nation, however, eliminates the objections which have been advanced to the use of Billitzer's value of the absolute potential.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE EXPLOSIVES LABORATORY, CHEMICAL DIVISION OF THE PITTSBURGH EXPERIMENT STATION, UNITED STATES BUREAU OF MINES]

THE SOLUBILITY OF TRINITROTOLUENE IN ORGANIC SOLVENTS[1]

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Introduction

Believing that there exists a serious lack in the fundamental data which should be available for all substances, and that such information will find practical application in the industries, serve for the development of methods of separating mixtures of such substances, or find other more purely scientific uses, the writers have undertaken the determination of some of the solubility constants now unknown. Accordingly, a study has been made of the solubility of α or 2:4:6 trinitrotoluene (TNT) in a number of the more common organic solvents.

Materials

Trinitrotoluene.—The trinitrotoluene used in the following determinations was a fine, crystalline product which had but a slight yellow color. Its setting point was 80.6°, as compared with 80.65° by Guia and Molinari,[4] and 80.35°±0.3° by Bell and Herty.[5] It was obtained by recrystallizing Grade I commercial trinitrotoluene from hot benzene after filtering off any insoluble matter present, evaporating with air the mechanically held benzene, crystallizing from boiling 95% alcohol, again dissolving in boiling 95% alcohol, and precipitating it from solution by pouring it into about 2 volumes of cold distilled water. The mixture was allowed to stand in a dark place for several hours in order to cool it thoroughly and effect complete crystallization. The crystals were then separated by filtration, washed several times with cold distilled water, and finally washed once with cold 95% alcohol to facilitate drying. They were allowed to dry in the air on filter paper away from strong light, and the faintly yellow, fluffy product was then transferred to desiccators over sulfuric acid, and allowed to stand in a dark place for several weeks before using. It was found that under these conditions, even when kept for 9 months or more, no further yellowing of the substance took place.

Solvents. Purification.—Commercial C.P. solvents were further purified, the method employed depending upon the solvent.

Water was redistilled and boiled immediately before use.

Ether was purified by being allowed to stand in contact with an excess of metallic sodium for longer than a week with frequent agitation. When there was no further evolution of gas, the pure ether was distilled.

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[1] Published by permission of the Director, United States Bureau of Mines.

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[4] Guia and Molinari, *Ber.*, **47**, 1718 (1914).

[5] Bell and Herty, *J. Ind. Eng. Chem.*, **11**, 1124 (1919).

Acetone was refluxed over anhydrous calcium chloride and then distilled.

Benzene and toluene were shaken with conc. sulfuric acid in the cold to remove any thiophene which might be present, and were then fractionally distilled.

The other solvents were purified by one or more fractional distillations until the constants obtained were considered to indicate sufficient purity.

Solvents of Low Dissolving Power

Method.—The standard method of determining solubility by removing samples of the solution when in equilibrium with the solid solute could be used when the solubility was comparatively low, so this method was adopted for water, ether, alcohol, carbon disulfide, carbon tetrachloride and chloroform. With most inorganic salts and some organic compounds there is some accurate method of analysis of the solution after it is weighed. There is no method of determining the amount of trinitrotoluene present except by actual weighing. Trinitrotoluene has a vapor pressure of 0.102 mm. of mercury at 99.5°[6], which is so low as compared with those of the above solvents that the solvent could be evaporated and the trinitrotoluene left.

The wagon-pipet was developed as an aid in taking samples and removing the solvent from these. The apparatus used is shown in Fig. 1, and weighs from 50 to 70 g. The cocks were ground so that they held a moderately high vacuum.

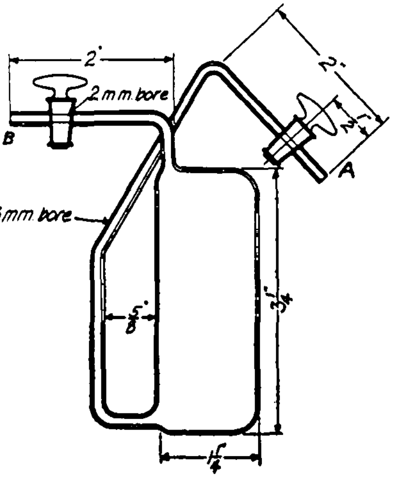

Fig. 1.

