

V. Summary.

1. The potential of the system



has been found to be 0.3988 ± 0.0002 .

2. The variations in the electromotive force of this system are probably due to a chemical change in the calomel electrode by which the potential increases with time.

3. This series of experiments indicates that within the limits of experimental error, probably within 1%, hydrochloric acid and potassium chloride are equally dissociated at tenth-normal concentrations.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE SOLUBILITIES OF LIQUIDS IN LIQUIDS. THE PARTITION OF THE LOWER ALCOHOLS BETWEEN WATER AND COTTONSEED OIL.

BY B. B. WROTH AND E. EMMET REID.

Received September 13, 1916.

Introduction.

According to the commonly accepted partition law a solute C is partitioned between two immiscible solvents, in contact with each other,

$$\frac{C_a}{C_b} = r = \frac{S_a}{S_b}$$

in which C_a and C_b are the concentrations of C in the solvents A and B, respectively, r is a constant ratio, and S_a and S_b are the solubilities of the solute in the two solvents. It has frequently been shown that r is constant only when the solute C exists in the two solvents in the same molecular aggregation. The equality of $C_a/C_b = r = S_a/S_b$ has been proved for iodine partitioned between water and carbon disulfide, bromoform, and carbon tetrachloride by Jakowkin.¹ His results are as follows:

From solubilities in				From partition experiments.
A.	B.	S_a .	S_b .	
CS ₂	H ₂ O	230	÷ 0.3387 = 679	685
CHBr ₃	H ₂ O	189.55	÷ 0.3387 = 559	558.5
CCl ₄	H ₂ O	30.33	÷ 0.3387 = 89.6	89.7

cepted to represent the ion-activity of the salt, there is reason to assume that the ion-activity of the acid is 0.0755."

A possible explanation of the slight discrepancy between the conclusion of his article and this one may be found in the value which he adopted for the contact potential of 0.1 N HCl-0.1 N KCl. It will be noted that our conclusion is based upon the assumption that this contact potential is -0.0284 volt. If a lower value of this contact potential, such as found by Bjerrum, is correct, then the potential of the calomel electrode toward a solution of 0.1 N KCl is greater than that of a calomel electrode toward a solution of 0.1 N HCl. In other words, if such is the case, 0.1 N HCl is slightly more dissociated than 0.1 N KCl.

¹ *Z. physik. Chem.*, 18, 590 (1895).

Of course, this law holds strictly only in the ideal case where the solvents A and B are absolutely immiscible and neither modifies the solvent power of the other in the slightest. If any appreciable amount of A dissolves in B, the solvent power of B for C is thereby altered and *vice versa*. Steiner¹ and Gordon² have shown that the solubilities of gases in water are much altered by the presence of even small quantities of salts in solutions. However, this is not contradicting the partition law, but simply saying that the value of S_a and of S_b should be the solubilities of C in A saturated with B and in B saturated with A, rather than the solubilities in the pure solvents.

Jakowkin³ has also shown that r changes progressively with the amount of solute C and that the value of r approaches S_a/S_b when larger and larger quantities of C are added. When C_a and C_b approach zero, r approaches another limit which is more properly its ideal value, as only when C_a and C_b are very small are the solvents A and B unaltered by the presence of C. When larger amounts of C are present A and B become mutually more soluble and the properties of both solvents are altered. In the present work the smallest practicable amounts of C were used.

Assuming $C_a/C_b = r = S_a/S_b$, since there are five quantities in this double equation, we may determine any three and calculate the other two. Thus if we measure C_a and C_b and thus find r we need to measure S_a in order to calculate S_b .

Such results must, of course, be considered in the light of the above considerations and be accepted with reserve. The present work was undertaken with the aim of applying this to the calculations of solubilities in the case of certain very soluble liquids. The results are considered as suggestive rather than as conclusive. They mean something, but just what they mean may be left for future consideration.

