It is of interest to note that in solutions as dilute as 0.1 *M* there is a marked difference between the behavior of those substances that are hydrated, and those that form hydrates to an inconsiderable extent only.

This investigation is being continued.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MANITOBA.]

SUPERSATURATED SOLUTIONS OF LIQUIDS IN LIQUIDS.

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It is comparatively easy to form supersaturated solutions of solids or gases in liquids, but, up to the present, attempts to form similar supersaturated solutions of liquids in liquids have met with little success.

Rothmund[1] has considered the possibility of the existence of such supersaturated solutions. His criterion for such a condition is based on the following considerations: A small drop of liquid is more soluble than a larger one and a solution can be supersaturated until it is in equilibrium with the smallest drops which are already formed in the liquid. When this concentration is exceeded, these drops rapidly grow, becoming less soluble as they do so and soon reduce the concentration of the supersaturated solution to that of a saturated one. In a case where the solubility increases with the temperature, the cooling of the solution causes drops to appear somewhat below the temperature of saturation for that particular concentration; but when the solution is heated, the larger drops will persist until slightly above the temperature of saturation. That is, there will be a difference between the temperatures at which the cloudiness appears and disappears and the greater the degree of supersaturation, the greater will be the difference in temperature.

In the case of all the liquids he investigated, this difference of temperature was very small; hence Rothmund concluded that there was no evidence of supersaturation.

Füchtbauer[2] carried out some experiments which seemed to give strong evidence of the existence of supersaturated solutions of liquids in liquids. He came to the conclusion that the difficulty in forming supersaturated solutions of liquids in liquids is due to the presence of dust particles or foreign nuclei of some sort, perhaps colloids.

A careful examination of the effect of dust particles on preventing the formation of supersaturated solutions of liquids in liquids was made by Fawcett.[3]

[1] *Z. physik. Chem.*, **26**, 443 (1898).

[2] *Ibid.*, **48**, 566 (1904).

[3] Thesis, University of Toronto, 1912. For summary see E. Fawcett, *Proc. Roy. Soc. Canada*, 1913. (I am indebted to Prof. F. B. Kenrick for a copy of this thesis.)

The method he used to detect supersaturation was similar to that used by Rothmund as already described above, that is, the determination of the difference between the temperatures at which the cloud appears and disappears when the temperature of the solution is changed. In every case there was a difference between the two temperatures, but it was of the order of the experimental error. He then attempted to remove the dust particles by various methods but again no evidence of supersaturation was obtained.

Liesegang[1] has pointed out that even if dust particles, or foreign nuclei of any kind, do facilitate precipitation of the second liquid phase, before the metastable limits of supersaturation are exceeded, yet that does not necessarily make it impossible to exceed these limits in a solution which contains such nuclei. For the nucleus prevents supersaturation only by forming a zone of approximately normal concentration at its surface, toward which the solute diffuses and as the rate of diffusion is not, after all, very fast, the influence of the nuclei in preventing supersaturation is dependent on the time in which the supersaturated state is obtained.

Experimental Determination of the Degree of Supersaturation of Some Liquids in Liquids.

Phenol in Water.—The *phenol* used in these experiments was a pure grade of material, which was fractionally distilled before use.

The water used in all this work was prepared as follows: Ordinary distilled water was subjected to fractional distillation in a still of the type designed by Bousfield, obtained from Messrs. Baird and Tatlock. Although this method is guaranteed to give water of a high degree of purity, it was not free from suspended particles visible to the naked eye. It was kept in well-stoppered hard glass bottles. High purity of the water could only be maintained where all later experimentation was done in sealed glass vessels. In other cases where cork stoppers were used, ordinary distilled water undoubtedly would have done just as well.

A thermostat with two parallel glass sides was regulated at 25°. It maintained a temperature constant to a few hundredths of a degree.

The solubility of phenol in water increases continuously with the temperature from 0° to the critical solution temperature.[2] Solutions of phenol and water saturated at 25° were formed in two ways:

1. By stirring with a current of air for half an hour. This air was first heated to the temperature of the thermostat by drawing it through a copper coil immersed in a bath at 25°.

