REPORT NO. R-1505

DATE 6 January 1939

SUBJECT

FR-1505

Report of

The Densities and Freezing Points of Solutions of Sodium Permanganate

by

S. R. Miller
J. C. White

NAVAL RESEARCH LABORATORY

BELLEVUE, D. C.

DECLASSIFIED

SECRET

Unclassified Unclassified Unclassified

[redacted]

9 January 1939

NRL Report No.P-1505
SERIAL No.8.

NAVY DEPARTMENT

BUREAU OF ENGINEERING

Report of

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NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D.C.

Number of Pages: Text - 4 Tables - 3

Authorization: BuOrd. Project Order 5037-Ord. and BuOrd.ltr.NP14(9)(R1) of 7 July 1934.

Date of Test: September, October, November, 1938.

Prepared by:

R. R. Miller, Assistant Chemist

J. C. White, Assistant Chemist

DECLASSIFIED

Reviewed by:

R. H. Canfield, Sr.Phys., Superintendent
Metallurgy and Thermodynamics Division

Approved by:

H. M. Cooley, Captain, USN, Director

Distribution:
BuOrd. (5)
BuEng. (2)

bms

Unclassified

Classification changed from Secret
to Unclassified
By authority of NRL Memo ltr.
File No. IV-1550-364/48 Dated 11-22-48

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APPENDICES

ABSTRACT

This report is the first of a number of reports intended to supply the various technical data required in planning the service application of the Navol Torpedo.

Graphs and Tables are presented giving the freezing points and densities of sodium permanganate solutions at various concentrations and temperatures, as determined at this Laboratory, no published data being available.

For possible use in freezing conditions, freezing points are given for a number of solutions containing additions of calcium and lithium chlorides as anti-freeze protection. The actual strength of sodium permanganate solution proposed for use in the service is 15%, which this work indicates will begin to freeze at 24° F. The addition of 15% calcium chloride will reduce this to about 7° F. below zero (Table 2).

AUTHORIZATION

1. The tests were authorized by Bureau of Ordnance Project Order 5037-Ord. and Bureau of Ordnance letter NP14(9)(R1) of 7 July 1934.

STATEMENT OF PROBLEM

2. The object of the research here reported is to secure information necessary in preparing and handling solutions of sodium permanganate, and in particular to determine conditions when freezing may be apprehended.

THE PHASE DIAGRAM OF THE SYSTEM SODIUM PERMANGANATE-WATER AND THE DENSITIES OF SODIUM PERMANGANATE SOLUTIONS

3. The temperature at which a solid phase appeared was determined for various solutions from 0% to 91% sodium permanganate. The solid phase was either ice, sodium permanganate trihydrate or sodium permanganate monohydrate depending upon the concentration of the solution.

4. The densities of sodium permanganate solutions were determined over a concentration range from 0% to 25% and over a temperature range of 0° C. to about 40° C.

5. The freezing point curve and solubility curves were obtained by recording the cooling curves for various concentrations of sodium permanganate. This was done with a four junction thermocouple and a Leeds and Northrup Recording Potentiometer. The thermocouple was calibrated, over the range used, against various fixed points using 0° C. as the reference junction. A smooth curve was obtained both above and below 0° C. The solutions were mechanically stirred during the cooling. A change in the cooling rate indicated a phase change.

6. The solutions used above were made up by mixing a weighed amount of sodium permanganate and a weighed amount of water. These solutions were also analyzed by titrating a weighed amount of solution against a weighed amount of standard sodium oxalate. Repeated analyses showed that the solutions could be made up accurately.

7. The sodium permanganate received for this work analyzed to be 88.0 percent. This material was dried in vacuo at 100° C. on a steam bath and on analysis was found to be 98.5%. Further drying at 100° C. did not increase the percentage.

8. Difficulty was experienced in obtaining cooling curves for solutions above 88%. Several points were obtained

for the eutectic point between the monohydrate and the anhydrous material. A freezing point for a 89.9% solution was obtained. This mixture was made by adding weighed amounts of the anhydrous material (98.5%) and the material received (88.0%).

