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RESEARCH MEMORANDUM

EFFECTS OF NITROGEN TETROXIDE AND WATER CONCENTRATION
ON FREEZING POINT AND IGNITION DELAY
OF FUMING NITRIC ACID

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

WASHINGTON
September 24, 1953

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUMEFFECTS OF NITROGEN TETROXIDE AND WATER CONCENTRATION ON FREEZING
POINT AND IGNITION DELAY OF FUMING NITRIC ACID

By Riley O. Miller

SUMMARY

The interrelated effects of water, from 0 to 10 percent by weight, and nitrogen tetroxide, from 0 to 25 percent by weight, in fuming nitric acid were investigated with respect to the freezing points of the acid and the ignition delays with several fuels. An equilibrium freezing-point surface for the acids in the composition range studied is presented. A minimum freezing point of -88.5° F occurs in the region of approximately 5 percent water and 17 percent nitrogen tetroxide, and a binary eutectic line extends from this region to nearly anhydrous acid containing 25 to 26 percent nitrogen tetroxide, which freezes at -82.5° F.

The ignition delays of fuel blends of 30 percent *o*-toluidine, 50 percent allylamine, and 50 percent ethylenimine, respectively, in triethylamine were determined at 70° and -40° F. These data show that the *o*-toluidine blend was most sensitive to both temperature and acid composition while the ethylenimine blend was least sensitive. Acids containing small amounts of water and large amounts of nitrogen tetroxide give shorter delays than acids containing large amounts of water and small amounts of nitrogen tetroxide; this effect is more pronounced at low temperature. The effects on ignition of varying either the water or the nitrogen tetroxide content of acid are less as the water is decreased and the nitrogen tetroxide is increased. The acid composition region giving low freezing points falls within the region of short ignition delay.

Several possible chemical causes for the opposing effects of water and nitrogen tetroxide on ignition are discussed.

INTRODUCTION

The freezing points and low-temperature fuel-igniting properties of fuming nitric acids are of current interest because of a demand to extend the use of these oxidants to rockets operating at low temperature. Varied amounts of nitrogen tetroxide and water are known to affect these properties; for example, recent experiments have shown that fuming nitric

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acids containing 3 to 4 percent water and 16 to 19 percent nitrogen tetroxide have low freezing points and ignite suitable fuels at temperatures of -76° F and lower (refs. 1 to 5), whereas the usefulness of white fuming nitric acids without additives is limited to higher temperatures. In order that the best possible specifications be established for rocket oxidizer acids, a knowledge of these properties should be acquired for fuming nitric acids containing various amounts of water and nitrogen tetroxide.

Published freezing-point data for fuming nitric acids in the composition ranges of usefulness to the rocket industry have been limited, for the most part, to the binary systems nitric acid - water (ref. 6) and nitric acid - nitrogen tetroxide (refs. 7 and 8); the latter data require corroboration (refs. 8 and 9). Data have been recently published also for the system nitric acid - nitrogen tetroxide (plus 2 percent water) (ref. 10). A need has continued to exist for studies of freezing points of the ternary system nitric acid - nitrogen tetroxide - water in the region of high nitric acid concentrations.

An experimental investigation, described herein, was made to determine the interrelated effects of nitrogen tetroxide and water on the freezing points and the fuel-igniting properties of fuming nitric acid. Experimental freezing-point data were obtained for nitric acids containing 0 to 10 percent water and 0 to 25 percent nitrogen tetroxide. These data were determined from temperature-time melting curves obtained in a sealed automatic-recording apparatus. Data more exhaustive than those heretofore published also were obtained to show the effect of the same acid compositions on the ignition of several fuels. These fuels were blends of 30 percent *o*-toluidine, 50 percent allylamine, and 50 percent ethylenimine, respectively, in triethylamine and have already been investigated at this laboratory with several acids (refs. 1, 3, and 4). They were selected for this study because of their diversity of composition, low-temperature fluidity, and desirable ignition characteristics. By use of a modified open-cup apparatus (refs. 1, 11, and 12), ignition delays were determined at 70° and -40° F; the more thorough study was made at -40° F, approximately the lowest temperature at which all the acids are fluid.

Acid composition ranges giving low freezing points are compared with the composition ranges giving short ignition delays at low temperature. Some hypotheses are proposed which may aid in explaining the effects of nitrogen tetroxide and water on ignition delay of fuming nitric acid.