2. By heating to a higher temperature and then cooling to the temperature of the bath. A dense cloud formed, showing that the solution was now saturated at 25°.

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[1] *Kolloid. Z.*, 3, 76 (1915).

[2] Alexjew, *Wied. Ann.*, 28, 305 (1886); also Rothmund, *Loc. cit.*

Various forms of tubes were used to hold the solutions. A very convenient form was found to be test tubes 20 cm. long and 2.5 cm. in diameter. Two Beckmann thermometers, graduated into hundredths of a degree, were regulated so that they read the same, at the same temperature, to less than a hundredth of a degree. One was placed in the thermostat, the other, through a tight fitting rubber stopper, in the test tube to be examined. The test tube was then cooled by bringing it into the room or by immersion in a beaker of water at a temperature below 25°.

The conclusion drawn from a large number of experiments of this kind was, that a clear saturated solution of phenol in water at 25° shows a distinct cloud on precipitation of the second phase before it has cooled a tenth of a degree.

Aniline and Water.—The solubility of aniline in water at ordinary temperatures increases with the temperature.[1] Solutions of aniline in water showed no marked evidence of supersaturation, although the measurements were not done with as much care as in the case of phenol solutions.

Nitrobenzene and Water.—The nitrobenzene used was a material from a well-known firm. It was shaken for several hours with calcium chloride and then distilled. As will be shown from experimental data, the solubility of nitrobenzene in water increases from temperatures well below 20° to one above 50° and that of water in nitrobenzene also increases over these limits. The method of procedure in the measurement of the supersaturation was therefore similar to that already described in the case of phenol and water.

(A) **at 25°.**—Five test tubes containing nitrobenzene and water were placed in the thermostat and the solutions in them well stirred with air for three hours. They were then tightly stoppered and allowed to stand till the solutions were clear. A Beckmann thermometer was placed in one of the tubes, which was then taken out of the thermostat and allowed to cool to room temperature. The bulb of the thermometer was so large that it probably did not accurately record the temperature of that particular part of the solution in which a cloud first appeared. Invariably a cloud quickly appeared in the lower layer of nitrobenzene with a little dissolved water, before any appreciable lowering of temperature was noticed; but the upper layer remained clear until a perceptible degree of supersaturation had been obtained. The results were as follows in three tubes examined:

No. of tube	1	2	3
No. of degrees of supersaturation	0.6°	0.1°	0.3°

(B) **at 20°.**—It was thought that the solution at 25° might not have been saturated, either because the stirring was not sufficient or because

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[1] Alexjew, *Loc. cit.*

the cork stopper had permitted vapor to escape. So two similar tubes were sealed up in the blowpipe. They were heated to 40°, shaken and allowed to settle, then placed in a thermostat[1] at 20°, constant to less than 0.1°. A dense cloud appeared, proving that the solutions were saturated, since the solubility of nitrobenzene in water appears to increase continuously from 0° to 50°. The solutions were allowed to stand in the thermostat until they were clear and investigated for supersaturation as described above.

	Tube (1)	Tube (2)
Supersaturation in lower layer...........	0.07°	0.00°
Supersaturation in upper layer...........	1.3°	0.3°

The Solubility of Nitrobenzene in Water.—No data exist on the solubility of nitrobenzene in water. Accurate measurement of the solubility of such a sparingly soluble substance is exceedingly difficult. The thermometers used in the solubility measurements were made of normal glass and graduated to 0.1°. They had been standardized in the Physikalisch-technische Reichsanstalt.

The solubility at 20° was determined by a method similar to that used by Rex.[2] The neck of a 1000 cc. flask was drawn out and to it was sealed an oblique T tube. One end of this was sealed and formed a graduated measuring tube which was carefully calibrated with weighed amounts of mercury. The terminal part of this measuring tube was 0.5 cm. wide and 5 cm. long. It then broadened out to a width of 1 cm. Thus the same apparatus could be used to measure changes of volume of two different orders of magnitude.