9. In Table 1, the temperatures are given at which a solid phase appears for a given percentage of sodium permanganate. For percentages below 41.2% the solid phase is ice; between 41.2 and 75.6% the solid phase is sodium permanganate trihydrate; between 75.6 and 91% the solid phase is the monohydrate. The values in Table 1 are taken from the curve drawn through the experimental points. The phase diagram is shown by Graph I. The solubility curve of the anhydrous material must fall somewhere within the shaded area. The anhydrous material decomposes before it melts.

"Anti-Freeze" Mixtures

10. The freezing points of several sodium permanganate solutions to which either calcium or lithium chloride had been added were determined. The results are shown in Table 2.

When as much as 10% lithium chloride is added to a 15% solution of sodium permanganate the freezing point is lowered by a considerable amount, but when lithium chloride is added to a 30% solution of sodium permanganate a solid salt phase appears at a higher temperature than the freezing point of the 30% solution of sodium permanganate itself. When more than 15% calcium chloride is added to a solution of sodium permanganate stronger than 25%, a solid salt phase appears at a temperature above -26° C. (-14.7° F.).

11. The densities of the sodium permanganate solutions were determined by the use of dilatometers. The dilatometers were calibrated by observing the height to which a given weight of water stood at a known temperature. The capillary stems were calibrated by weighing the amount of water contained between fixed points at several places on the stem. The coefficient of cubical expansion for the dilatometers were also determined by measuring the volume of a known weight of water at 25.3° C. and at 1.35° C.

12. Five different concentrations of sodium permanganate were used. These were put in the dilatometers by means of a fine capillary tube. Both the solution and dilatometer were kept at 0° C. during the operation in order to keep the very dark solutions from getting on the upper portion of the calibrated tube. The solutions were apt to cling to the sides of the tube and thereby make it difficult to read the volume as well as lead to error in the volume

[redacted]

read. The dilatometers were then placed in the thermostat set at 1.35° C. and allowed to come to that temperature. This was ascertained by observing the volume in the capillary. A cathetometer was used to determine the volume between graduations on the capillary tubes. The volumes were easily read to 0.001 cc.

The volumes were determined at 1.35° C., 13.0° C., 25.3° C. and 37.45° C. for each of the five solutions by use of five dilatometers. In order to be sure the temperatures were constant in each case the volumes were read until a constant volume was obtained. After the volumes were determined, the dilatometers plus the solutions were weighed. To be sure that there was no loss in weight of the solutions while standing in the dilatometers, they were weighed again the following day. No loss occurred.

13. All weights were corrected to vacuum and the volumes corrected for the cubical expansion. The volumes of the dilatometers were approximately 45 cc and the capillary stems 1 cc. The temperature of the thermostat at each temperature was constant to within ±.02° C.

14. The absolute densities as determined are given in Table #2 and plotted in Graph No. 2. In Table #4 are values taken from Graph No. 2.

CONCLUSIONS

15. The phase-diagram shows that solutions of sodium permanganate of concentrations lying between zero and 48% do not begin to freeze (crystallize) until the temperature is below 32° F. The composition hitherto used in experiment (15%) freezes at about 24° F. In case of extreme winter conditions, the freezing point can be reduced to below zero fahrenheit by addition of 15% calcium chloride which is known not to interfere with operation of the torpedo.

TABLE 1

% $NaMnO_4$	Freezing Point °C	% $NaMnO_4$	Freezing Point °C	% $NaMnO_4$	Freezing Point °C
0	-0.21	34	-12.40	66	32.4
2	-0.62	36	-13.30	68	34.1
4	-1.15	38	-14.20	70	35.4
6	-1.70	40	-15.2	72	35.6
8	-2.40	41.2	-15.8 E	74	35.3
10	-3.05	42	-14.0	75	34.6
12	-3.80	44	-10.0	75.5	34.0
14	-4.60	46	- 5.8	75.6	33.8 E
16	-5.45	48	- 1.6	76.0	35.3
18	-6.30	50	+ 2.6	78.0	44.5
20	-7.10	52	6.8	80	54.0
22	-8.00	54	11.0	82	63.3
24	-8.85	56	15.2	83	66.5
26	-9.75	58	19.4	84	67.7
28	-10.6	60	23.3	86	68.3
30	-11.5	62	26.9	88	68.0
32		64	30.0	90	66.1
				91	34. F
				92	Not determined

Solid Phase Ice.

Solid Phase Trihydrate.

Solid Phase Monohydrate.