In a series of experiments in which ethyl alcohol was partitioned between cottonseed oil A, and water B, r was found to be 28.3. The average of a series of experiments gave the solubility of alcohol in the oil, S_a as 21.1 g. per 100 cc. Calculation gives S_b as the solubility of the alcohol in 100 cc. water as 600 g. There are many substances of which water dissolves several times its own weight. For instance, 100 cc. of water dissolve 339 g. of cadmium chlorate at 0° and 549 g. at 65°. In these cases, however, though the solubility is great, it is still limited. One hundred grams of water dissolve 907 g. of calcium iodide at 0° but stops there, and if we shake it with 910 g., 3 g. of the salt are left over, while the 100 g. of water dissolve 600 g. of alcohol, but if more alcohol is added it too disappears in the solution.

¹ *Wied. Ann.*, 52, 275 (1894).

² *Z. physik. Chem.*, 18, 520 (1895).

³ *Ibid.*, 18, 590 (1895).

An examination of the phenomena shows that there is an essential difference between a solid solute and a liquid solute in contact with a solvent. The solid solute, except such substances as gelatine, does not absorb or dissolve the solvent, while the liquid solute plays the role of solvent and the result is two solutions. Thus, if dry ether be added to water, the ether which is not dissolved does not remain anhydrous, but dissolves a considerable amount of the water. The figure 600 obtained for the solubility of alcohol in water, is for anhydrous alcohol in contact with its solution in water. If the alcohol were separated from the water by a semipermeable diaphragm, through which the alcohol alone could pass, this condition might possibly be realized.

Such numbers as these, representing a sort of ideal solubilities, are of interest for the comparison of the properties of the members of a series. They have a practical value in the study of extractions.

The lower alcohols have been studied in the hope of being able to arrange them in a series, so as to show the variation of solubility with molecular weight.

It is difficult to find a suitable liquid for the solvent A, since most liquids that are insoluble in water, dissolve too much of the alcohols. Cottonseed oil was chosen on account of its insolubility in water, its non-volatility, and its accessibility. It served the purpose only fairly well since it is rather difficult to handle and gives up a small amount of volatile matter when steam distilled. It mixes with the higher alcohols, so only partition ratios could be determined with these.

Meyer¹ in a study of the influence of temperature upon the partition coefficient has determined the distribution ratio of ethyl alcohol between olive oil and water. His determinations were made at 3° and 30° with the following results:

	G. substance per 100 cc. of		C_w/C_o .	Mean.
	Water layer.	Oil layer.		
3°	2.69	0.09	29.8	42.7
3°	3.90	0.07	55.7	
30°	2.64	0.14	18.8	21.3
30°	3.82	0.16	23.8	

The wide variation in his results is due to the fact that he determined the alcohol in the oil layer by difference, throwing all the error on the smaller quantity.

His results at 30° approximate those obtained in the present work for the similar cottonseed oil.

Materials.

Cottonseed Oil.—The ordinary oil was purified by distilling with steam for about two hundred hours. When the density of the distillate ap-

¹ *Arch. exp. Path. Pharm.*, 46, 344 (1901).

proached the density of pure water, the oil was assumed to be ready for use. A small amount of alkali in water was added to neutralize and dissolve any free acid, and the oil filtered through a dry paper in a hot water funnel.

Later in the work it was found that Wessen oil required only one day of distilling with steam before being ready for use, and it was then used in the place of the ordinary commercial oil.

Ethyl Alcohol.—The ethyl alcohol was refluxed with lime for a period of several days and distilled. It had a density of $0.78543^{25}/4$ corresponding to 99.92% alcohol.

Methyl Alcohol.—Difficulty was experienced in dehydrating methyl alcohol. It was first refluxed with lime for several days, then with anhydrous copper sulfate, then finally with metallic calcium. Density $0.79580^{25}/4$ corresponding to 99.95% alcohol.

Propyl, Isobutyl and Isoamyl Alcohols.—All three alcohols were refluxed with metallic calcium for several days and assumed to be practically anhydrous. Their densities were $0.80715^{25}/4$, $0.79949^{25}/4$ and $0.81225^{25}/4$, respectively, not corrected for air displacement.

Procedure.