The apparatus was weighed and the main body of the flask nearly filled with distilled water. Some nitrobenzene saturated with water at 20° was poured down a capillary funnel into the measuring tube. The apparatus was then evacuated, sealed up in the blowpipe and weighed. After bringing the apparatus to the temperature of 20°, the volume of the nitrobenzene was read off. The nitrobenzene was now allowed to run into the main part of the flask. This was heated to 30°, well shaken up, and after some time put in the thermostat at 20°. A dense cloud formed, showing that the solution was saturated. The flask was shaken in the thermostat for many hours and the volume of the residual nitrobenzene determined in the measuring tube. The great source of error was in the presence of small drops that would not coalesce.

The result of one determination was that 100 g. of solution dissolve 0.16 cc. of the nitrobenzene saturated with water. The specific gravity

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[1] This thermostat was controlled by an alternating current thermoregulator which has been described in THIS JOURNAL, **37**, 1520 (1915). A better form was described by McDermott in THIS JOURNAL, **37**, 2381 (1915). I have adopted his form and find it gives great satisfaction.

[2] *Z. physik. Chem.*, **55**, 358 (1906).

of nitrobenzene saturated with water at 20° was found to be 1.201. Subsequent work shows that the amount of water in this nitrobenzene may be neglected. Hence, the solubility of nitrobenzene in water thus obtained was 0.19 g. per 100 g. of solution.

So far, the method is very similar to that employed by Rex. He determined solubilities at 30° in the same way, but the following method will be found useful in certain cases: Qualitative experimentation soon shows that the solubility of nitrobenzene in water increases continuously from 20° to 30°. Water, therefore, was saturated with nitrobenzene at 30° and the clear solution forced over into the flask above described. This was sealed off, cooled to 20° and the volume of the precipitated nitrobenzene determined. A preliminary experiment gave 0.021 cc.; a more careful one, 0.025 cc. or 0.03 g., as the increase in the solubility of nitrobenzene in water from 20° to 30°. While this value must be considered fairly satisfactory, the absolute value for the solubility at 30° depends on the value at 20°.

As a check on these values, the solubility of nitrobenzene in water at about 55° was determined by the cloud method so well described by Rothmund.[1] Known weights of pure nitrobenzene and water were sealed up in a tube and the temperature found, at which the cloud of precipitation of the second phase appeared and disappeared.

Wt. of nitrobenzene, 0.290 g.; wt. of water, 107 g.; cloud appeared, 54.2°; cloud disappeared, 55.5°; mean, 55°. These temperatures were not sharply marked.

The collected results are:

Temperature	20	30	55
Solubility of nitrobenzene in water. (Grams per 100 g. soln.)	0.19	0.22	0.27

These results should only be regarded as showing the order of the values for the solubility, but the method is capable of yielding good results.

The Solubility of Water in Nitrobenzene.—This was determined by the cloud method outlined above. For the lower temperatures the heating bath was water; for the higher, melted paraffin.

Conc. soln. (g. H_2O : 100 g. soln.)	Temp. of appearance of cloud.	Temp. of disappearance of cloud.	Mean of the two.
0.174	8.4°	9.3°	8.8°
0.194	14.2°	15.2°	14.7°
0.299	29.8°	31.8°	30.8°
0.401	43.2°	45.3°	44.2°
0.713	62.3°	64.4°	63.3°
1.53	105.0°	108.2°	106.6°

Carbon Disulfide and Water.—The carbon disulfide used in these experiments was a pure grade which was shaken up for many hours with successive portions of sulfuric acid until the acid showed no color on such

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[1] Rothmund, "Löslichkeit und Löslichkeitsbeeinflussung," 1907, p. 30.

treatment. It was then washed free from acid with distilled water, shaken for six hours with calcium chloride and distilled.