[redacted]

TABLE 2

% $NaMnO_4$	% $CaCl_2$	Freezing Points Cent.	Freezing Points Fahr.
15.65	0	- 4.7	+ 23.5
13.5	15.2	-21.7	- 7.0
11.75	26.4	-50.	- 58.0
25.70	0	- 8.6	+ 16.5
22.15	12.9	-26	- 14.7
	% LiCl		
14.52	0	- 4.0	+ 24.8
13.1	10.0	-20.0	- 4.0

TABLE 3

% $NaMnO_4$	34.4° 1.35°	55.4° 13.00°	77.5° 25.30°	99.4° F. 37.45° C.
5.32	1.0404	1.0390	1.0361	1.0319
10.58	1.0843	1.0817	1.0776	1.0725
14.62	1.1148	1.1110	1.1062	1.1005
17.62	1.1471	1.1429	1.1371	1.1310
25.60	1.2243	1.2108	1.2110	1.2034

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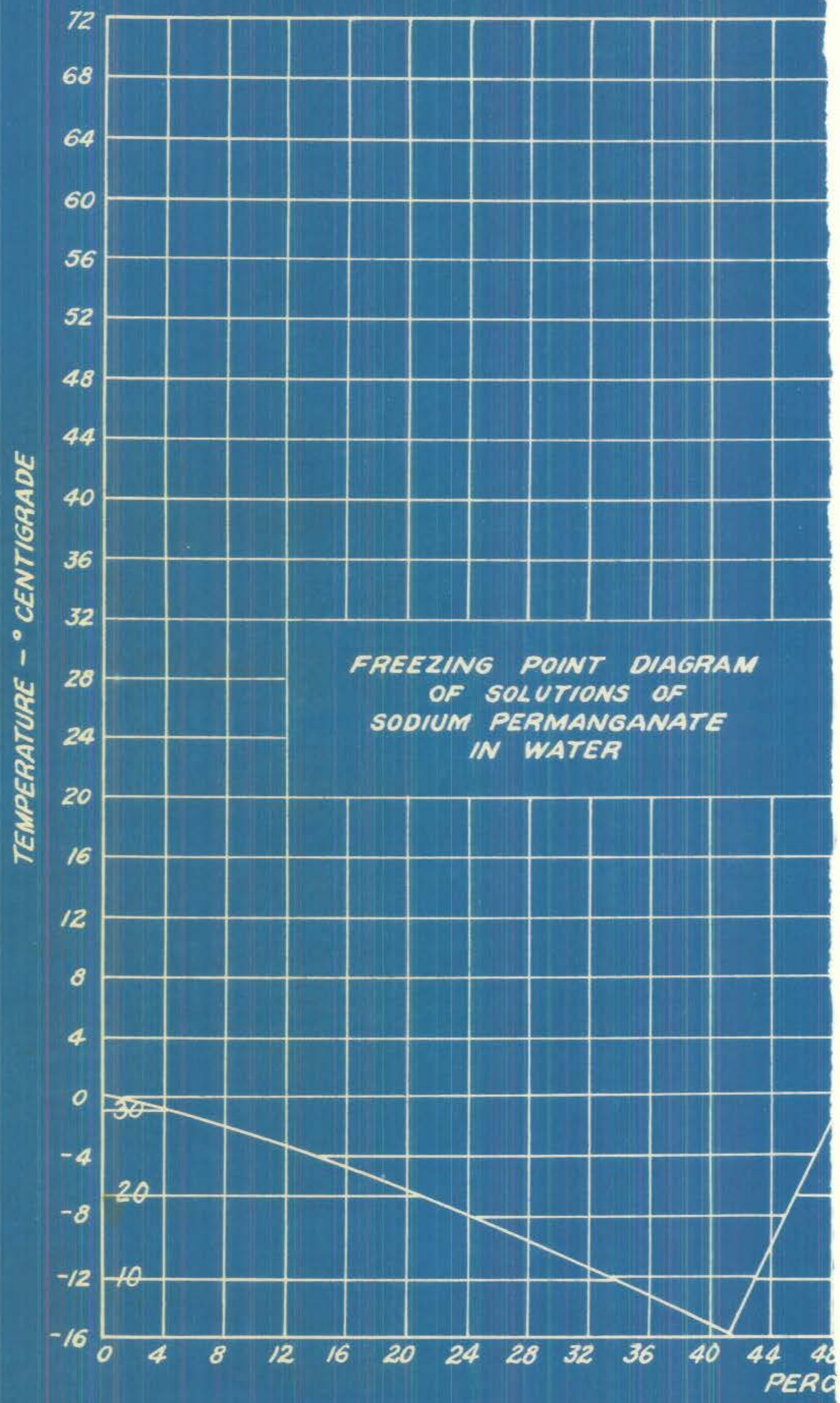
TABLE 4