Procedure.—Three samples were prepared by placing the solvent in bottles and adding sufficient substance to leave an excess of the solid material at the temperature at which the determinations were to be made. These were then usually heated to a temperature higher than that desired for the determination, placed in the thermostat and allowed to cool. They were shaken frequently for several hours and the solid allowed to settle for at least 2 hours before samples were taken. Often 1 bottle was not heated above the thermostat temperature, but allowed to reach equilibrium from a lower temperature. The mouths of the bottles were kept above the surface of the thermostat liquid because rubber stoppers could not be used and there was danger of leakage through corks. This prevented the use of constant-agitation devices.

The pipet was weighed, then evacuated by a suction pump, and a short piece of rubber tubing containing a loose plug of cotton was placed on Tube *A*. This rubber tube was inserted in a bottle, and Cock *A* quickly opened and the pipet allowed to become about $^2/_3$ full of the solution. *A* was then closed, the rubber removed, and the trinitrotoluene and solvent were washed from the end of Tube *A* with a fine jet of alcohol, this in turn being removed with ether.

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[6] Menzies, This Journal, **42**, 2218 (1920).

When the pipet and contents had cooled to room temperature, Cock *A* was opened to restore atmospheric pressure, and the whole was weighed. The weight of samples so taken varied from 30 to 50 g.

The pipet was clamped in a horizontal position and a tube carrying a current of dry air was connected to Tube *A*, both cocks being opened. When all of the visible solvent had been evaporated, the pipet was placed in an oven at 60° and the drying continued with a current of warm, dry air for at least 1 hour. The pipet containing the trinitrotoluene was then cooled in a desiccator and weighed, after which it was again dried in the oven for at least an hour, cooled and weighed. These weights usually checked within 2 mg., but when they did not the drying and weighing were repeated.

Precautions.—Some precautions were necessary in order to keep within the limits of accuracy. These limits were practically fixed by the temperature reading and control of the thermostat within 0.1°. This was accomplished by the use of a carefully calibrated thermometer and the use of a large mercury-toluene regulator which was responsive to a temperature change of about 0.05°.

The weighings were made on an analytical balance, with standardized weights. It was unnecessary to correct to vacuum weights, but when the solubility was extremely low, as in the case of water, it was found necessary to use another tube as a counterpoise to overcome the effects of surface moisture and to keep the accuracy within the limits of the temperature variation.

Of equal importance to the temperature control is the necessity of certainty that equilibrium has been attained before samples of the solution are taken. All lots of material were kept at constant temperature for at least 20 hours before being sampled; and equilibrium was checked with each solvent by determinations made by approaching the equilibrium temperature from each direction. Those determinations made with rising temperature are indicated in the following tables by an asterisk.

Table I

Approach to Equilibrium of Solution in Ether

° C.	G. of TNT per 100 g. of ether Rising	Falling	
26.0	3.915	3.945	3.906
33.0	5.161	5.156	5.139

Where the solubility was low there was no indication of difficulty in reaching equilibrium, but with chloroform, in which the solubility was much higher, there was an apparent lag. A series of determinations was made to note the time rate of reaching equilibrium in this case. The thermostat was set at 30° and the solution A, made up at 22°, was placed in the bath. Solution B was heated to 40° with constant agitation and allowed to cool to 30° in the bath. There was a large excess of trinitrotoluene present in each solution. The solutions were shaken constantly, and as soon as they had reached the bath temperature, samples were taken, followed by other samples after intervals with shaking.

Table II

Lag in Reaching Equilibrium

Elapsed time Hours	A	B	Elapsed time Hours	A	B
	29.79	34.04	15	29.89	29.91
1	29.70	32.20	39	29.86	29.95
3	29.69	31.25	..	....	....
7	29.83	30.15	..	....	....

Page and Keightley[7] have shown that results may not be identical when equilibrium is approached from opposite sides. Emerson[8] found that organic mixtures such as stearic acid and alcohol tended to exist with a high degree of supersaturation unless a very large excess of the solid solute was present.

Solubility Results

Water

Trinitrotoluene is but slightly soluble in water. Copisarow[9] states that 100 g. of water dissolves 0.021 g. at 15°, and 0.164 g. at 100°. Both of these figures are somewhat higher than those obtained by the present writers.

TABLE III

SOLUBILITY IN WATER[10]

° C.	A	B	C	Av.
0.3	0.0114	0.0097	0.0109	0.0110
5.9	0.0116	0.0104	0.0119	0.0113
20.0	.....	0.0116	0.0124	0.0120
33.1	0.0214	0.0196	0.0209*	0.0203
44.2	0.0335	0.0334	0.0351	0.0340
45.0	0.0382	0.0370	0.0359	0.0370
53.0	0.0539*	0.0530	0.0535	0.0534
57.15	0.0621	0.0609	.....	0.0614
73.25	0.0964*	0.0958	0.0968	0.0963
94.4	0.1413	0.1375	0.1337	0.1375
99.5	0.1482	0.1455	.....	0.1467

Ether

No report of previous quantitative work was found in the literature, but it has been variously stated by different writers that trinitrotoluene is slightly, easily, or very soluble in ether.

