontal lines being the e and s coördinates. In order to measure $a' = \delta s/\delta e'$, one takes the slope of FP at P, with respect to the s and the e' coördinates, while $m = \delta e/\delta s'$ is the slope of AP at P in terms of the s' and e coördinates. The ether layer is treated similarly.

The values of the quantities involved are

$a' = 0.130$ $\alpha' = 0.106$
$b' = 0.000599$ $\beta' = 0.000128$
$m' = 0.172$ $\mu' = 1.9$
$n' = -0.000535$ $\nu' = 0.00048$

As is apparent, these values are only slightly different from those used in evaluating Equation 4, and they lead, when substituted in Equation 7, to practically the same result, namely,

$$dR/dt = 0.0257.$$

Equation 7, therefore, satisfactorily derives the total effect of temperature changes upon the distribution ratio, from the effects of temperature upon the solubilities involved, the composition of the solvent being kept constant, and from the separate effects of changing solvent at constant temperature.

2. The Effect of Concentration.

We are now in a position to investigate the effect upon the distribution ratio, of changes in concentration of succinic acid, the temperature being kept constant. This should be a fruitful field for research, since much of the progress of science in recent years has resulted from studies of the deviations of phenomena from simple but only approximate expressions of the fundamental laws.

Distribution ratios have usually been expressed directly as the ratios of experimentally determined concentrations in mols. or grams per liter of solvent. So long as one works in dilute solutions, and is satisfied with constants which vary 2 or 3%, this method is good enough. Of course, the correct method is to reckon in mol. fractions of the total, since this quantity measures the activity of a substance in an ideal solution. We have given our results in both units, for the sake of comparison. It will be observed that while the ratio, reckoned by volume (Fig. 5), or by weight (see Tables VI to VIII), falls off rapidly with rising concentration of acid, the mol. ratio, uncorrected for dissociation, is constant within the experimental error (Fig. 6), which emphasizes the danger of assuming that all methods of reckoning concentrations are interchangeable in "dilute" solutions of 5% or thereabouts.

But the constancy of the ratio reckoned in mol. fractions can hardly have real significance. A correction for dissociation must be applied, whereupon the ratio of undissociated mols. is found to increase slightly (Fig. 6). The correction for association of water will be in the opposite sense. Let us recalculate R in mol. fractions for two points found at 20°, under the assumption that the molecular weight of water is 36.

$H_2O = 18$.			$(H_2O)_2 = 36$.		
s.	*σ.*	*R.*	*s.*	*σ.*	*R.*
0.00431	0.00319	1.351	0.00846	0.00327	2.592
0.01211	0.00889	1.363	0.02358	0.00917	2.574

The distribution ratio could be made constant by assuming an average molecular weight for water intermediate between 18 and 36. But even if this correction should exactly balance that due to dissociation, the resulting constancy would have to be considered as a mere accident, because the composition of the solvents in both layers changes with the acid concentration.

Without a membrane permeable to acid, but not to water or ether, it would be impossible to measure directly distribution ratios between solvents of constant composition. Such a membrane might conceivably be found in a liquid immiscible with water and ether, but able to dissolve succinic acid. In the absence of such a membrane, we can nevertheless get a very good idea of this, the true distribution ratio, as follows: Take any point on the curve of distribution ratios, noting σ in the ether layer.

Find from Fig. 4 the value of ω for such a solution. Using the value R, calculate s, in the water layer, and find from Fig. 3 the value of e for such a solution. Next draw through the points thus determined lines so inclined to the vertical axes that they would meet these at the points $\sigma = 1$ and $s = 1$, respectively. When drawn thus, they automatically represent solutions having the same composition of solvent. The intersections of these lines with the curves for saturated, undissociated succinic acid fix the solubilities σ_0 and s_0 of undissociated succinic acid in solvents of the given constant compositions. If such a pair of saturated solutions, ethereal and aqueous, were separated by a membrane permeable to succinic acid *only*, they would be in equilibrium. The corresponding ratio of succinic acid concentrations is the distribution ratio (measured in mols. of undissociated acid) between solvents of the given constant compositions when saturated with acid. Such a calculation is made for points A, B, and C; and the new points A′, B′, and C′ are plotted in their proper positions in Figs. 3, 4, and 6.

Point.	R.	σ.	ω.	s.	e.	σ_0.	s_0.	$s_0/\sigma_0 = R'$.	Point.
C	1.358	0.00606	0.055	0.00823	0.01907	0.00827	0.0120	1.451	C′
B	1.351	0.00319	0.049	0.00431	0.0185	0.00762	0.0119	1.562	B′
A	1.347	0.00000	0.044	0.00000	0.01772	0.00710	0.0118	1.662	A′

Some curve (probably not far from a straight line) connecting C and C′ represents the distribution ratio of succinic acid between an ether layer in which $\epsilon/\omega = 0.939/0.055$ and a water layer in which $w/e = 0.8986/0.0191$ from the concentrations $\sigma = 0.00606$ and $s = 0.0823$ up to saturation. So also for the lines BB′ and AA′ (Fig. 6).

The distribution ratio thus calculated is seen to increase strongly with increasing concentration of acid, whereas theory would seem to demand that this ratio be independent of the concentration of acid. The truth of this latter statement will not be impaired by making the correction for association of water, as discussed above. For if the calculation just described is made with the assumption that the molecular weight of water is as improbably high as 6×18 or 108, $R = 7.16$ at infinite dilution, and 8.41 at saturation, *i. e.*, the ratio is still found to rise rapidly with the acid concentration, in spite of the tendency, already shown, for increasing molecular weight of water to make R fall with increasing values of σ. Therefore the ratio must increase for any value of M between 18 and 108.