Weighed amounts of oil and water were placed in a 200 cc. glass stoppered bottle. With the lower alcohols several volumes of oil were used to one of water, so as to increase the alcohol in the oil layer. To this mixture a quantity of alcohol, weighed from a pycnometer, was added. A piece of sheet rubber was stretched over the stopper and securely tied around the neck of the bottle. The bottles were then placed in the shaking machine and shaken for one hour in a constant temperature bath at 25° . The bottles were completely submerged in the bath during the shaking. It was found that it required three weeks' standing at 25° for the layers to separate clear. To obviate this delay, the bottles containing the mixture were centrifuged at 1350 revolutions per minute until the layers became clear. The temperature of the centrifuge was not regulated but was usually not far from 25° .

It was found to require about six hours' centrifuging for the ethyl and methyl alcohol mixtures while the propyl, isobutyl and isoamyl required about three hours.

The bottles were then placed in the 25° bath until ready for analysis.

Estimation of Alcohol in Oil Layer.—The oil layer containing the alcohol was drawn off by means of a special pipet, shaped something like an Ostwald pycnometer. A suitable amount of the oil was weighed out of the pipet into a Kjeldahl flask, out of which it was distilled with steam. The flask was provided with an efficient trap to prevent splashing over. The receiver was provided with a cork having a small opening, and was placed in an ice bath to diminish evaporation.

The alcohol in the weighed distillate was estimated either by the usual density method or by the interferometer. For the interferometer work a table was prepared for each alcohol. Small weighed bulbs were filled with the anhydrous alcohol, sealed and weighed. These bulbs were broken in glass stoppered bottles containing weighed amounts of water. The interferometer readings of a number of these mixtures were plotted against the percentages of the alcohols. From this a table was calculated, which was used in determining the composition of the distillate.

The interferometer readings with weighed mixtures of alcohols and water are given in the following table:

	Methyl Alcohol.					Isobutyl Alcohol.			
CH ₃ OH %	0.821%	1.50	3.99		C ₄ H ₉ OH %	1.89%	2.95	3.18	4.21
Reading	0.62	1.08	2.87		Reading	7.31	11.30	12.17	16.40
Reading for 1%	0.75	0.72	0.72		Reading for 1%	3.86	3.82	3.82	3.89
	Propyl Alcohol.					Isoamyl Alcohol.			
C ₃ H ₇ OH %	1.84%	2.67	3.39	4.24	C ₅ H ₁₁ OH %	1.42%	2.31		
Reading	5.75	8.57	11.07	14.48	Reading	5.96	9.72		
Reading for 1%	3.12	3.20	3.26	3.41	Reading for 1%	4.19	4.20		

When cottonseed oil is distilled with steam, no matter how long the process is continued, the distillate always contains a small amount of something which changes its density slightly and also gives a reading in the interferometer. The composition of this distillate remains nearly constant for a long time. The densities of the alcoholic distillates were corrected for this by taking densities of distillates obtained with the same lot of oil containing no alcohol. In the interferometer work the steam distillation of the sample of the oil layer was continued for a considerable time after all of the alcohol had passed over. A specimen of the distillate collected at the end of this distillation was used, instead of pure water, in the other cell of the interferometer. Since the interferometer is a differential instrument, the reading thus obtained represented the amount of alcohol present.

A weighed portion of the filtered water layer was distilled in the Kjeldahl flask and the alcohol determined as above.

For the experiments with ethyl alcohol the pycnometer was used and for the other alcohols the interferometer for estimation of the alcohol.

The absolute solubilities of ethyl and methyl alcohol in the oil were found by adding a weighed amount of alcohol to a weighed amount of oil in a small separating funnel. The mixture was then shaken in a constant temperature bath at 25° for two hours.

The funnels were allowed to remain in the bath until the layers became clear. A sample of the oil layer was then drawn off into a Kjeldahl flask and steam distilled, the amount of alcohol being determined as in the above experiments. The funnel was weighed before and after to

get weight of sample. Since alcohol evaporates from this saturated oil solution very readily, much care was taken to effect this transfer with the least possible exposure to the air, but even then it was difficult to obtain concordant results.

Weighed portions of the alcohol layers were evaporated in wide-mouth weighing bottles on a steam bath. The film of oil gained weight on long heating. This materially interfered with the accuracy of the results.