In contradistinction to the other liquids dealt with in this paper, the solubility of carbon disulfide in water decreases continuously from 0° to 50°. Chancel and Parmentier[1] determined the solubilities by chemical estimation of the amounts of disulfide in the saturated solutions. Rex[2] measured the volumes dissolved on solution as already described in this paper. A glance at Curve I shows that the results obtained by the two methods do not agree, either for the form of the solubility curve or for the absolute values of the solubility. I found that the solubility increases again above 50°, because solutions saturated at 60° or 70° showed a dense cloud on cooling. More work on the solubilities of these sparingly soluble substances is greatly to be desired.

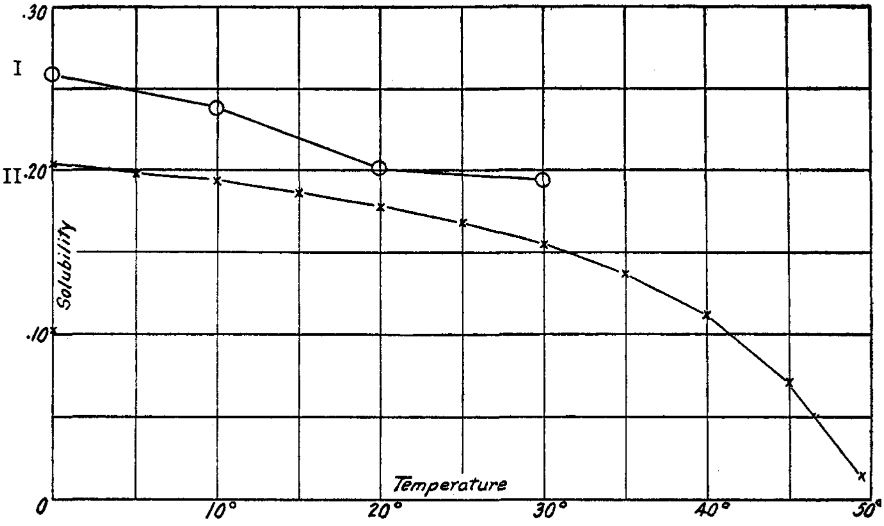

Fig. 1.—Solubility of Carbon Disulfide in Water.

Curve I, Rex's values (grams carbon disulfide in 100 g. solution).

Curve II, Chancel and Parmentier's values (grams carbon disulfide in 100 liters solution).

Test tubes 20 cm. long and 2.5 cm. in diameter were nearly filled with a mixture of carbon disulfide and water and closed with a good tight fitting cork. The solutions were cooled to about 10°, shaken (prolonged shaking is not required) and allowed to settle. When now the tubes were put in a thermostat at 20° constant to 0.1°, a dense cloud appeared in the water layer, which must, therefore, have been saturated with carbon disulfide at that temperature. The cloud slowly settled and disappeared. Often, however, a slight milkiness remained. So, just before heating

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[1] *Compt. rend.*, **99**, 892 (1894); 100, 773 (1885).

[2] *Z. physik. Chem.*, **55**, 358 (1906).

the solutions above 20°, they were cooled to 10–15° for a short time, when the water solution became very clear.

The solutions were heated above 20° in the following way: A tall, narrow beaker was partly filled with water at a temperature of about 18° and water at a temperature of about 70° was poured upon this down a wire, at the base of which was a small watch glass. This watch glass was held in a horizontal position by the wire and broke the fall of the water, so that two layers of water at very different temperatures were obtained. Into the beaker was plunged one of the test tubes described above. A cloud at once appeared in the top of the upper layer, *i. e.*, the solution of carbon disulfide in water, and slowly moved down the tube. The temperature of the water just ahead of this cloud was investigated by a small boiling point thermometer with a bulb only 8 mm. in length, so that the temperature in a local spot in the liquid could be determined. It was found that clear spaces beneath the cloud had temperatures as high as 23–24° while it must be remembered that this solution was saturated at 20°.

Two of the experiments were performed with sealed tubes, which were broken open at the top to admit the thermometer just before heating above 20°. In this way any errors arising from the use of corks were eliminated, but these solutions behaved the same as those kept in corked tubes.

Effect of Mechanical Jar on Supersaturated Solutions of Liquids in Liquids.

