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THE FREEZING POINTS OF HYDRAZINE-AMMONIUM PERCHLORATE MIXTURES

by

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ABSTRACT

A freezing point curve for solutions of ammonium perchlorate in hydrazine was determined safely in a remotely-operated apparatus. The freezing point of hydrazine is lowered to -25.61°C by ammonium perchlorate at a molal concentration of 3.855 (31.15 wt-%). The plot of freezing points *vs* molality of ammonium perchlorate follows a straight line.

INTRODUCTION

The freezing point is defined as being identical with the melting point; the melting point is taken as the temperature when the last particle of frozen material vanishes, or when the temperature of the medium detectably increases at constant energy input. Other, more precise definitions could be given, but the ones noted here apply to the experimental procedure adopted in this work.

The usual methods for determining the freezing points of various compounds require proximity of the operator to the apparatus employed and the solutions that are being measured. In order to determine the freezing points of the potentially-explosive mixtures of ammonium perchlorate and hydrazine, equipment was fabricated that can be operated remotely without sacrificing accuracy of data. The insidious nature of hydrazine perchlorate was recognized from the start of this work and precautions were taken to protect the operator from the explosive hazard presented by the triboelectrical ignition of crystals which inevitably separate at the freezing point.

The freezing points of solutions ranging from a concentration of 0% to 30% ammonium perchlorate in hydrazine were measured by means of a 5-thermel system which was calibrated against pure materials of accepted freezing-point values.

EXPERIMENTAL

Apparatus

The over-all design of the freezing-point apparatus is shown in Figure 1. The 10-rpm motor with a cam and spring-loaded follower is used to obtain the up-down stirring action found to be most suitable for these determinations. The reciprocating glass stirrer surrounds the glass-enclosed thermocouple probe, which contains five 2-mil thermocopules wired in series to increase the thermoelectric output to values which can easily be measured by a 1-mv recorder. The space within the double-walls of the sample tube is evacuated; this permits the sample to be cooled and warmed at a slow rate. The sample tube is initially charged with ammonium perchlorate and the Teflon injection port is used for the introduction of hydrazine; in this way, accurate mixtures are prepared without hazard. A lab-jack is used to raise and lower the cold bath; Dry Ice can be added (by means of tongs and gloved hand) through the entry port at the rear of the apparatus as required.

The wiring diagram for continuous temperature measurement is shown in Figure 2. Each thermopile consists of five copper-constantan couples in series; a reference thermopile is kept at ice temperature. Since the signal generated is often greater than 1 millivolt, a precision potentiometer is used as a variable source to "buck" the output and leave an effect of less than 1 mv. The recorder and potentiometer are located at some distance away from the freezing-point apparatus.

By noting the bucking voltage from the potentiometer and the voltage indicated by the recorder, a precise determination of the signal being generated by the thermopile can be determined at any time. Since the reference side of the thermopile is maintained at $0^{o}C$, and the temperature is being measured over a wide range above and below $0^{o}C$, a reversing switch is placed in the circuit to make possible recording of a continuous curve at all times.

Calibrants

The materials for calibration were selected to cover a wide range of freezing points:

benzene	$+5.48^{\circ}C$	benzyl alcohol	$-15.3^{\circ}C$
water	$0.0^{\circ}C$	1,2-dichloroethane	$-35.3^{\circ}C$
aniline	$-6.2^{\circ}C$	chloroform	$-65.3^{\circ}C$

and were either "spectroquality" or "analytical-reagent" grade. The water was freshly-distilled for this purpose.

Samples

The hydrazine used in the freezing point determinations (Matheson, Coleman, and Bell) assayed as follows:

H_2O	1.91%
NH_3	0.06
$C_6H_5NH_2$	0.16

The ammonium perchlorate (Fisher Scientific, analytical-reagent grade) was used as received; its composition is known to be in excess of 99.5% (from prior work at JPL).