Results.

The results are given in the table below.

The experiments are given in the order in which they were made and none are omitted except preliminary experiments at beginning of first two series.

In Column 1 is given volume of oil, which was obtained by dividing the weight of oil put in by 0.922, the density of the oil used. In Column 4 is given weight of alcohol for the total oil layer, calculated from the analysis of a weighed portion of the oil layer, while in Column 5 is the amount of alcohol for the total water layer found in the same way. The sums of these amounts of alcohol are given in Column 6. These sums should equal the amounts put in, which are given in Column 3. The amounts found are usually less, indicating loss of alcohol somewhere in the operations. It is likely that most of this alcohol is lost in handling the water layer as this had to be filtered. Excess of alcohol found over that put in may be explained by error in pycnometer estimation or by presence of volatile matter other than alcohol in the distillate. The distillates from the oil layer were usually about 60 cc. so that the total alcohol present amounted to only about 2% in the distillate.

Columns 7 and 8 contain the amounts of alcohol calculated from 100 cc. of oil and water, and the ratio of these is given in Column 9, as the partition ratio for alcohol between oil and water.

As the greatest error seemed to be in the handling of the water layer, the ratios in Column 10 were also calculated, assuming that the values in Column 4 for alcohol in oil layers are correct and estimating the alcohol in water layer by difference, *i. e.*, the difference between the values in Columns 6 and 4. The values calculated in this way are usually higher and are somewhat more regular.

The values of the partition ratios have not been calculated by difference in the case of isobutyl and isoamyl alcohols since the amounts of these alcohols in the two layers are more nearly equal, and the probable errors of estimating the alcohols in the two layers were nearly the same.

Some results which appear erratic are in parentheses and have not been used in making the averages.

PARTITION OF METHYL ALCOHOL BETWEEN COTTONSEED OIL AND WATER.

1. Vol. oil.	2. Vol. H ₂ O.	3. Wt. CH ₃ OH.	4. Wt. CH ₃ OH in oil.	5. Wt. CH ₃ OH in H ₂ O.	6. Wt. CH ₃ OH found.	7. Wt. CH ₃ OH in 100 cc. oil.	8. Wt. CH ₃ OH in 100 cc. H ₂ O.	9. Ratio direct.	10. Ratio difference.
81.95	12.03	2.871	0.163	2.085	2.248	0.199	17.28	86.6	(112.0)
83.03	12.58	3.589	0.210	2.945	3.155	0.253	23.34	92.2	105.8
82.09	13.05	4.244	0.245	3.369	3.614	0.298	25.73	86.2	102.4
83.10	11.77	3.516	0.220	2.851	3.071	0.264	24.15	91.3	105.5
82.67	14.04	4.102	0.228	3.307	3.535	0.275	23.48	85.2	100.0
82.38	12.43	3.688	0.213	3.148	3.361	0.258	24.44	94.0	104.4
83.25	12.32	3.501	0.237	2.849	3.086	0.284	23.06	(81.4)	(92.8)
Mean,								89.2	103.6

SOLUBILITY OF METHYL ALCOHOL
IN COTTONSEED OIL AT 25°.

Wt. Oil sample.	Wt. CH ₃ OH found.	Wt. CH ₃ OH in 100 g. oil.	Wt. CH ₃ OH in 100 cc. oil.
44.36	2.269	5.13	4.73
43.39	2.026	4.67	4.31
42.17	2.420	5.81	5.36
41.47	2.238	5.36	4.95
Mean,		5.24	4.84

SOLUBILITY OF COTTONSEED OIL
IN METHYL ALCOHOL AT 25°.

Wt. sample.	Wt. oil found.	Wt. oil in 100 g. CH ₃ OH.	Wt. oil in 100 cc. CH ₃ OH.
7.016	0.0575	8.26	6.57
8.166	0.0701	8.65	6.88
6.7405	0.0513	(7.51)	(5.98)
6.1605	0.0356	(7.45)	(5.93)
11.2777	0.0959	8.57	6.82
Mean,		8.32	6.62
Mean,		8.45	6.74

PARTITION OF ETHYL ALCOHOL BETWEEN COTTONSEED OIL AND WATER.