TABLE IV

SOLUBILITY IN ETHER

° C.	A	B	C	Av.
0.3	1.757	1.765	1.728	1.75
5.9	2.136	2.134	2.123	2.13
20.3	3.335	3.347	3.307	3.33
26.0	3.915*	3.945	3.906	3.92
33.0	5.161*	5.156	5.139	5.15

Alcohol

Copisarow[9] states that the solubility in alcohol is 1.6 parts at 22° and 10 parts at 58°. It is inferred that absolute alcohol was used for these

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[7] Page and Keightley, *J. Chem. Soc.*, **25**, 566 (1872).

[8] Emerson, THIS JOURNAL, **29**, 1750 (1907).

[9] Copisarow, *Chem. News*, **112**, 247 (1915).

[10] In this and subsequent tables the solubility is given in terms of g. of trinitrotoluene in 100 g. of solvent, unless otherwise stated in the text.

determinations. The present writers decided to use 95% alcohol, as this is the strength in common use in the laboratory and the plant, and values found for this would have a more direct practical application than those for absolute alcohol. Accordingly, pure grain alcohol was used, having a specific gravity of 0.816 at 15/15°. This corresponds[11] to a concentration of 95.07% of alcohol by volume.

TABLE V

SOLUBILITY IN 95% ALCOHOL

°C.	A	B	C	Av.
0.3	0.69	0.75	0.66	0.70
32.0	...	1.99	1.98	1.99
40.1	2.97	3.04	2.94	2.98
45.0	3.80	3.61	3.70	3.70
50.0	4.64	4.59	...	4.61
55.0	6.07	6.09	...	6.08
59.8	8.14	8.16	8.12	8.14
65.0	11.43	11.40	11.36	11.40
74.0	18.60	18.65	18.49	18.58

Carbon Disulfide

With the exception of one determination[12], whereby it was found that the solubility at 17° is 0.386 g. per 100 g. of carbon disulfide, no report of previous work with this solvent was discovered, though several writers mention the fact that trinitrotoluene is but very sparingly soluble in carbon disulfide. The above value agrees very well with that found by the present writers.

TABLE VI

SOLUBILITY IN CARBON DISULFIDE

°C.	A	B	C	Av.
0.3	0.158	0.146	0.145	0.15
5.6	0.198	0.204	0.202	0.20
11.1	0.218	0.276	....	0.27
24.5	0.625	0.619	0.613	0.62
30.1	0.837*	0.841	0.840	0.84
35.0	1.123	1.131	1.117	1.12
40.0	1.541	1.536	1.522	1.53
45.0	2.043	....	1.997	2.02
46.3	2.196	2.208	2.199	2.20

Carbon Tetrachloride

Although carbon tetrachloride is used in one of the commercial processes of purifying trinitrotoluene, no work has been published on the solubility in this solvent.

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[11] U. S. Bur. Standards, *Circ.*, **19,** 9 (1911).

[12] Beilstein and Kuhlberg, *Ann.*, **155,** 27 (1870).

Table VII

Solubility in Carbon Tetrachloride

° C.	A	B	C	Av.
0.3	0.216	....	0.214	0.22
5.6	0.278	0.277	0.276	0.28
11.1	0.374	0.375	0.373	0.37
24.5	0.764	0.764	....	0.76
30.1	1.007	1.009	1.007	1.01
35.0	1.323	1.322	1.320	1.32
40.0	1.746	1.759	1.752	1.75
45.0	2.368	2.374	2.370	2.37
50.0	3.257	....	3.220	3.24
57.0	5.324	5.335	5.326	5.33
59.2	6.394	6.423	6.387	6.40
61.7	8.166	8.112	....	8.14
67.0	13.671	13.694	13.676	13.68
72.5	20.713	20.756	20.694	20.72
78.2	29.841	29.912	29.623	29.76

Chloroform

The studies up to this point were with solvents in which the solubility of the solute was either low or comparatively slight. During the work with trinitrotoluene in chloroform, difficulties were encountered owing to the much higher solubility.