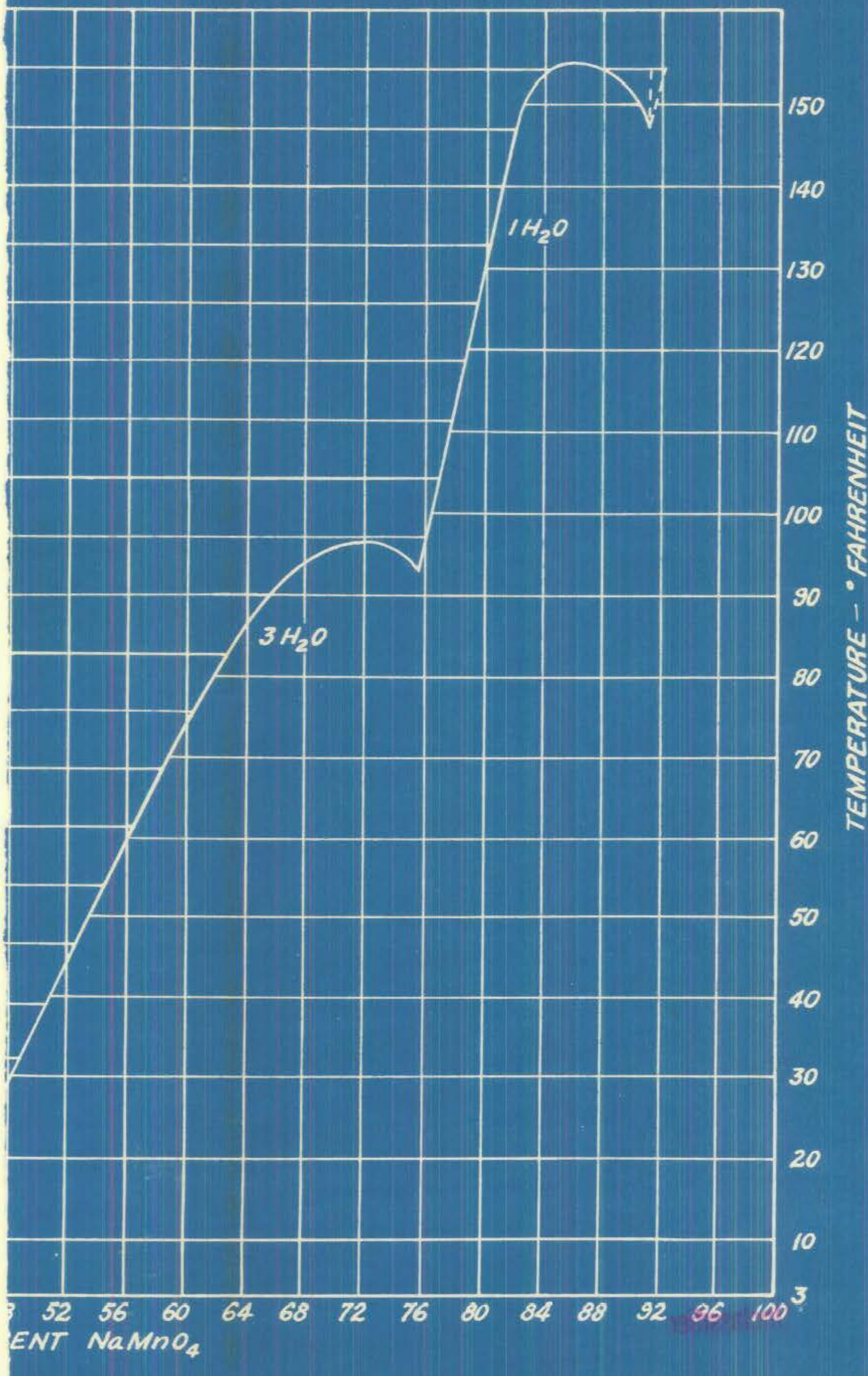
Density of $NaMnO_4$ Solutions

Freezing Points °C	Concentration 2%	4%	6%	8%	10%	12%	14%	16%	18%	20%	22%	24%	26%	28%
2	1.0154	1.0307	1.0463	1.0625	1.0795	1.0966	1.1143	1.1323	1.1501	1.1694	1.1888	1.2079	1.2276	1.2470
4	1.0152	1.0304	1.0460	1.0621	1.0790	1.0961	1.1136	1.1317	1.1497	1.1688	1.1879	1.2070	1.2265	1.2459
6	1.0149	1.0300	1.0457	1.0617	1.0784	1.0957	1.1128	1.1310	1.1490	1.1680	1.1870	1.2060	1.2254	1.2448
8	1.0146	1.0296	1.0453	1.0613	1.0780	1.0952	1.1120	1.1303	1.1484	1.1672	1.1860	1.2050	1.2243	1.2436
10	1.0143	1.0291	1.0450	1.0609	1.0776	1.0947	1.1112	1.1295	1.1478	1.1664	1.1852	1.2040	1.2232	1.2425
12	1.0140	1.0288	1.0447	1.0604	1.0770	1.0941	1.1104	1.1288	1.1469	1.1655	1.1842	1.2029	1.2221	1.2413
14	1.0136	1.0283	1.0442	1.0600	1.0766	1.0936	1.1097	1.1278	1.1460	1.1647	1.1832	1.2019	1.2211	1.2402
16	1.0132	1.0280	1.0439	1.0597	1.0759	1.0928	1.1088	1.1270	1.1450	1.1637	1.1822	1.2008	1.2200	1.2390
18	1.0127	1.0277	1.0433	1.0592	1.0752	1.0921	1.1081	1.1261	1.1440	1.1628	1.1812	1.1997	1.2189	1.2379
