LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor

LW-8009
Chemistry - General

This Document consists of
11 Pages No. 75 of
93 Copies, Series A

FREEZING POINT DATA
FOR UNH - H₂O - HNO₃ SYSTEMS

Photostat Price \$ 1.80
Microfilm Price \$ 1.80
Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

By: M. K. Harmon

Date: December 17, 1947

CLASSIFICATION CANCELLED
DATE 12-3-55
For The Atomic Energy Commission
H. F. Canale
Chief, Declassification Branch

CLASSIFICATION CANCELLED
DATE
For The Atomic Energy Commission
H. F. Canale
Chief, Declassification Branch

CAUTION

This document contains information affecting the National Defense of the United States. Its transmission or the disclosure of its contents in any manner to an unauthorized person is prohibited and may result in severe criminal penalties under applicable Federal laws.

CHEMICAL DEVELOPMENT DIVISION
TECHNICAL DEPARTMENT
GENERAL ELECTRIC COMPANY
HARTFORD WORKS

RESTRICTED DATA **SECRET**
This document contains restricted data as defined in the Atomic Energy Act of 1946.

This document contains "Restricted Data" within the meaning of the Atomic Energy Act of 1946 (Public Law #386). Its transmission or the revelation of its contents in any manner, not authorized by that act, is prohibited by law.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISTRIBUTION OF DOCUMENT HW-8309

INTERNAL

Copy No.

1. A. B. Greninger
2. O. H. Greager
3. Carleton Shugg, Manager
4. Patent Group, Chicago
5. T. W. Hauff
6. F. W. Albaugh
7. R. E. Curtis
8. R. H. Beaton
9. R. B. Richards
10. J. M. Frame

Copy No.

11. A. R. Maguire
12. E. F. Curren
13. F. W. Woodfield
14. M. K. Harmon
15. 700 File
16. W. I. Patnode - 300 File
17. Extra
18. Extra
19. Pink Copy
20. Yellow Copy

EXTERNAL

- 21 - 30. Argonne National Laboratory
- 31 - 33. Atomic Energy Commission, Washington
34. Battelle Memorial Institute
- 35 - 44. Brookhaven National Laboratory
- 45 - 46. Carbide and Carbon Chemicals Corp. (K-25 Area)
- 47 - 48. Carbide and Carbon Chemicals Corp. (Y-12 Area)
- 49 - 60. Clinton Laboratories
- 61 - 63. General Electric Co., Schenectady
64. Iowa State College
- 65 - 67. Los Alamos
68. Madison Square Area
69. Massachusetts Institute of Technology
70. Monsanto Chemical Co., Dayton
- 71 - 72. National Bureau of Standards
73. Patent Advisor, Washington
74. Research Division (for NEPA), Oak Ridge
- 75 - 89. Research Division, Oak Ridge
- 90 - 93. University of California, Radiation Laboratory

DO NOT PHOTOCOPY

~~SECRET~~

HW-8309
Chemistry - General

FREEZING POINT DATA FOR UNH - H₂O - HNO₃ SYSTEMS

Summary

(Twenty-five)

Data are presented in Chapter II of the Project Handbook, on the freezing points of UNH-H₂O solutions, but none are available concerning the effect of HNO₃ on this system. In this series of experiments, therefore, 25 solutions were prepared and their freezing points were determined. The composition of these test samples ranged from 10% to 75% UNH, and from 0 to 3 M HNO₃. In all cases, cooling curves were obtained, and the "setting point" wherever possible was determined as the true freezing temperature. Crystal formation was observed closely with the aid of a strong light source, and the temperature at which crystals were first noted was taken as the freezing point for those solutions whose cooling curves exhibited no setting point.

In general, the results show that within the limits of nitric acid concentration investigated, solutions containing UNH equal to or greater than 57.5% by weight display a steady increase in freezing temperatures with increase in the concentration of HNO₃, and that solutions containing 30% or less UNH show a uniform lowering of freezing points as the HNO₃ content is increased. Solutions whose compositions lie between 30% and 57.5% UNH all exhibit minima, the positions of which depend upon the molarity of nitric acid present.

Experimental

Two sets of apparatus were designed and prepared _____ the first (Figure 1) for solutions freezing above 15°C., and the second (Figure 2) for those freezing below 15°C. The thermometers used (one for high temperatures, and one for low) were both calibrated against Eastern Laboratory standards, and both proved to be accurate to within 0.1°C. in their respective ranges.

The test solutions were prepared to approximate given pre-determined compositions (e.g. 30% UNH - 1.0 M HNO₃), the freezing points were obtained, and the samples were then submitted to the Laboratories Division for analysis.

~~SECRET~~

In performing the test, the sample was heated (if the freezing point was above room temperature) and was placed in the apparatus (Fig. 1). Air, dried by passing through concentrated H_2SO_4 , was forced into the outer jacket at a constant rate, evaporating the ether, and causing a gradual but steady lowering of the temperature of the solution. Temperature was plotted as a function of time, giving the cooling curve shown in Figure 3, and the "setting point" (caused by the heat of formation of the solid phase) was taken as the true freezing point.