Table VIII

Solubility in Chloroform

° C.	A	B	C	Av.
0.3	6.32	6.34	6.31	6.33
32.0	37.52	38.21	37.63	37.7
40.1	66.35	....	66.82	66.6
45.0	101.8	102.11	100.6	101
50.0	150.42	....	149.42	150
55.0	218.26	217.3	218.48	218
59.8	295.21	297.24	295.44	296
65.0	440.13	445.31	440.82	442

Solvents of High Dissolving Power

Benzene, toluene, acetone, aniline and pyridine dissolve much larger amounts of trinitrotoluene per unit of solvent than does any of the solvents previously considered; chloroform is a solvent of dissolving power intermediate between the two classes. Preliminary work soon made it apparent that the wagon-pipet method could not be used in cases of very high solubility because (*a*) it was impossible to transfer a large or representative sample into the tube, and (*b*) a slight error in determining the weight of solvent in such a sample causes a large error in the solubility value derived from the determination.

The Cooling-curve Method.—The solubility of solids in liquids has been determined by heating a solution above its saturation temperature, gradually cooling until crystals just appeared, noting the temperature, and then checking this point by slowly raising the temperature until the crystals just dissolved. This has been applied to the solubility of organic solids in organic liquids by Goldschmidt and Cooper, who determined the solubility of carvoxime in limonene.[13]

In many cases there is a tendency to form supersaturated solutions. This may be prevented, as described by Menschutkin,[14] by the formation of a crystal of the solute above the surface of the liquid by means of local cooling and then causing contact of the solution with the seed so formed.

It was found, however, that in the case of trinitrotoluene and solvents of high dissolving power, this method would not prevent a considerable supercooling previous to crystal production unless the time factor was large.

Guia[15] and Molinari,[4] melted mixtures of trinitrotoluene and dinitrotoluene, cooled them, and took as the solidification point the temperature at which crystallization started. Later, Bell and Herty,[16] working with the same substances, cooled the melt at the rate of approximately 2° per minute and noted that supercooling occurred. The temperature of the mixture rose to a maximum after the appearance of crystals and then decreased at a rate slower than that of the molten mixture. By plotting time against temperature they were able to extrapolate the second rate

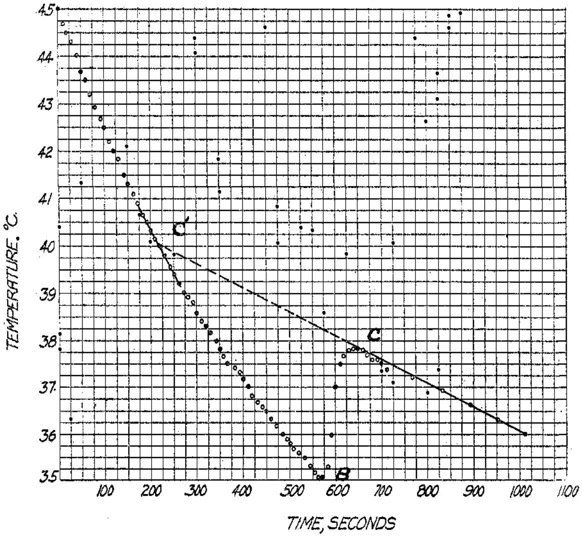

Fig. 2.—A TNT-chloroform cooling curve.

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[13] Goldschmidt and Cooper, *Z. physik. Chem.*, **26**, 713 (1898).

[14] Menschutkin, *Z. anorg. Chem.*, **49**, 207 (1906).

[15] Guia, *Gazz. chim. ital.*, [1] **45**, 339 (1915).

[16] Ref. 5, p. 1125.

of cooling through the high point, *C* on Fig. 2, and so obtain a temperature value, *C′*, which they gave as the true solidification or melting point of the mixture.

Determinations were made by the cooling-curve method as developed by Bell and Herty. Air cooling was employed, as it was found that the rate of cooling was sufficiently slow and agitation of the mixture in a flask was easier than when determinations were made in a double-walled test-tube. The method of seeding of Menschutkin was used, as otherwise there was from 10° to 15° of supercooling. The addition of broken glass in order to give greater friction and a rough surface, and to prevent caking of the liquid-crystal mixture was tried, but this did not prevent super-cooling.

It was found that the point *C* (Fig. 2) could be easily checked within a maximum error range of 0.2°; but due to the caking effect obtained when the concentration was above about 75 g. of trinitrotoluene per 100 g. of chloroform, uniform agitation and, hence, uniform cooling throughout could not be obtained and so the point *C′* could not be derived. A series of determinations covering a range from 22.4° to 67.05° was made.