20	1.0121	1.0274	1.0429	1.0587	1.0744	1.0912	1.1074	1.1252	1.1430	1.1618	1.1802	1.1986	1.2178	1.2367
22	1.0116	1.0270	1.0422	1.0580	1.0737	1.0902	1.1068	1.1243	1.1421	1.1608	1.1792	1.1975	1.2166	1.2354
24	1.0110	1.0267	1.0416	1.0573	1.0729	1.0892	1.1060	1.1232	1.1411	1.1598	1.1781	1.1964	1.2154	1.2342
26	1.0104	1.0261	1.0410	1.0566	1.0722	1.0882	1.1053	1.1223	1.1400	1.1587	1.1770	1.1952	1.2142	1.2330
28	1.0098	1.0254	1.0403	1.0560	1.0713	1.0873	1.1044	1.1215	1.1392	1.1577	1.1760	1.1940	1.2130	1.2319
30	1.0092	1.0247	1.0397	1.0552	1.0706	1.0865	1.1035	1.1207	1.1382	1.1566	1.1749	1.1929	1.2118	1.2307
32	1.0087	1.0240	1.0390	1.0544	1.0698	1.0858	1.1028	1.1198	1.1373	1.1554	1.1738	1.1918	1.2105	1.2294
34	1.0082	1.0232	1.0383	1.0538	1.0692	1.0850	1.1018	1.1190	1.1364	1.1543	1.1727	1.1906	1.2093	1.2280
36	1.0076	1.0224	1.0376	1.0530	1.0683	1.0843	1.1009	1.1181	1.1354	1.1532	1.1715	1.1894	1.2080	1.2266
38	1.0068	1.0216	1.0368	1.0522	1.0677	1.0835	1.0999	1.1172	1.1343	1.1520	1.1702	1.1881	1.2070	1.2251

[redacted]