It is well known that supersaturated solutions of solids and gases in liquids are particularly sensitive to a mechanical jar. A single experiment shows this very well in the case of a gas dissolved in a liquid.

If a solution of air in water, saturated at atmospheric pressure, is placed in a stout tube such as a Nessler tube, and if the pressure is lowered by connecting it to an aspiration pump, then a supersaturated solution is obtained. A few bubbles form and rise to the surface, after which the solution remains quiet. If now the tube is struck sharply on the side with a glass rod, hundreds of bubbles appear inside the liquid.

It was noticed in the case of solutions of phenol and nitrobenzene in water, that sometimes, on striking the thermometer a blow, clouds seemed to come off it. The existence of such a phenomenon was clearly established in the case of solutions of carbon disulfide in water, in the following way: A 500 cc. flask was filled with a clear solution of carbon disulfide, saturated at 20°. A stout glass rod (7 mm.) was flattened on the bottom to a disk about 1$^1/_2$ cm. wide. It was supported in the solution through a cork. When the flask was placed in a beaker of water at 35°, a cloud formed at the top of the solution and moved slowly down. Now, while the disk of the rod was still in a clear part of the solution, the top was struck a sharp blow with a small iron clamp, upon which clouds were observed to come from the bottom of the rod and to form also in the solution below it. Sometimes the cloud formed after a few seconds, nearly a centimeter below the disk.

Calculations of the Degrees of Supersaturation Theoretically Possible for Solutions of Liquids in Liquids.

Kenrick[1] has suggested that there is no essential difference between supersaturated solutions of solids in liquids and those of liquids in liquids, but that "the cause of the small degree of supersaturation of liquids is connected with the comparatively small surface tension of the interface between liquid and liquid." Ostwald[2] was the first to derive a formula showing the change in the solubility of a particle of solid or liquid with size. This formula has been corrected by Freundlich,[3] who gives one of the following form:

$$\ln \frac{S_1}{S} = \frac{2M\sigma}{R\theta\rho r}$$

S is the solubility of a substance for particles of infinite radius.
S_1 is the solubility for particles of radius r.
M is the molecular weight of the substance in solution.
σ is the interfacial surface tension.
R is the gas constant (8.3×10^7 ergs/degree).
θ is the absolute temperature of the solution.
ρ is the density of the particles.
(All quantities are expressed in absolute units.)

From this formula, the supersaturation, theoretically possible, has been calculated for the following substances, assuming that in each case a particle of radius 15×10^{-7} cm. can be formed spontaneously in the supersaturated solution:

$$R = 8.3 \times 10^8 \frac{\text{ergs}}{\text{degree}};\ \theta = 298°;\ r = 15 \times 10^{-7} \text{ cm.}$$

Solution.	σ.	M.	ρ.	Percentage supersaturation calc.	Supercooling calc.	Supercooling found.
Calcium sulfate in water..	550[4]	136	2.32	600	...	.....
Isobutyric acid in water..	1.76[4]	88	0.95	0.8	...	.....
Nitrobenzene in water....	23[5]	123	1.20	12	8°	0.1° to 1.4°[6]
Water in nitrobenzene....	23	18	1	2	0.8°	0.0° to 0.7°[6]
Carbon disulfide in water.	38.4[5]	44	1.23	7	$\begin{bmatrix}6°\\25°\end{bmatrix}$[7]	3°
Water in carbon disulfide.	38.4	18	1	4	...	.....

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[1] *University of Toronto Studies*, **99**, 4 (1913).

[2] *Z. physik. Chem.*, **34**, 504 (1900).

[3] H. Freundlich, "Kapillarchemie," **1909**, p. 144.

[4] F. Kenrick, *Loc. cit.*

[5] Mlle. L. van der Noot, *Bl. Acad. Belg.*, **4**, 501.

[6] The results obtained at 20° are also included.

[7] The 6° is obtained from the values for the solubility of carbon disulfide in water

In these calculations it has been assumed that a drop with a radius of the order 1.5×10^{-6} can be formed spontaneously in the solution. It will be well now to review allied phenomena to see if there is any ground for such a belief.