TABLE IX

SOLUBILITY IN CHLOROFORM BY THE COOLING-CURVE METHOD

° C.	G.
22.4	24.8
33.6	51.8
37.8	74.5
41.5	101
47.2	152
51.2	201
55.1	260
58.2	306
60.6	364
62.8	450
64.6	519
66.4	647
67.05	685

These results show too high a solubility at a given temperature, but the method is of practical value in cases where other methods are not applicable and only approximate results are desired, and it has the advantage of being very rapid. It is also of value in establishing the formation of molecular complexes in cases where the determination of the true solubility curve would require too long a time or be impossible with other methods. The results so obtained are valuable for comparison in the derivation of a true solubility curve.

Benzene

Efforts were first made to determine the values for the solubility of trinitrotoluene in benzene by means of the wagon-pipet, but the method was not found to be applicable above 20°. Accordingly, these attempts were discontinued and determinations were made by the cooling-curve method. The results were calculated to the percentage basis given in the following table and are also plotted as a concentration curve, *A*, on Fig. 3.

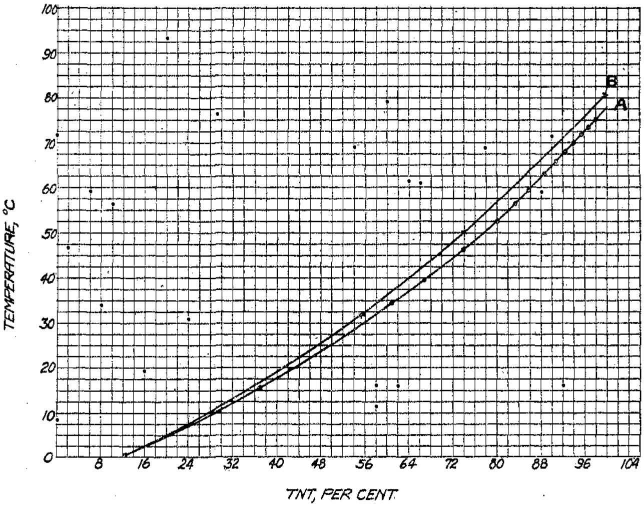

Fig. 3.—Concentration curve of TNT in benzene.

TABLE X

APPROXIMATE SOLUBILITY IN BENZENE

° C.	TNT, %	° C.	TNT, %
16.8	36.71	63.30	88.85
30.4	55.55	65.8	90.93
34.7	60.24	67.9	92.41
39.75	66.74	70.0	94.00
46.15	73.90	71.8	95.41
52.65	80.00	73.05	96.30
56.15	83.33	75.1	97.84
59.3	85.88	...	...

In order to derive the curve showing true equilibrium, 3 solutions of different concentrations were prepared in the cooling-curve apparatus, heated to a point considerably above the saturation temperature, and then immersed in a thermostat bath maintained several degrees above the saturation temperature for that concentration as shown by the curve derived by the cooling-curve method. The temperature of the thermostat bath was then so varied that, after long standing, there was a slight crystal growth on the seed of trinitrotoluene present in each case and, on raising the temperature 0.1°, the crystal growth so produced dissolved. The temperature at which there was just appreciable growth after 24 hours was taken as the saturation temperature for that concentration.

TABLE XI

TRUE SOLUBILITY IN BENZENE

TNT, %	Saturation temp. on cooling curve ° C.	Saturation temp. found by thermostat ° C.
55.55	30.4	31.95
73.90	46.15	50.1
88.85	63.3	67.2

Wagon-pipet determinations at 0.4° gave a value of 14.5 g. per 100 g. of benzene, or 12.6%. This point, the three saturation temperatures found above and the value 80.6° for 100% concentration were then plotted on Fig. 3. A smooth curve, B, somewhat parallel to that obtained by plotting the cooling-curve data was then drawn through these points and represents the curve of true equilibrium.

Intermediate points on this curve were obtained by interpolation and calculated in terms of g. of trinitrotoluene per 100 g. of benzene, and are given in the complete solubility table.

Toluene

The solubility in this solvent was found to be of the same order as that for benzene, and determinations were made by the cooling-curve method to obtain the relative solubility. The concentration values so obtained follow.

TABLE XII

APPROXIMATE SOLUBILITY IN TOLUENE

° C.	TNT, %	° C.	TNT, %
1.5	22.91	62.5	85.44
21.0	37.05	64.3	87.50
34.4	51.87	66.0	88.94
37.4	55.69	68.0	91.01
40.4	60.16	71.0	93.24
45.8	67.16	72.6	94.93
52.5	75.06	74.5	96.66
56.5	79.59	75.4	97.51
60.1	83.30	..	...