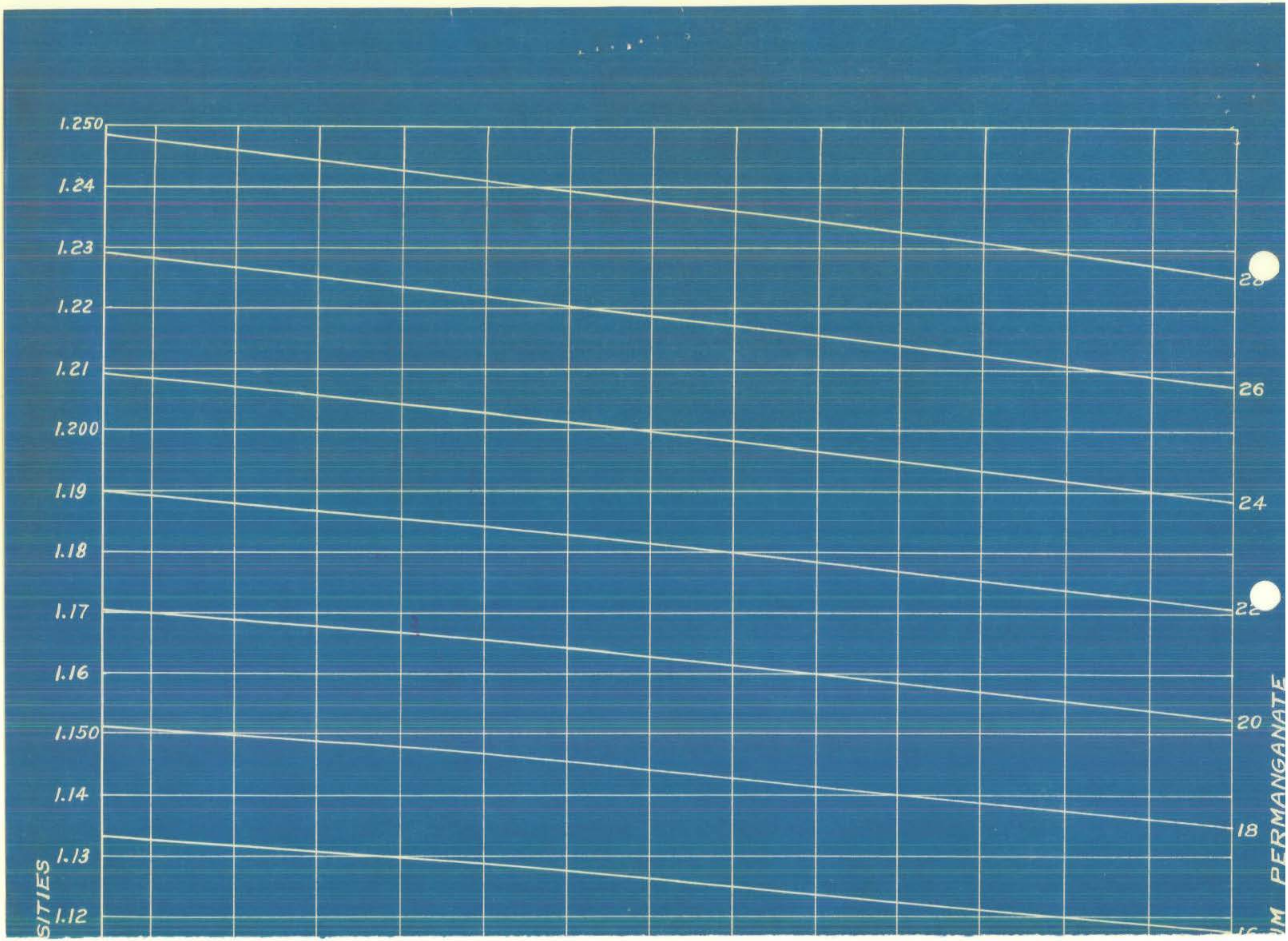


FREEZING POINT DIAGRAM
OF SOLUTIONS OF
SODIUM PERMANGANATE
IN WATER
TEMPERATURE - ° CENTIGRADE
72
68
64
60
56
52
48
44
40
36
32
28
24
20
16
12
8
4
0
-4
-8
-12
-16
30
20
10
0
4
8
12
16
20
24
28
32
36
40
44
PERC



150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
3
1 H_2O
3 H_2O
52 56 60 64 68 72 76 80 84 88 92 96 100
ENT $NaMnO_4$
TEMPERATURE - °FAHRENHEIT