The Spontaneous Formation of Nuclei in Gases.

The conditions of condensation of water vapor in air and other gases have been carefully investigated by C. T. R. Wilson[1] and Barus.[2] Their experiments showed that nuclei are always present in large numbers, sufficient to condense the vapor when it has about eight times its normal density. He showed that drops with a radius of the order 10^{-8} cm. would, according to accepted formulae, be in equilibrium at this eightfold density and that such drops would contain but a few molecules. He suggested that such drops might be formed spontaneously through the accidental collision of molecules.

J. J. Thomson[3] has offered the following theory to explain the phenomena attending the condensation of water vapor from gases:

> "When a liquid film gets very thin, its surface tension no longer remains constant but depends on its thickness. For very thin films, theory indicates[4] that the surface tension would be proportional to the square of the thickness, while the experiments of Reinold and Rücker[5] showed that the surface tension had a maximum value for a thickness comparable with that of the dark spot in soap films. More recent experiments by Johannot[6] have made it probable that, considering the surface tension as a function of thickness, there is more than one maximum.
>
> "We see now when we take the variation of surface tension into account that even the slightest supersaturation will produce some condensation, but that these drops will be exceedingly small and will evaporate as soon as the supersaturation ceases."

He then shows that if supersaturation increases, drops may finally be formed of such radius that they will continue to grow as long as supersaturation exists and will produce a dense cloud. On the contrary, on the evaporation of a drop, *it may persist at a temperature somewhat above*

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obtained by Chancel and Parmentier (*Compt. rend.*, **99**, 892 (1884); **100**, 773 (1885)), the 25° from the values obtained by Rex (*Z. physik. Chem.*, **55**, 355 (1906)). The value 0.201 found by Rex at 20° is incorrectly copied as 0.101 in the *Chem. Zentralbl.*, **1906**, p. 1594.

[1] *Phil. Trans.*, (*A*) 265 (1897) and (*A*) 403 (1899).

[2] *Publ. Carnegie Institution of Washington* No. 40, 149 (1906); also No. **62**, No. **96**, I and II and *Smithsonian Contributions*, **34** (1905).

[3] Thomson, "Conduction of Electricity through Gases," 183 (1906).

[4] See Lord Rayleigh, *Phil. Mag.*, **5**, 33.

[5] Rücker and Reinold, *Phil. Trans.*, **177**, II, 627 (1886). Bakker (*Phil. Mag.*, [6] **17**, 341 (1909)) disputes this conclusion. From prolonged mathematical consideration he concludes that "it follows that the capillary layer must always be complete and the apparition of the black spots cannot be explained otherwise than as the consequence of a temporary and local diminution of the surface tension in the considered points in consequence of the temporary and local increase of evaporation in these points."

[6] *Phil. Mag.*, **47**, 501 (1899).

the saturation temperature for that concentration of water vapor, but that a temperature will finally be reached where it will disappear.

Opalescence near the Critical Temperature.

As is well known, gases in the critical condition show a marked opalescence: "It appears only inside a few tenths of a degree and certain volume limits from that point. Also under suitable conditions just before the disappearance of the meniscus, it appears in the liquid just as well as in the gas after the disappearance of the liquid into the common phase."[1]

A similar phenomenon appears in solutions of liquids in liquids near the critical solution temperature, which is thus described by Rothmund:[2]

> "This cloudiness appears blue in incident, and brown-red in transmitted light. It is strongest in the immediate neighborhood of the critical temperature and decreases slowly as the temperature changes till it completely vanishes. Still, this takes place gradually and a definite point cannot be established at which it can no longer be seen. It can often be clearly recognized at temperatures which are ten degrees or more removed from the critical temperature. - - - As a rule, it does not appear at the separation of a new liquid phase from a solution but only in the neighborhood of the critical point.
>
> "From the whole behavior of this phenomenon it is evident that it is to be sharply differentiated from the precipitation of drops of the second phase which precedes the separation into two layers. The latter is accompanied by a thick clouding which immediately makes the liquid opaque and in a longer or shorter time leads to the formation of a sharp surface of separation. On the other hand it is always possible to see through a critically clouded solution. - - - From the theoretical standpoint, too very strong objections can be raised against that idea. For if one has to deal here with precipitated drops of the same kind and with the same properties as the drops which are visible under the microscope, these could not remain stable as small drops but must grow."