Using these values as guides, the true solubility was determined for concentrations of 55.69% and 69.20% by the method of noting the formation of crystals after long standing at a constant temperature. These two concentrations gave saturation temperatures of 39.2° and 51.5°, respectively. These values, with a value of 80.6° for 100% trinitrotoluene, determine the concentration curve which represents true equilibrium. Solubility values, obtained from this by interpolation and calculation to the basis of g. per 100 g. of toluene, are given in the complete solubility table.

Acetone

Trinitrotoluene is more soluble in acetone than in any solvent so far considered. A series of determinations of the relative solubility made by the cooling-curve method gave the following values.

TABLE XIII

APPROXIMATE SOLUBILITY IN ACETONE

° C.	TNT, %	° C.	TNT, %
21.2	53.60	61.05	89.21
29.1	60.91	63.5	91.08
35.6	67.32	66.25	92.80
40.1	71.73	67.8	93.96
43.7	75.12	69.8	95.16
44.45	75.75	71.5	96.23
49.8	80.43	73.05	97.17
55.1	84.81	75.4	98.56
57.2	86.51	...	...

Solutions having concentrations of 56.196% and 77.55% of substance were then prepared in air-tight flasks and found to have saturation points of 25.25° and 49.7°, respectively, by the method described for benzene. Using these points, a value for 0.4° found by means of the wagon-pipet, and the value, 80.6° for 100% trinitrotoluene, a concentration curve was drawn representing true equilibrium of trinitrotoluene and acetone over this range. Values taken from this curve by interpolation and calculated to the basis of g. per 100 g. of acetone are given in the complete solubility table.

Aniline

It is known that aniline forms a complex with trinitrotoluene of the formula[17] $C_6H_5NH_2.C_6H_2CH_3(NO_2)_3$ and a melting point of 83° to 84°.

Starting with a concentration of about 5200 g. of trinitrotoluene per 100 g. of aniline, a large number of determinations were made by the cooling-curve method. The method worked very well as the concentration was decreased, giving a smooth curve, until a concentration giving a point, C, of about 68° was reached. When the concentration was decreased further, there was no evidence of supercooling with consequent rise in temperature of the mixture after crystals had begun to separate; the temperature would fall to a certain point, remain constant for a short time, and then continue to decrease. It was noticed that as the concentration was decreased, the temperature at which the solid began to separate was higher in each case, until at a concentration of 244 g. per 100 g. of aniline (which corresponds to the composition of the complex given above), solid commenced to separate at about 83.5°, and the temperature of the mixture remained constant for some time. Upon further decreasing

[17] Hepp, *Ann.*, **215**, 365 (1882).

the concentration, solid began to separate at 83.5° and the temperature of the mixture continued to decrease, so that no definite point of equilibrium below 83.5° for a concentration of only 200 g. per 100 g. of aniline could be obtained. When the concentration was decreased to about 100 g. per 100 g. of aniline, it was found that the familiar phenomenon of supercooling below the true saturation temperature occurred, and there was a consequent rise in the temperature of the mixture after the formation of crystals had begun. Further determinations at lower concentrations were then made by this method. The results obtained follow, and are shown as the lower curve on Fig. 4.

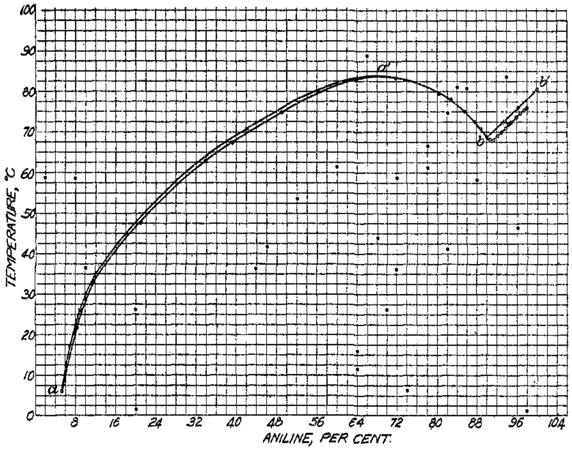

Fig. 4.—TNT–Aniline.