Calibration Procedure

Three to four milliliters of one of the materials of accepted melting point is introduced into the double-walled test tube. The thermocouple and stirring rod are placed in position along with the tube cap. The stirring motor is then started and the sample temperature is determined by turning on the recorder and applying the proper bucking voltage from the precision potentiometer. The Dry-Ice/alcohol cold bath is raised into position and the temperature of the calibrant material is followed by maintaining on-scale deflections of the recorder pen with the bucking voltage. At the temperature where freezing occurs, the steady cooling slope of the curve being traced changes because of the release of the calibrant material's heat of fusion. In almost all instances, supercooling is observed and the recorder will actually indicate a temperature rise (see Figure 4). When the calibrant material becomes a slush, the temperature remains nearly constant. The cooling bath is then removed and the material is allowed to become warm. When the last particle of frozen material vanishes, the warming curve traced by the recorder will exhibit a sharp change of slope (Figure 4). The millivolt reading, found by extrapolation as shown in Figure 3 corresponds to the freezing point of the material.

The millivolt readings that correspond to the melting points of the calibration materials are summarized in Table I. These data are represented as the calibration curve shown in Figure 3.

Sample Procedure

For the determinations of the freezing points of hydrazine-ammonium perchlorate mixtures, the operator is shielded by heavy Plexiglas (Figure 1) and the apparatus is located in a hood. The hood door is kept closed as much as possible during the determinations.

According to the concentration desired, a sample of ammonium perchlorate is weighed into a previously-dried double-walled test tube and placed in position in the apparatus, and the stirring motor is turned on. A dry, 10-ml gas tight syringe is partially filled with about 3 ml of hydrazine and weighed. The hydrazine is injected into the sample tube via the Teflon entry port, and the syringe is re-weighed.

The ammonium perchlorate is allowed to dissolve and the freezing point of the solution is determined in the same manner as described in the calibration procedure. At completion of the determination, water is injected into the sample tube to dilute the solution and render it insensitiive to shock. After the water has been added, the apparatus is disassembled and cleaned.

RESULTS AND DISCUSSION

As shown in Figure 5, the freezing-point curve plotted from the data on a wt-% basis deviates slightly from a straight line. However, since the reaction between NH_4ClO_4 and N_2H_4 proceeds nearly completely according to the following equation:

$$N_2H_4 + NH_4ClO_4 \rightleftharpoons N_2H_5ClO_4 + NH_3$$

when the molality of the ammonium perchlorate dissolved is calculated on the basis of the quantity of hydrazine remaining after the reaction and this is plotted *vs* the freezing point, a much straighter line is obtained as shown in Figure 6.

The freezing point data are summarized in Table II.

Table I

Calibration Data for Thermocouple System

Reagent	M.P., $^{\circ}$C*	Millivolts
Benzene	5.48	+0.520
Water	0.00	-0.025
Aniline	-6.2	-0.630
Benzyl Alcohol	-15.3	-1.530
1,2-Dichloroethane	-35.3	-3.540
Chloroform	-63.5	-6.250

*As recorded in the Handbook of Chemistry and Physics, 38th Edition, Chemical Rubber Co., Cleveland, Ohio, 1957.

Table II

Melting Points of N_2H_4-ClO_4 Solutions

$\%NH_4ClO_4$	$\%N_2H_4$	Molality NH_4ClO_4	Melting Point, ^oC
5.68	94.32	0.512	- 3.05
4.61	95.39	0.412	- 3.09
4.44	95.56	0.396	- 2.78
9.06	90.94	0.850	- 5.75
9.99	90.01	0.944	- 6.11
17.18	82.82	1.765	-12.00
14.71	85.29	1.467	-10.21
18.49	81.51	1 930	-13.05
20.20	79.80	2.154	-14.48
20.34	79.66	2.170	-14.41
24.61	75.39	2.783	-20.10
25.15	74.85	2.862	-21.34
25.87	74.13	2.974	-20.27
28.00	72.00	3.310	-24.80
29.07	70.93	3.488	-23.95
31.19	68.81	3.855	-25.61