Vol. oil.	Vol. H ₂ O.	Wt. C ₂ H ₅ OH.	Wt. C ₂ H ₅ OH in oil.	Wt. C ₂ H ₅ OH in H ₂ O.	Wt. C ₂ H ₅ OH found.	Wt. C ₂ H ₅ OH in 100 cc. oil.	Wt. C ₂ H ₅ OH in 100 cc. H ₂ O.	Ratio direct.	Ratio difference.
79.18	36.63	2.7916	0.174	2.548	2.722	0.2196	6.963	31.2	32.4
78.34	35.69	3.1062	0.199	3.07	3.269	0.2539	8.572	(33.7)	(31.8)
80.68	38.42	2.7375	0.178	2.56	2.738	0.2203	6.642	30.1	30.1
82.04	38.04	2.8203	0.145	2.59	2.735	0.1765	6.789	(38.4)	(39.7)
78.79	36.60	2.9125	0.178	2.56	2.739	0.2265	6.974	(30.7)	(34.2)
79.20	35.32	3.0570	0.231	2.838	3.069	0.2916	8.012	27.4	27.3
80.57	34.82	3.2196	0.243	3.032	3.275	0.3017	8.682	28.7	28.2
79.14	35.29	2.8352	0.189	3.041	3.230	0.2384	8.585	(36.0)	(31.2)
79.54	37.14	2.5780	0.166	2.280	2.446	0.2083	6.147	29.5	31.0
79.10	38.33	2.8757	0.178	2.590	2.768	0.2251	6.738	29.9	31.2
83.61	37.89	3.1138	0.250	2.795	3.045	0.2991	7.354	24.6	25.1
80.68	35.96	2.6997	0.224	2.48	2.704	0.2783	6.876	24.7	24.5
81.95	38.73	2.8583	0.195	2.655	2.850	0.2515	6.835	27.1	27.2
Mean,								28.1	28.5
Mean,								28.3	

SOLUBILITY OF ETHYL ALCOHOL
IN COTTONSEED OIL AT 25°.

Wt. oil sample.	Wt. C ₂ H ₅ OH found.	Wt. C ₂ H ₅ OH in 100 g. oil.	Wt. C ₂ H ₅ OH in 100 cc. oil.
34.06	9.64	23.4	21.6
37.77	8.90	(26.4)	(24.3)
40.56	8.50	23.3	21.5
39.02	8.44	24.7	22.8
46.13	9.02	22.2	20.5
47.64	8.65	21.0	19.4
		<hr/>	<hr/>
	Mean,	22.9	21.2

SOLUBILITY OF COTTONSEED OIL
IN ETHYL ALCOHOL AT 25°.

Wt. sample.	Wt. oil.	Wt. oil in 100 g. C ₂ H ₅ OH.	Wt. oil in 100 cc. C ₂ H ₅ OH.
11.2595	0.9976	(9.72)	(7.62)
6.0616	0.5591	(10.16)	(7.97)
9.8321	1.0190	11.56	9.08
7.9535	0.8487	11.94	9.38
		<hr/>	<hr/>
	Mean,	11.75	9.23

PARTITION OF PROPYL ALCOHOL BETWEEN COTTONSEED OIL AND WATER.

Vol. oil.	Vol. H ₂ O.	Wt. C ₃ H ₇ OH.	Wt. C ₃ H ₇ OH in oil.	Wt. C ₃ H ₇ OH in H ₂ O.	Wt. C ₃ H ₇ OH found.	Wt. C ₃ H ₇ OH in 100 cc. oil	Wt. C ₃ H ₇ OH in 100 cc. H ₂ O.	Ratio, direct.	Ratio, difference.	
82.32	25.94	3.908	1.248	2.620	3.868	1.516	10.07	6.64	6.74	
83.02	25.05	3.507	1.202	2.038	3.240	1.447	8.112	(5.60)	6.34	
83.45	26.36	3.599	1.216	2.343	3.559	1.457	8.897	6.10	6.21	
83.05	25.31	4.206	1.407	2.645	4.052	1.694	10.41	6.14	6.50	
85.10	25.02	3.969	1.342	2.632	3.974	1.576	10.49	6.65	6.65	
83.21	25.21	3.752	1.251	2.480	3.731	1.503	9.809	6.53	6.57	
								<hr/>	<hr/>	
								Mean,	6.41	6.50