TABLE XIV

APPROXIMATE SOLUBILITY IN ANILINE

° C.	TNT, %	° C.	TNT, %
6.0	5.41	68.1	90.71
21.8	8.05	67.8	91.63
33.25	11.72	68.6	92.34
47.6	20.97	69.9	93.31
62.85	33.99	70.85	94.05
67.4	39.00	71.0	94.14
74.75	48.99	71.9	94.72
83.5	70.95[a]	72.5	95.19
79.6	80.37[a]	72.7	95.36
78.0	82.78[a]	73.5	95.98
75.0	85.63[a]	74.6	96.88
72.5	87.55[a]	75.3	97.65
70.2	88.85[a]	76.0	98.11
68.5	90.00[a]	...	...

[a] There was no supercooling evident in making these determinations, so these results represent true saturations.

Four solutions of definite concentrations were made up, heated above their saturation temperatures, and the true saturation temperature for each was determined by means of crystal growth as described for benzene. This was very difficult, as aniline and trinitrotoluene form an almost opaque solution and the presence of small crystals, which are a deep red, cannot easily be detected when they first appear.

TABLE XV

TRUE SOLUBILITY IN ANILINE

° C.	TNT, %	° C.	TNT, %
26.0	9.01	72.5	93.30
71.0	42.20	76.0	96.21

These results were then plotted as shown on Fig. 4. Using these points, the true saturation concentration at 83.5°, and the 100% value of 80.6°, the 2 upper curves, *A-A′* and *B-B′*, were drawn. The intermediate values were obtained by interpolation and are given in the complete solubility table.

The use of aniline as a solvent in purification work or for other purposes is not to be recommended, as the trinitrotoluene so treated is always contaminated and reddish.

Pyridine

By means of the cooling-curve method, a series of determinations of the relative solubility in pyridine was made.

TABLE XVI

APPROXIMATE SOLUBILITY IN PYRIDINE

° C.	TNT, %	° C.	TNT, %
21.2	60.17	65.5	90.96
30.6	66.95	67.5	92.41
37.25	71.94	69.5	93.81
42.5	75.06	71.6	95.23
49.5	80.04	73.7	96.64
54.9	83.47	75.0	97.50
58.2	85.80	75.7	98.01
62.7	88.97	76.2	98.35

Using these values as guides, several concentrations of the 2 substances were prepared and their saturation points were determined by means of the thermostat. At 33.2°, 48.15° and 64.9° the percentages found were 67.06, 77.79 and 89.20, respectively. These values were plotted, and a line drawn through them and the value 80.6° for 100% trinitrotoluene gave the true equilibrium curve. It was found impossible to make determinations by means of the wagon-pipet as, due to the very low vapor pressure of pyridine (12 mm. of mercury at 18.5°), the pyridine could not be completely volatilized without considerable loss of trinitrotoluene. Furthermore, when pyridine and trinitrotoluene are heated above room temperature, some decomposition ensues and the mixture becomes black. For this reason it was found very difficult to determine the true saturation points given above, by means of the thermostat.

By interpolation from the true concentration curve so found, a series of values was calculated to the basis of g. per 100 g. of pyridine. These are given in the complete solubility table.

Trinitrotoluene-pyridine Complex.—An unstable complex having the composition, $C_6H_2CH_3(NO_2)_3.C_5H_5N$, was isolated. It is formed when trinitrotoluene and pyridine are brought into contact at a temperature lower than 40°, or by causing a solution of trinitrotoluene in pyridine to deposit crystals at a temperature lower than this.

The molecular compound so obtained is light brown and unstable toward the atmosphere and heat. It has a strong odor of pyridine, due to decomposition. It is, however, stable in an atmosphere saturated with pyridine. It melts with decomposition between 40° and 42°. It was prepared as follows.

Pyridine was almost or completely saturated with trinitrotoluene at 40° and 20°. Crystals were then deposited by cooling the solutions to 25° and 0°, respectively. These were quickly separated, crushed and dried by means of filter paper, and the powder exposed to the air as little as possible. When the product would no longer "pack," it was placed in an air-tight container, from which samples were withdrawn for analysis and determination of the melting point.

TABLE XVII

TRINITROTOLUENE-PYRIDINE COMPLEX

	Sample I	II	Calc.
Temperature range ° C.	40 to 25	20 to 0	
Melting point, ° C.	40 to 42	40 to 42	
TNT, %	74.12	74.19	74.18

That this complex is formed when the 2 substances are merely brought into contact without solution was shown by agitating pyridine with an excess of trinitrotoluene at 0° and 22°. The undissolved solid was separated, crushed, and quickly dried with filter paper. It had the appearance of the product described above, melted with decomposition over the range 40° to 42° in each case, and on analysis gave 78.77% and 77.96% of trinitrotoluene, respectively, showing an almost quantitative formation of the complex.