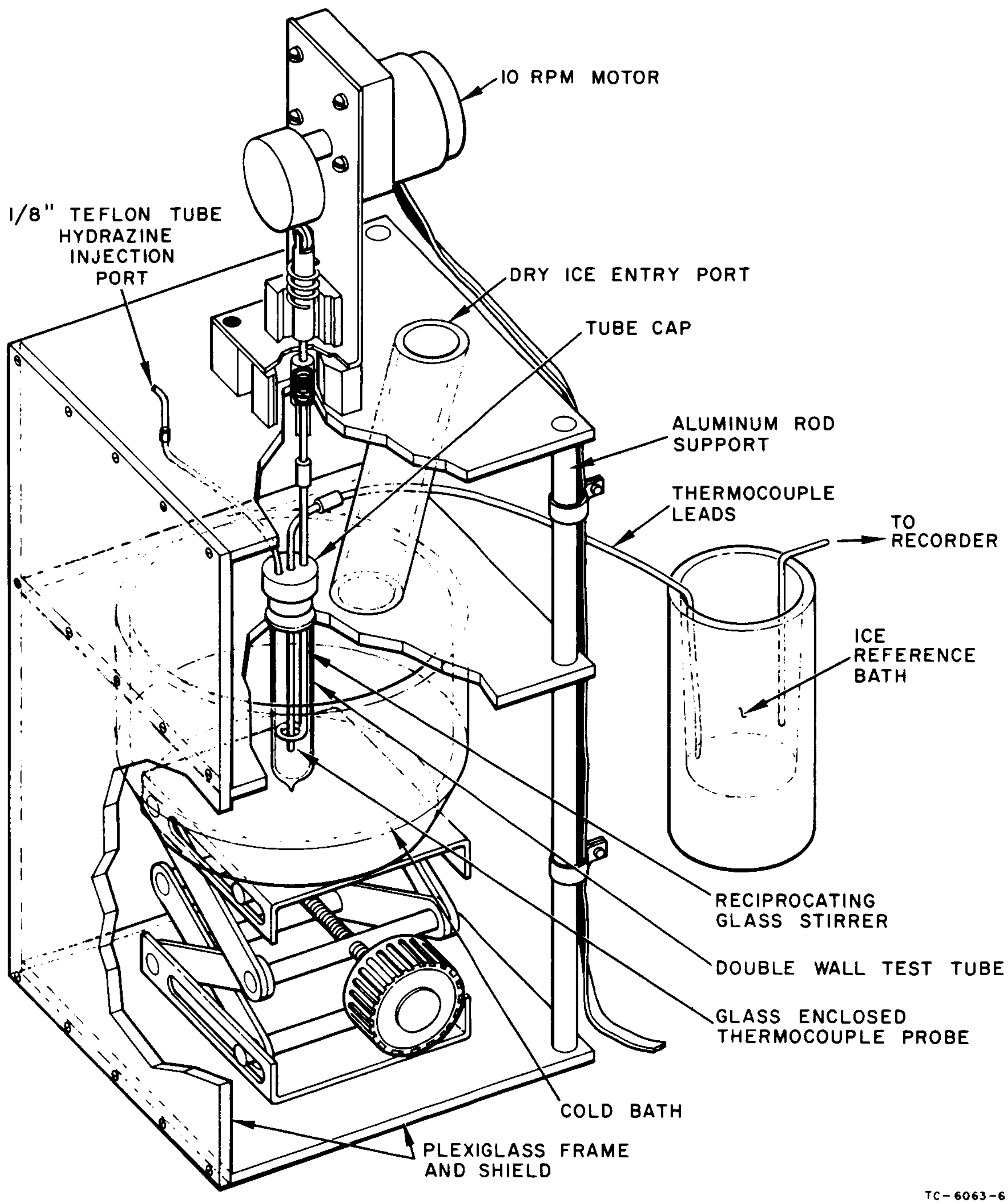

FIG. 1 FREEZING POINT APPARATUS

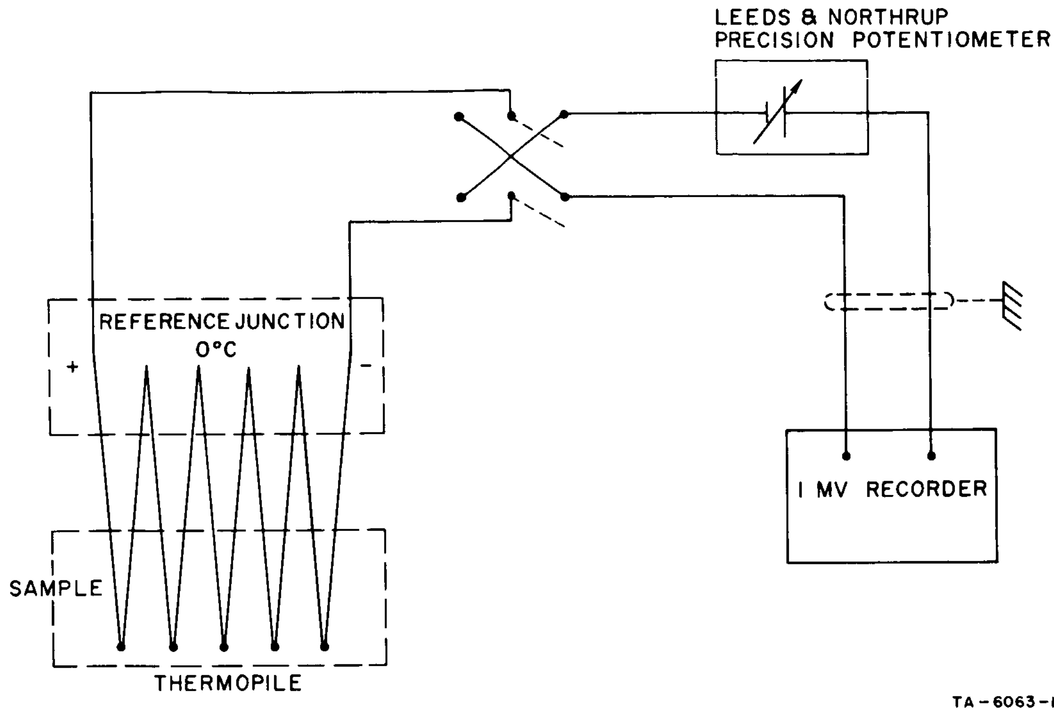

FIG. 2 WIRING DIAGRAM FOR