Konowalow[3] has attempted to explain this peculiar opalescence as due to the influence of foreign dust particles.

F. G. Donnan[4] has given a complete theory of the opalescence observed at the critical point of a liquid and Rothmund has applied it further to explain the opalescence at the critical solution temperature.

Donnan makes the following assumptions:

(*a*) Below the critical temperature, the interfacial tension between the two phases is positive for all values of the radius of curvature.

(*b*) At the critical temperature the interfacial tension becomes zero for all ordinary curvatures, but remains positive for very small values of the radius of curvature. *It will be seen that this assumption involves*

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[1] Smoluchowski, *Ann. phys.*, [4] **25**, 217 (1908). This article contains a good list of references.

[2] Rothmund, "Löslichkeit u. Löslichkeitsbeeinflussung," 1907, p. 76. This is the best exposition of the subject and contains complete references.

[3] Drude's *Ann.*, 10, 360 (1903).

[4] *Chem. News*, 90, 139 (1904).

the further one, that at the temperature of disappearance of the meniscus at a boundary surface of ordinary curvature, the two phases do not become identical.

(*c*) At temperatures slightly above the critical, the interfacial tension is still positive for very small radii of curvature, but negative for all ordinary curvatures, while at a still higher temperature it becomes negative for all curvatures.

Granted these assumptions, the existence of permanent opalescence above the ordinary critical temperature follows at once. It will be seen that there is a great deal in common between the theories of Donnan and Thomson.

Smoluchowski[1] has brought forward the idea that the opalescence observed at the critical temperature and that observed at the critical solution temperature are due to the inequalities of density, which, according to the kinetic theory, must exist in matter, due to the movements of the molecules. He has brought forward evidence that these fluctuations become noticeable when a liquid is in the critical state, on account of the greatness of the compressibility at that point, through which regions with considerable difference in density may be nearly in equilibrium with each other.

The critical opalescence according to him is not caused by true drops but by "diffuse heaps of indeterminate size, since for every volume there corresponds a different density." Further, "it is not unreasonable to suppose that the life of such agglomerations is greater in the critical condition."

Smoluchowski gives the following criticisms of Donnan's hypothesis:

> "This hypothesis seems to me unsatisfactory in several respects: In the first place we are dealing here not with two different substances, but with one substance whose two phases have already become identical at the critical point. What is this liquid then? Its existence above the critical temperature must first be proved. And why does the opalescence also appear below that temperature? Moreover, the ordinarily accepted views on capillary force seem to correspond to a decrease in the surface tension with decrease in the radius of curvature, rather than with the reverse. Finally, we will not go into a prolonged discussion of these questions, since Donnan's hypothesis in view of the simple molecular kinetic explanation of those phenomena seems to be completely unnecessary."

Apparently he has misunderstood Rothmund's application of Donnan's hypothesis, for regarding the unchangeability of the phenomena with time he says:

> "This condition renders more difficult Rothmund's explanation of the phenomenon through suspended drops, since, according to Lord Kelvin's rule, the large drops must grow at the expense of the smaller; that is, the phenomenon must change in the course of time."

That Smoluchowski's views afford a profound view into the nature of

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[1] *Loc. cit.*

matter cannot be doubted, but it is not yet clear that they afford a complete explanation of the critical opalescence. In the first place, no evident reason has been given as to why the life of an agglomeration should be greater at the critical point. Moreover, if the fluctuations in density in the case of a gas become more noticeable at the critical point because of the great compressibility at that point, how can similar reasoning be applied to explain the opalescence at the critical solution temperature?