Analysis of this complex consisted of exposing a weighed sample to the atmosphere for 10 hours, heating at 60° for 3 hours, cooling and reweighing. The residue in each case was proved to be trinitrotoluene by determination of its melting point and by the development of the characteristic color with sodium hydroxide solution.

When studied under the microscope, this complex was found to consist of a mass of crystallites so small that their crystal characteristics could not be determined. This was true even when large and fairly regular crystals of the complex were grown slowly, and when residual trinitrotoluene from the analysis of this complex was examined, it was found to be in this extreme state of division also.

TABLE XVIII

SOLUBILITY DATA

Grams of Trinitrotoluene per 100 g. of Solvent

Interpolated values

° C.	Water	Aniline	Pyridine	Toluene	Acetone
0	0.0100	5.0	..	28	57
5	0.0105	5.5	..	32	66
10	0.0110	6.1	..	38	78
15	0.0120	7.4	..	45	92
20	0.0130	8.1	137	55	109
25	0.0150	9.4	158	67	132
30	0.0175	11.4	181	84	156
35	0.0225	14.1	215	104	187
40	0.0285	18.0	255	130	228
45	0.0360	22.7	302	163	279
50	0.0475	28.7	370	208	346
55	0.0570	35.9	462	272	449
60	0.0675	44.5	600	367	600
65	0.0775	55.3	833	525	843
70	0.0875	69.3, 807, 1043	1250	826	1350
75	0.0975	92.3, 595, 2074	2460	1685	2678
80	0.1075	130.0	..	..	..
85	0.1175	...	..	..	..
90	0.1275	...	..	..	..
95	0.1375	...	..	..	..
100	0.1475	...	..	..	..

° C.	Benzene	Carbon tetrachloride	95% Alcohol	Chloroform	Carbon disulfide	Ether
0	13	0.20	0.65	6	0.14	1.73
5	24	0.25	0.75	8.5	0.20	2.08
10	36	0.40	0.85	11	0.26	2.45
15	50	0.50	1.07	15	0.35	2.85
20	67	0.65	1.23	19	0.48	3.29
25	88	0.82	1.48	25	0.63	3.80
30	113	1.01	1.80	32.5	0.85	4.56
35	144	1.32	2.27	45	1.13	..
40	180	1.75	2.92	66	1.53	..
45	225	2.37	3.70	101	2.02	..
50	284	3.23	4.61	150	..	..
55	361	4.55	6.08	218	..	..
60	478	6.90	8.30	302	..	..
65	665	11.40	11.40	442	..	..
70	1024	17.35	15.15	...	..	..
75	2028	24.35	19.50	...	..	.

An attempt was made to find a break in the curve indicative of the existence of this compound. As stated before, the wagon-pipet method could not be applied. Accordingly, the cooling-curve method was employed, but the data obtained, while indicating a very slight break in this region, were not sufficiently accurate to prove this conclusively.

Summary

Complete solubility data were obtained for trinitrotoluene in 11 solvents frequently used. A summary is given in the foregoing table showing the values at 5° intervals. In the course of the work it was necessary to use different methods depending upon the nature of the solvent and the relative solubility.

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AN IMPROVED OPTICAL LEVER MANOMETER

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In considering some measurements on the adsorption of toluene vapor by plane glass surfaces, as described in the paper immediately following, it was found that none of the manometers described in the literature was entirely suitable. The McLeod gage is inaccurate with easily condensable vapors. The hot wire manometer[1] is hardly sensitive enough. The thermionic pressure gage[2] would decompose the toluene. The use of the Knudsen gage[3] offered many difficulties. The Rayleigh manometer[4] and the optical lever manometer of Shrader and Ryder[5] appeared to be the only ones that could be used. After some experimentation, the optical lever manometer was selected.

This manometer as previously described is essentially a U-tube mercury manometer. Floating on one of the mercury surfaces is a glass ball, which is attached to a mirror pivoted on 2 knife edges in such a way that

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[1] Pirani, *Verh. I. Deut. Phys. Ges.*, 4, 686 (1906).

[2] Buckley, *Proc. Nat. Acad. Sci.*, 2, 683 (1916).

[3] Knudsen, *Ann. Physik*, 32, 809 (1910).

[4] Rayleigh, *Phil. Trans.*, 196A, 905 (1901).

[5] Shrader and Ryder, *Phys. Rev.*, 13, 321 (1919).