CONTINUOUS TEMPERATURE MEASUREMENTS

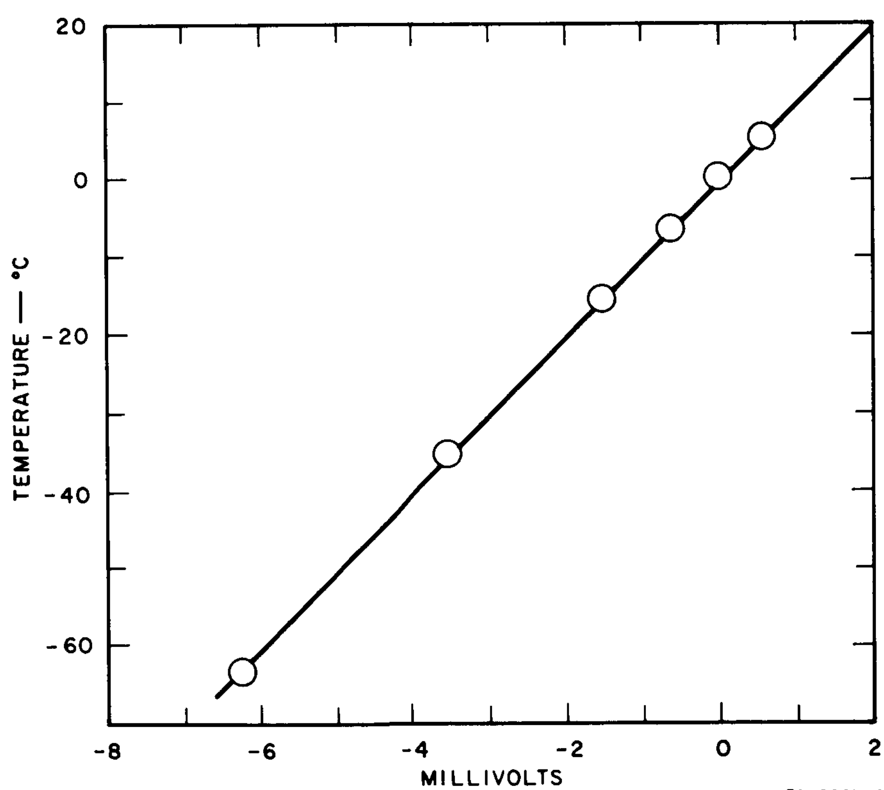

FIG. 3 THERMOCOUPLE CALIBRATION CURVE

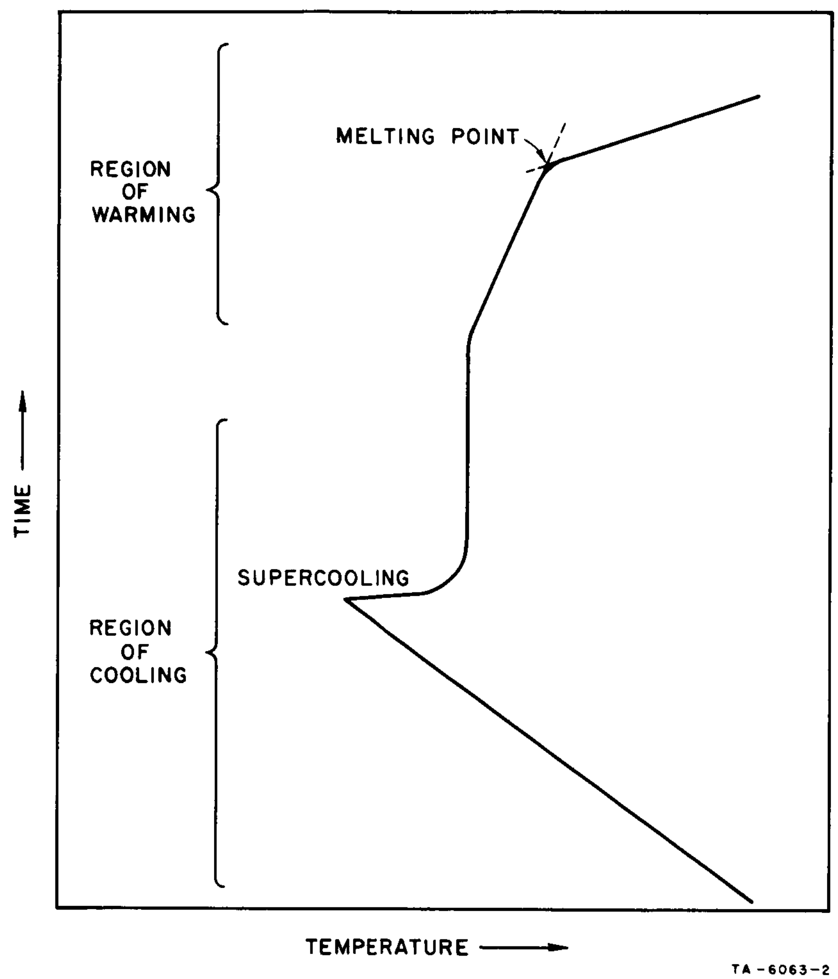