Furthermore, his objections to Donnan's theory are not convincing. It has already been pointed out that his contention that small drops must be unstable because of the increase of vapor pressure is not true, if Donnan's assumptions are granted. One of these assumptions, the increase in the value of the surface tension and the stability of drops above the saturation temperature, has been dealt with in detail by Thomson.

The other assumption of Donnan, that the two phases do not become identical at the critical point, has not received sufficient consideration hitherto. It is well known that surface tension produces a hydrostatic pressure inside a spherical drop, in magnitude equal to $2T/r$, where T = surface tension and r = radius of drop. Apart from theoretical considerations, a glance at Fig. 2 will show that the liquid behind a convex surface must have a greater density than that bounded by a plane surface. The tube is full of liquid which is supported in the tube (neglecting the surface tension at the top) by the convex surface at the bottom. Since the liquid at the bottom is subjected to the hydrostatic pressure of the superincumbent liquid, it is compressed. This increase in density, negligible for ordinary curvatures, may become quite noticeable when the radius of curvature is small, as the following calculation shows:

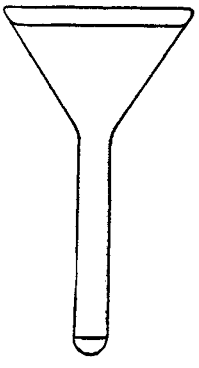

Fig. 2.

For water at ordinary temperature, surface tension = 70 dynes/cm.; compressibility = 4×10^{-11} in absolute units. So that the hydrostatic pressure inside a drop of 10^{-6} cm. radius would be 1.5×10^{-8} dynes/cm^2., or about 150 atmospheres and the corresponding increase in density about 0.6%. For a radius[1] of 10^{-7} cm. on the pressure would be 1500 atmospheres and the increase in density 6%.

Thus the density of a liquid in the form of a small drop is greater than when it is bounded by a plane surface, and further, such physical properties of a liquid as solubility, vapor pressure and surface tension depend on the radius of the drop so that a small drop would not be identical with the vapor phase at a point, where the liquid, bounded by a

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[1] Johannot (*Phil. Mag.*, 47, 501 (1899)) showed that stable films may be as thin as 6×10^{-7} cm.

plane surface and the vapor phase, become identical—which is just what Donnan has postulated.

Is it not more than likely that both these hypotheses present phases of the truth and that, as Smoluchowski has pointed out, local dense spots of varying volume and density are formed in a nearly saturated solution and that some of these, when once formed, are stable, for the reasons which Thomson and Donnan have given? As to the size of these drops, it seems possible, since it is related to the surface tension, that the size may vary with different liquids and also with the temperature for the same liquid. The amount of supersaturation possible is regulated by the size of these drops.

Summary.

1. The degrees of supersaturation of four solutions of liquids in water have been measured. In the cases of nitrobenzene and carbon disulfide, the existence of supersaturation has been definitely established.
2. The solubility of nitrobenzene in water has been measured at three different temperatures.
3. The solubility of water in nitrobenzene has been measured at six different temperatures.
4. Various important theories have been correlated and an attempt made to use them to explain the phenomena observed.
5. A change in the density and other physical properties of small drops with the radius has been suggested as fulfilling one of the conditions in Donnan's theory of the critical opalescence.

WINNIPEG, MANITOBA.

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THE CONDUCTANCE OF SOLUTIONS OF CERTAIN IODIDES IN ISOAMYL AND PROPYL ALCOHOLS.

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1. Introduction.

The study of the conductance of largely ionized solutes in aqueous solution has shown that the results over the range of concentration from 0.001 to 0.1 normal can be expressed fairly well by the equation $\frac{(c\gamma)^n}{c(1-\gamma)} = K$, first proposed by Storch.[1] In this expression c denotes the concentration, and γ the conductance ratio Λ/Λ_0; K is a constant, and n is another constant which has a value which varies somewhat with the nature of the solute, but almost always lies between 1.40 and 1.55.[2] In the case

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[1] *Z. physik. Chem.*, 19, 13 (1896).

[2] Noyes, THIS JOURNAL, 30, 343 (1908).