by 5.6 ± 0.1 cal./deg. per mole at 70° K., and it is concluded that this value will not be appreciably different at the absolute zero.

We wish to express our thanks to the Giant Powder Company for supplying us with crystalline glycerol.

BERKELEY, CALIFORNIA

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

THE SOLUBILITY OF TRINITRO-PHENYLMETHYL-NITRAMINE (TETRYL) IN ORGANIC SOLVENTS[1]

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Introduction

Work on this subject was undertaken as the logical continuation of work previously done on the solubility of trinitrotoluene in organic solvents. Tetryl is one of the newer high explosives, and as it is now used to a considerable extent, to have its fundamental data available is important. A search of the literature showed that its solubility in the common solvents was expressed in a qualitative rather than a quantitative manner. Accordingly, quantitative measurements of the solubility of this substance in a number of the common organic solvents at different temperatures were made, and solubility curves were derived from the data so obtained.

Materials

Tetryl.—A good grade of commercial tetryl was purified by recrystallization from hot benzene after filtration to separate any insoluble matter. The crystals were dried in air to remove benzene held mechanically. They were then recrystallized from boiling 95% ethanol, redissolved in hot 95% ethanol, and the solution was poured into about 2 volumes of cold distilled water. The mixture was allowed to stand in a dark place for several hours to cool for complete crystallization. The crystals were caught on a Büchner funnel, washed several times with cold distilled water, and given a final rinsing with cold 95% ethanol in order to facilitate drying. The mass of crystals was dried on filter paper, and kept in desiccators over sulfuric acid in a dark place.

Efforts to obtain colorless tetryl proved unsuccessful. The material precipitated from the hot ethanol by water appeared colorless, but as soon as it was filtered a faint yellow color developed, even when the work was carried out in a dark room.

The final product of this purification was a mass of very light, flaky crystals of a very faint yellow tint. The setting point was found to be 128.72°.

Solvents.—The solvents used in this work were the same lots of purified solvents used in the study of the solubility of trinitrotoluene.[4] For a list of the physical constants and methods of purification, see that paper.

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

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[4] THIS JOURNAL, 45, 44 (1923).

Method

The method adopted was that of obtaining solutions in equilibrium with an excess of the solute at a definite temperature, removing samples by means of the wagon-pipet, weighing, evaporating off the solvent, and reweighing the dry tetryl. The procedure and precautions have been given in the previous paper on the solubility of trinitrotoluene.[4]

In the following tables, the presence of an asterisk after a solubility value indicates that the value was obtained by approaching equilibrium from a temperature lower than that at which the determination was to be made.

TABLE I

SOLUBILITY OF TETRYL IN WATER

	G. of tetryl per 100 g. of water			
°C.	A	B	C	Av.
0.5	0.0051	0.0053*	0.0048	0.0051
9.6	0.0069	0.0071	0.0067*	0.0069
14.8	0.0073*	0.0078	0.0063	0.0071
20.5	0.0070	0.0082	0.0070	0.0074
30.0	0.0087*	0.0083	0.0082	0.0084
35.0	0.0092*	0.0095	0.0095	0.0094
40.0	0.0098	0.0106	0.0117	0.0107
45.0	0.0137	0.0133*	0.0135	0.0135
50.0	...	0.0202	0.0197	0.0200
60.05	0.0387	0.0347	0.0327	0.0350
65.05	...	0.0442	0.0444	0.0443
69.5	0.0531	0.0516	0.0546	0.0531
84.2	0.0935	0.0968	....	0.0952
96.7	0.1603*	0.1635	....	0.1619
98.55	0.1754	0.1755	....	0.1755

TABLE II

THE SOLUBILITY OF TETRYL IN ETHER

	G. of tetryl per 100 g. of ether			
°C.	A	B	C	Av.
0.4	0.1917	0.1919	0.1890	0.1918
9.6	0.3174*	0.3129	0.3220	0.3174
14.8	0.3930	0.3839*	0.3786	0.3852
20.5	0.4241*	0.4222	0.4195	0.4219
29.05	0.4624*	0.4666	0.4750	0.4680
30.0	0.4757*	0.4718	....	....
..	0.4690	0.4688	....	0.4713

TABLE III

SOLUBILITY OF TETRYL IN 95% ETHANOL[5]

	G. of tetryl per 100 g. of 95% ethanol			
°C.	A	B	C	Av.
0.5	0.333	0.366	0.273	0.324
25.0	0.651*	0.646	0.648	0.648
33.0	0.849	0.843	0.837*	0.843

[5] The writers decided to use 95% ethanol rather than absolute ethanol, as this is the strength in common use in the laboratory and plant.