FIG. 4 TYPICAL FREEZING POINT CURVE

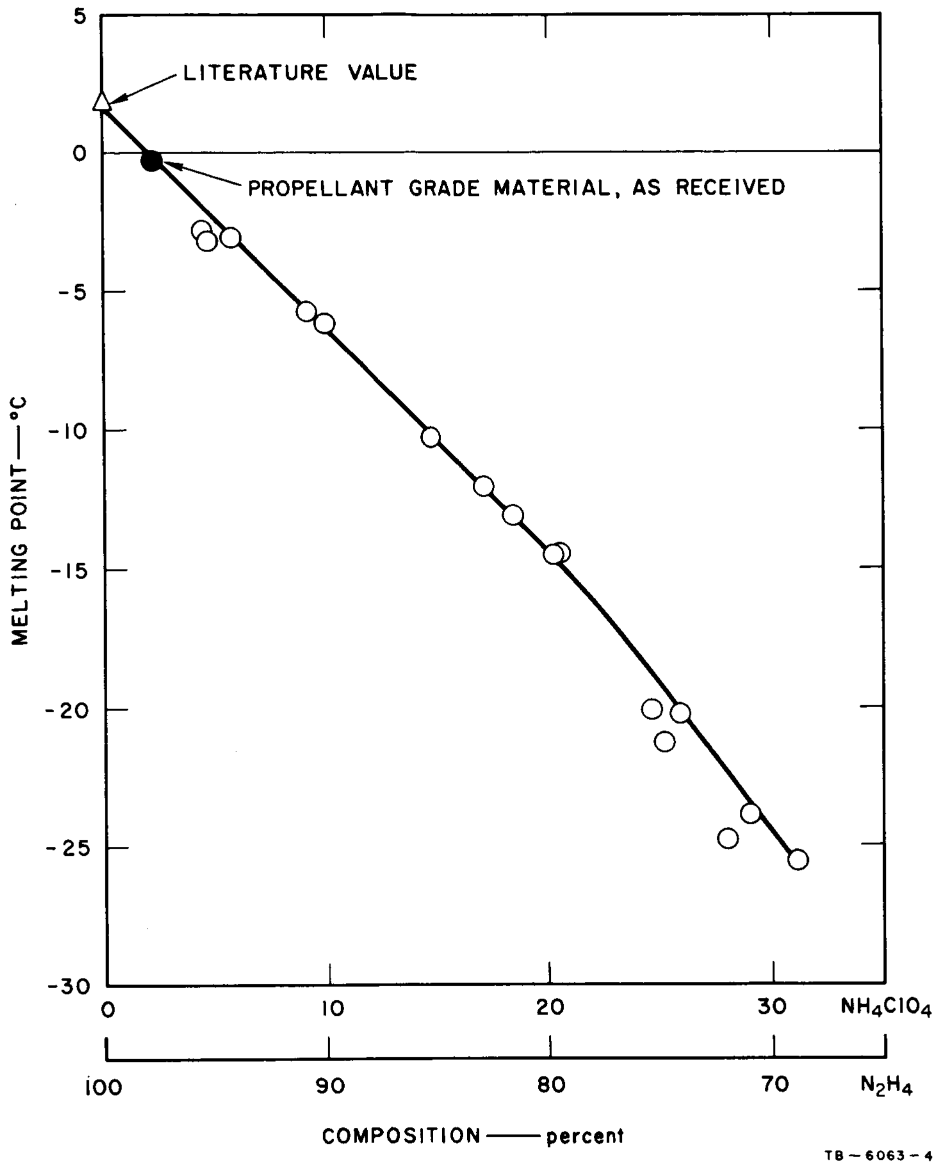

FIG. 5 FREEZING POINTS OF A.P.-N_2H_4 MIXTURES BASED ON WT-PERCENT COMPOSITION