PARTITION OF ISOBUTYL ALCOHOL BETWEEN COTTONSEED OIL AND WATER

Vol. oil.	Vol. H ₂ O.	Wt. C ₄ H ₉ OH.	Wt. C ₄ H ₉ OH in oil.	Wt. C ₄ H ₉ OH in H ₂ O.	Wt. C ₄ H ₉ OH found.	Wt. C ₄ H ₉ OH in 100 cc. oil.	Wt. C ₄ H ₉ OH in 100 cc. H ₂ O.	Ratio, direct.	
83.96	75.53	3.020	1.155	1.748	2.903	1.375	2.307	1.67	
82.57	78.63	3.208	1.160	1.916	3.076	1.405	2.429	1.72	
81.30	77.96	2.923	1.038	1.759	2.797	1.276	2.250	1.76	
81.53	75.77	2.653	0.953	1.554	2.507	1.168	2.043	1.74	
83.02	75.02	2.846	1.069	1.604	2.673	1.288	2.135	1.65	
81.89	72.80	3.281	1.225	1.789	3.014	1.495	2.450	1.64	
								<hr/>	
								Mean,	1.70

PARTITION OF ISOAMYL ALCOHOL BETWEEN COTTONSEED OIL AND WATER.

Vol. oil.	Vol. H ₂ O.	Wt. C ₅ H ₁₁ OH.	Wt. C ₅ H ₁₁ OH in oil.	Wt. C ₅ H ₁₁ OH in H ₂ O.	Wt. C ₅ H ₁₁ OH found.	Wt. C ₅ H ₁₁ OH in 100 cc. oil.	Wt. C ₅ H ₁₁ OH in 100 cc. H ₂ O.	Ratio, direct.	
81.48	74.65	2.699	1.789	0.835	2.624	2.195	1.1156	0.508	
81.77	72.37	2.801	1.940	0.722	2.662	2.372	0.9995	0.421	
82.60	71.88	2.469	1.609	0.660	2.269	1.947	0.9153	0.470	
82.99	74.19	2.899	1.884	0.822	2.706	2.273	1.105	0.486	
82.52	75.32	2.516	1.631	0.751	2.382	1.976	0.9946	0.503	
80.98	77.06	2.778	1.813	0.772	2.585	2.224	0.9986	0.445	
								<hr/>	
								Mean,	0.472

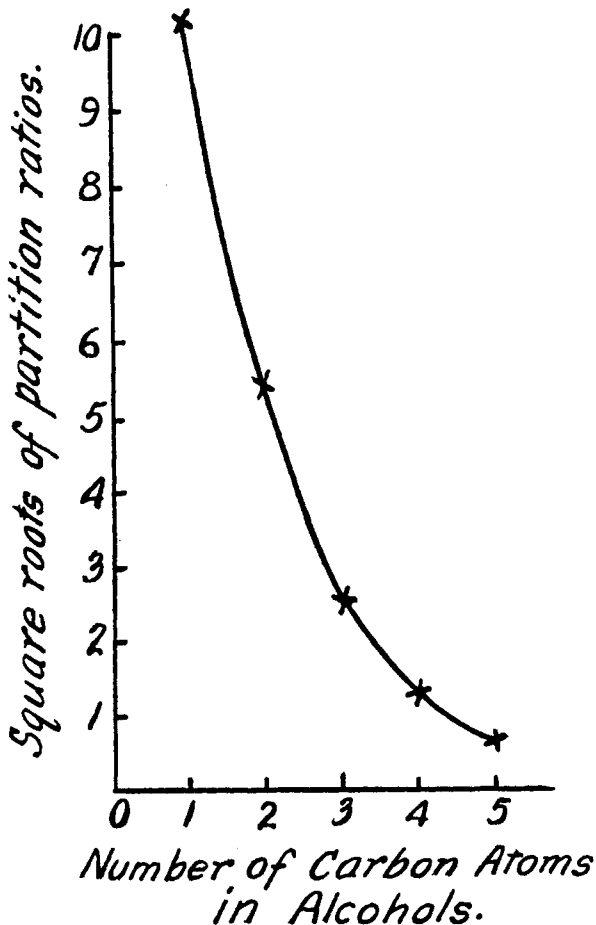
Discussion of Results.