TABLE III (*Continued*)

	G. of tetryl per 100 g. of 95% ethanol			
°C.	A	B	C	Av.
39.0	1.08	1.05	1.10	1.08
45.1	1.46	1.31*	1.41	1.39
51.0	1.85	1.78*	1.80	1.81
56.05	...	2.24	2.22	2.23
61.0	2.75	2.77	2.74*	2.76
66.1	3.49	...	3.52	3.50
70.05	4.22	...	4.23	4.23
73.25	5.09	4.85*	4.92	4.95
77.1	5.70	5.89	...	5.80

TABLE IV

SOLUBILITY OF TETRYL IN CARBON DISULFIDE

	G. of tetryl per 100 g. of carbon disulfide			
°C.	A	B	C	Av.
0.4	0.0098	0.0095	0.0089	0.0094
15.0	0.0172*	0.0173*	0.0185	0.0177
28.0	0.0264*	0.0254*	0.0315	0.0277
32.2	0.0337*	0.0331	0.0330	0.0333
37.0	0.0436*	0.0440*	0.0437	0.0437
40.0	0.0549	0.0559	0.0563	0.0557
46.1	0.1020*	0.1072*	....	....
..	0.1024	0.1074*	....	0.1048

TABLE V

SOLUBILITY OF TETRYL IN CHLOROFORM

	G. of tetryl per 100 g. of chloroform			
°C.	A	B	C	Av.
0.4	0.281	0.294	0.272	0.282
15.0	0.450*	0.462*	0.507	0.473
28.0	0.738*	0.742*	...	0.740
32.2	0.851*	0.852	0.867	0.856
40.0	0.198*	1.215	1.215	1.209
50.0	1.760*	1.783	1.798	1.780
58.8	2.528	2.540	2.527	2.53

TABLE VI

THE SOLUBILITY OF TETRYL IN CARBON TETRACHLORIDE

	G. of tetryl per 100 g. of carbon tetrachloride			
°C.	A	B	C	Av.
0.5	0.0071	0.0075	....	0.0073
25.0	0.0299*	0.0309	....	0.0304
33.0	0.0446	0.0452	....	0.0449
39.0	0.0554*	0.0565	0.0567	0.0566
45.1	0.0728*	0.0735	0.0731	0.0733
51.0	0.0952*	0.1005	0.0989	0.0997
56.05	0.1299	0.1316	....	0.1307
61.0	0.1557*	0.1600	0.1594	0.1597
66.1	0.1969*	0.2011	0.2014	0.2012
70.05	0.2427	0.2411	0.2418	0.2419
73.25	0.2777	0.2769	0.2772	0.2773

From solubility curves derived from the foregoing values, values at 5° intervals were obtained by interpolation and used to form the following table of solubilities of tetryl.

TABLE VII

G. OF TETRYL PER 100 G. OF SOLVENT

Interpolated values

° C.	Water	95% Ethanol	Carbon tetra-chloride	Chloro-form	Carbon disulfide	Ether
0	0.0050	0.320	0.007	0.28	0.0090	0.188
5	0.0058	0.366	0.011	0.33	0.0120	0.273
10	0.0065	0.425	0.015	0.39	0.0146	0.330
15	0.0072	0.496	0.020	0.47	0.0177	0.377
20	0.0075	0.563	0.025	0.57	0.0208	0.418
25	0.0080	0.65	0.031	0.68	0.0244	0.457
30	0.0085	0.76	0.039	0.79	0.0296	0.493
35	0.0094	0.91	0.048	0.97	0.0392	...
40	0.0110	1.12	0.058	1.20	0.0557	...
45	0.0140	1.38	0.073	1.47	0.0940	...
50	0.0195	1.72	0.095	1.78	....	...
55	0.0270	2.13	0.124	2.23	....	...
60	0.0350	2.64	0.154	2.65	....	...
65	0.0440	3.33	0.193	..	....	...
70	0.0535	4.23	0.241	..	....	...
75	0.0663	5.33	0.297	..	....	...
80	0.0810	...	...	..	....	...
85	0.0980	...	...	..	....	...
90	0.1220	...	...	..	....	...
95	0.1518	...	...	..	....	...
100	0.1842	...	...	..	....	...

Summary

Complete solubility curves were obtained for tetryl in 6 solvents frequently used, the solubility being comparatively slight in all cases, and in general of a lower magnitude than that found for trinitrotoluene in the same solvent and under the same conditions.

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