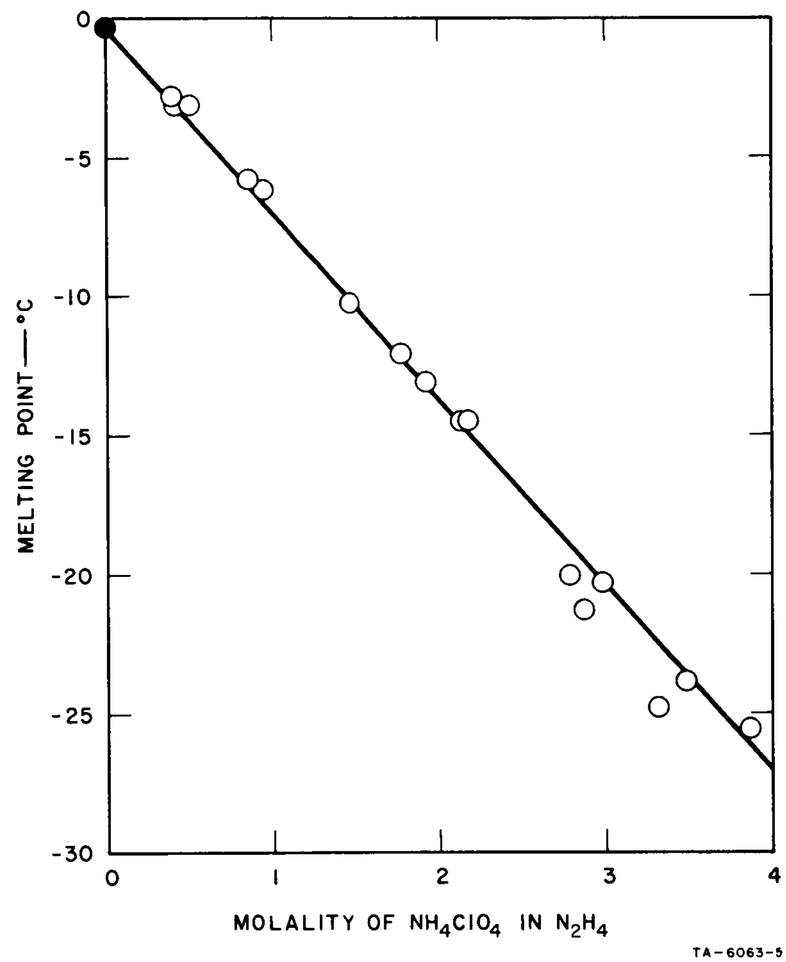

FIG. 6 FREEZING POINTS OF A.P.-N_2H_4 MIXTURES BASED ON MOLALITY OF NH_4ClO_4 IN N_2H_4