The operation of the apparatus shown in Figure 2 was simple but effective. The tube containing the sample was pushed down in the center beaker until the spring was compressed, holding the screen securely in place. This beaker was then placed in the eutectic bath, and the salt solution as formed was forced by the compressed air into the annulus surrounding the test sample, the ice being held back by the screen. As the air was alternately cut off and on at the rate of about 3 times per minute, the cooling mixture was raised and lowered inside the inner jacket, providing smoother and more rapid cooling by the more efficient removal of heat (see Figure 3b.). This method, however, still leaves much to be desired, since in many cases (particularly those freezing below $-10^{\circ}C.$) the cooling rate was so slow that supercooling never occurred, and no "setting point" was obtained. Thus, the solution had to be observed with the aid of the micro lamp, and the point of incipient crystallization had to be taken as the freezing point. The Spencer microscope light beam made the crystal formation strikingly apparent and easily detectable by a phenomenon similar to the Tyndall effect in colloidal dispersions.

Table 1 presents the data obtained on the test solutions; i. e., freezing point, specific gravity, HNO_3 concentration, etc. In Figure 4, these data are shown as a plot of freezing points vs. percent UNH for a series of HNO_3 concentrations. It was found that for a solution containing no nitric acid, the composition resulting in the minimum freezing point ($-20^{\circ}C.$) was approximately 57.5% UNH, a total molarity of solute of 1.8. However, as can be seen from this graph, the freezing minima are lowered, corresponding to the decrease in UNH content as the HNO_3 concentration is increased, until a freezing point of $-27^{\circ}C.$ is reached for a solution of 30% UNH and 3 M HNO_3 , equivalent to a total molarity of 3.6. These facts are strikingly illustrated by Figure 5, a cross section of Figure 4, for which the values of all nitric acid molarities except 0.0, 0.3, 1.0 and 3.0 were obtained by interpolation.

The observed values for solutions containing no nitric acid agree fairly well with those found in the Project Handbook, the greatest variance occurring in the range of 55 - 65% UNH; this difference may have been due to the presence of free HNO_3 (not exceeding 0.005 M) retained by our salt on its recrystallization from distilled water. As a whole, however, the data presented in this report are felt to be of sufficient accuracy and precision to provide an extremely reliable definition of the freezing characteristics of any solutions falling within the range investigated.

~~SECRET~~

RW-8309
Chemistry - General

Table 1

Freezing Point Data for UNH - H₂O - HNO₃ Systems

UNH Sol'n No.	Density	UNH		HNO ₃		Freezing Point	
	25°C.	g./l.	per cent	g./l.	moles	°C.	°F.
1	*1.8707	1317.4	70.4	63.0	1.0	33.8	92.8
2	*1.8481	1285.0	69.6	50.48	0.8	32.5	90.5
3	*1.8733	1461.2	78.0	0.0	0.0	32.5	90.5
4	1.7658	1215.4	68.8	0.0	0.0	18.3	64.6
4b	1.7680	1217.1	68.8	0.0	0.0	16.3	61.0
5	1.6988	1110.1	65.35	0.0	0.0	5.7	42.2
6	1.7491	1130.1	64.61	48.20	0.77	19.2	67.8
7	1.2357	369.48	29.90	0.0	0.0	- 5.0	23.0
8	1.2659	367.97	29.07	57.72	0.92	-11.3	11.9
9	1.0669	107.85	10.1	0.0	0.0	- 1.0	30.2
10	1.0994	107.2	9.75	62.52	0.99	- 5.2	22.7
11	1.2579	107.54	8.6	177.3	2.81	-16.5	2.3
12	1.3287	393.6	29.6	178.5	2.84	-26.1	-15.0
13	*1.7644	1101.8	62.6	172.63	2.74	33.5	92.3
14	*1.8956	1351.6	71.3	140.48	2.23	44.5	112.0
15	1.0758	107.52	10.0	18.18	0.29	- 2.2	- 7.6
16	1.1493	370.5	32.2	17.72	0.28	- 6.5	20.3
17	1.7092	1107.7	64.8	17.66	0.28	11.0	51.8
18	1.7903	1249.7	69.8	18.34	0.29	23.5	74.3
19	1.5789	912.26	57.78	0.0	0.0	-20.0	- 4.0
20	1.5477	849.84	54.91	15.13	0.24	-20.7	- 5.2
21	1.4699	689.04	46.88	60.62	0.96	-21.1	- 6.0
22	1.5317	693.69	45.29	191.39	3.04	1.6	34.9
23	1.3862	461.09	33.3	188.67	2.99	-22.5	- 8.5
24	1.5628	828.09	52.9	49.97	0.79	- -	- -
25	1.5621	806.2	51.5	66.54	1.05	-13.3	8.1

* Determined at the freezing point.

~~SECRET~~

~~SECRET~~

FREEZING POINT APPARATUS
(Above 15° C.)

Figure 1

~~SECRET~~

~~SECRET~~

W-8309
Chemistry - General

FREEZING POINT APPARATUS
(Below 15°C.)

Figure 2

UNH Solution No. 1
70 % UNH
1 M HNO₃

9

11

~~SECRET~~
TEMPERATURE °C

HNO₃ - MOLES PER LITER

~~SECRET~~

HW-8309
Chemistry - General