We have therefore established that succinic acid is not distributed in constant ratio between water and ether, when the calculation is made in a rigorous manner. This can mean only that the ratio of activity to concentration in aqueous solution falls with increasing concentration, or more strictly, that this deviation is greater in water than in ether solution. It would be interesting to see whether the inconsistency could be explained by data at all concentrations on the exact molecular state of every substance involved. Solvation undoubtedly is largely responsible.

3. The Molecular State of Water in Ether Solution.

It is interesting to attempt to apply Rothmund's[1] mutual solubility equation to the solubility data. Since this equation is derived by assuming that each substance follows Henry's law in unchanging solvents, and since we have just proved that succinic acid does not follow this law in aqueous solutions, it is useless to expect good results from the water layer. But the irregularities are probably less in the ether layer, since ether is a normal (unassociated) liquid.

The solubility of acid in ether saturated with water is 0.00889, in pure ether it is 0.00264, all at 20°. Call these quantities σ_0 and σ.

Then Rothmund's law requires that

$$\sigma_0 \log (\sigma/\sigma_0) = \omega_0 \log (\omega/\omega_0),$$

where ω's, as before, refer to the water. We cannot evaluate then without knowing the true molecular weight of water, but we can get their ratio without this, and can then use the equation to obtain an indication of the true molecular weight.

On the basis of $H_2O = 18$, we have $\omega_0 = 0.060$, $\omega = 0.044$; but the last value is too large. For what is wanted is the solubility of water from the same phase which was in equilibrium with the triply saturated solution. When water already saturated with ether is further saturated with succinic acid, its solubility in another phase is reduced, according to Nernst, in proportion to the mol. fraction of new substances added, in this case about 1.5%. The amount of water from the triply saturated aqueous solution which would dissolve in pure ether through a membrane permeable to water only would therefore be not 0.044 but 0.0434.

$$\sigma_0 \log (\sigma/\sigma_0) = 0.00468 \log (\omega/\omega_0) = 0.141,$$

whence $\omega_0 = 0.033$ instead of 0.060.

This means that 60 molecules of H_2O furnish 33 molecules of water, which therefore consist almost entirely of $(H_2O)_2$. This result is not to be taken as accurate, but it agrees quite well with estimates made by other workers[2] using different methods.

4. Summary.

1. Measurements are given of the solubilities of ether, water, and succinic acid in two and three component systems between 15° and 25°.
2. Measurements are given of the distribution ratio of succinic acid between water and ether at various concentrations and temperatures.
3. An equation is derived in two stages of approximation and verified showing the temperature coefficient of the saturated distribution ratio as a function of the temperature and mutual solubility coefficients of each substance in each layer.

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[1] *Z. Elektrochem.*, **7**, 675 (1901); see also Nernst, *Z. physik. Chem.*, **38**, 487 (1901).

[2] See the bibliography by Richards and Palitzsch. THIS JOURNAL, **41**, 64 (1919).

4. It is shown that the distribution ratio, when calculated on a basis of unchanging solvents, increases sharply with the concentration of acid, even after corrections for dissociation of acid and association of water.

5. It is shown to be probable that the average state of association of water dissolved in ether is somewhat less than two.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY.]

CHEMICAL REACTIONS AT LOW PRESSURES. IV. THE CLEAN-UP OF NITROGEN BY A HEATED MOLYBDENUM FILAMENT.[1]

BY IRVING LANGMUIR.

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In previous papers[2] it has been shown that a tungsten filament heated in a fairly high vacuum to a temperature at which vaporization occurs, causes a disappearance or clean-up of practically all the common gases except the inert gases such as argon. This phenomena has often been used in this laboratory to obtain a particularly high vacuum.[3]

It is well known that molybdenum at its melting point evaporates very rapidly, in fact much more rapidly than tungsten at its melting point. If then molybdenum vapor shows the same tendency as tungsten vapor to react with gases, the use of a heated molybdenum filament would seem to offer a still more promising method of obtaining a high vacuum. With this end in view, experiments were undertaken to study the clean-up of nitrogen by a heated molybdenum filament. It was soon found that this metal was much less suitable than tungsten for the purpose. Whereas with tungsten the clean-up is quite rapid at any temperature sufficiently high to produce perceptible volatilization of the metal, with molybdenum enough material may evaporate to darken the bulb considerably before any clean-up is observed. It was found, however, by raising the temperature of the filament still higher that rapid clean-up does occur, and that just as in the case of tungsten, the *rate of clean-up is independent of the pressure* of the gas. This fact seemed very peculiar, for the explanation that had previously been given for the case of tungsten, namely that the nitrogen combines quantitatively with the metallic vapor as fast as it is produced, certainly does not apply here.

The resistance of the filament in the experiments with molybdenum

[1] Most of the experimental work described in this paper was carried out during 1913 and 1914. A very brief summary of the results was published in THIS JOURNAL, **37**, 1157 (1915).

[2] THIS JOURNAL, **34**, 1310 (1912); **35**, 105, 931 (1913); *Trans. Amer. Inst. Elec. Eng.*, **32**, 1895 (1913); *Z. anorg. Chem.*, **85**, 261 (1914).

[3] See for example Langmuir, *Physik. Z.*, **15**, 519 (1914).