PLATE I



1.250
1.24
1.23
1.22
1.21
1.200
1.19
1.18
1.17
1.16
1.150
1.14
1.13
1.12
SITIES
28
26
24
22
20
18
UM PERMANGANATE

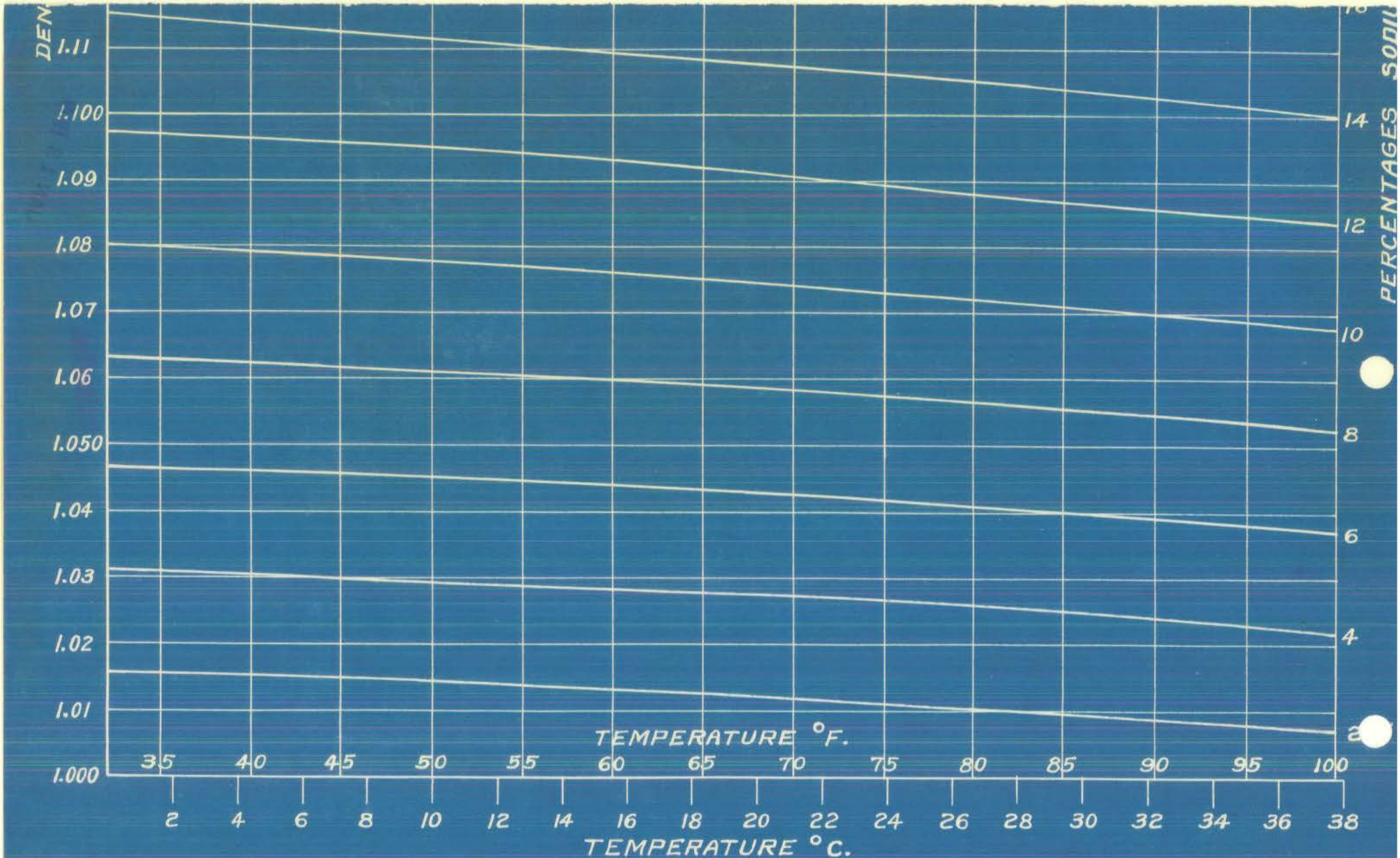

DEN
1.11
1.100
1.09
1.08
1.07
1.06
1.050
1.04
1.03
1.02
1.01
1.000
PERCENTAGES SODI
14
12
10
8
6
4
2
TEMPERATURE °F.
35 40 45 50 55 60 65 70 75 80 85 90 95 100
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38
TEMPERATURE °C.

PLATE 2