The average results are brought together in table.

PARTITION RATIO BETWEEN WATER AND COTTONSEED OIL.					
Alcohol.	Methyl.	Ethyl.	Propyl.	Isobutyl.	Isoamyl.
Ratio.....	103.6	28.3	6.41	1.70	0.47
Square root of ratio.....	10.18	5.32	2.53	1.30	0.68

The ratios decrease rapidly as the number of carbon atoms in the alcohol increase, each ratio being approximately one-fourth of the preceding ratio.

Taking these ratios as fractions, the numerators which represent the solubilities of the alcohols in water, increase as number of carbon atoms decrease, while the denominators, or the solubilities of the alcohols in the oil increase in the opposite directions. For this reason the square roots of these ratios have been plotted against number of carbon atoms in the



curve below.

The solubility of methyl alcohol in cottonseed oil appears to be 4.84 g. per 100 cc. while for ethyl alcohol it is 21.2 or about four times as great. We have $4.84 \times 103.6 = 505$ and $21.2 \times 28.3 = 600$. From this 505 g. methyl alcohol and 600 g. ethyl alcohol should dissolve in 100 cc. water. These represent, in the same approximation, what may be termed ideal solubilities. At any rate the numbers 4.84 and 103.6 represent something real as determined by experiment and their product must have some meaning also. Further work will have to be done before these results can be satisfactorily inter-

puted. It is surprising that methyl alcohol gives the smaller number 505, while ethyl alcohol gives the larger number 600. It was expected that methyl alcohol would give the larger number as the fact that methyl alcohol is more difficult to salt out of a solution than ethyl, seems to indicate a greater affinity for water and hence a greater solubility in water. The difficulty may be in the numbers 4.84 and 21.2, the directly determined solubilities of the two alcohols in the oil. These do not represent the amounts of alcohol taken up by the oil when in contact with the pure alcohols, but the amounts in the oil when the oil is in contact with solutions of the oil in the two alcohols. If we consider molecular solubilities, the order is what we should expect, since $505 \div 32 = 15.8$ and $600 \div 46 = 13.0$.¹ Taking the higher and more concordant values we find that 100 g. of methyl alcohol dissolve 8.45 g. of cottonseed oil and 100 g. ethyl alcohol, 11.75 g.

Experiments showed that propyl, isobutyl, and isoamyl alcohols mix with cottonseed oil in all proportions. This prevented the determinations of their direct solubilities. The solubilities of isobutyl and isoamyl alcohols in 100 cc. water are given in the tables as 9.55^{18° and 2.67^{22° . According to the above reasoning, the solubilities of these two alcohols in the oil should be $9.55 \div 1.70 = 5.6$ and $2.67 \div 0.47 = 5.6$. This shows that we must be guarded in drawing conclusions and that there are factors which are not taken into consideration in the reasoning as stated above.

These alcohols, when they contain a few per cent. of water, do not mix with the oil. The phenomena of mutual solubility are quite complex and require much further study. This work is being continued in this laboratory.

Summary.

1. The partition ratios of methyl, ethyl, propyl, isobutyl and isoamyl alcohols between water and cottonseed oil at 25° are found to be 103.6, 28.3, 6.41, 1.70 and 0.47, respectively.

2. These are found to change regularly with increased number of carbon atoms.

3. The solubilities of methyl and ethyl alcohols in cottonseed oil are 4.84 and 21.2 g. per 100 cc. oil.

4. The attempt has been made by using these numbers and the partition law to calculate the ideal solubilities of the lower alcohols in water.

BALTIMORE, MD.

¹ Suggestion of Associate Editor.