EXPERIMENTAL PROCEDURE

Measurement of Freezing Point

The freezing-point apparatus (fig. 1(a)) consisted of a sealed glass cell in which the acid was contained and instrumentation which

automatically recorded the temperature of the acid as a function of time. In the glass cell were a stirring rod and a well which contained a nickel resistance thermometer. The stirring rod was reciprocated by a low-speed motor and the rod was sealed from the atmosphere through a hypodermic syringe barrel and plunger. The instrumentation consisted of the resistance thermometer, a bridge circuit unit, and self-balancing recording potentiometer. The bridge circuit converted changes in resistance to changes in potential so that the potentiometer could make a continuous record of temperature as a function of time.

A calibration of the complete apparatus was made by freezing pure hydrocarbons of known freezing point in the apparatus; the mean deviation from the calibration curve was 0.8° F. The acid was cooled by raising a bath of liquid nitrogen around the outside of the cell. The cell was jacketed so that the rate of heat transfer could be controlled by the degree of vacuum in the jacket; for most of the experiments, however, a full vacuum was used. The acid was warmed by removing the liquid nitrogen bath and exposing the outside of the cell jacket to atmospheric air. Two complete cooling and warming curves were run for each acid. Usually the acid was cooled until it was completely frozen as a white solid. Examples of cooling and warming curves are presented in figure 2; two separate cooling and warming curves are shown for one of the red fuming nitric acids investigated. Curve I shows the usual behavior of the acid. The segment AB indicates the cooling of the acid as a liquid. At B the acid has been supercooled and starts to freeze, the temperature rising to C. The segment CD shows that a phase is freezing. This segment can be extrapolated backward to give approximately the initial freezing point E. The record was interrupted at D, and presumably during the period of interruption a second phase froze thus forming a binary eutectic. On the warming curve this melted at F. The last of the solids disappeared at G, the final melting point, which is 2° F higher than E, the extrapolated initial freezing point. In some cases the initial freezing point and final melting point were closer together than this.

Curve II (fig. 2) illustrates an interesting phenomenon that was sometimes encountered during the freezing-point experiments. Here the acid remained supercooled to temperatures lower than -100° F until at B' a phase (2) started to freeze; when the segment C'D' was extrapolated backward, the indicated freezing temperature was -104° F. This "pseudo" freezing temperature was much lower than the initial freezing temperature E from the upper curve. The pseudo freezing temperature probably is the temperature at which a phase (2) freezes out of the liquid, which is still supercooled with respect to phase (1); phase (1) would have frozen first from the system under equilibrium conditions. The warming portion of curve II shows that the phases have readjusted themselves, and the binary eutectic and final melting points F' and G', respectively, correspond to the points F and G of curve I. The difference in the slope of the curves reflects a difference in the rate of heat transfer. Curve II shows that

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initial freezing point data are not always equilibrium values and therefore final melting points are better criteria for equilibrium freezing points. The equilibrium freezing points reported herein are actually final melting points; each point is the average of at least two determinations. Unless otherwise specified, these averages are within $\pm 0.5^{\circ}$ F of the individual measurements.

Measurement of Ignition Delay

Ignition-delay experiments were made in a modified open-cup apparatus (fig. 1(b)). The fuel (1 ml) in a sealed ampule is submerged underneath the surface of the acid (3 ml) contained in an ignition-type pyrex test tube. The ampule is broken by a weight striking a stainless steel rod which rests on the ampule. The ignition delay is measured as the interval from the time the ampule starts to break to the time the first continuous flame starts in the test tube. Prior to the firing, the fuel and acid are brought to a desired temperature by immersing the lower part of the assembly in a constant-temperature bath. Instantaneous measurements and continuous oscillograph records are made of the ignition-delay interval; unless otherwise specified, the data reported herein were taken from continuous records of light emission as a function of time. More complete descriptions and discussions of the apparatus are contained in references 1, 11, and 12.

Materials

Fuels. - The fuels used in the ignition-delay experiments were blends of 30 percent by volume o-toluidine, 50 percent allylamine, and 50 percent ethylenimine, respectively, in triethylamine. The blends were prepared from purified compounds procured from commercial sources.

Acids. - The acids used in these experiments were prepared by mixing, at low temperature, calculated quantities of three stock solutions: (1) a nearly absolute nitric acid, (2) a nearly anhydrous red fuming nitric acid (42.1 percent nitrogen tetroxide), and (3) a c.p.-grade 69.9-percent nitric acid.

The absolute acid (1) was prepared by distilling c.p.-grade white fuming nitric acid from an equal volume of sulfuric acid in a sealed all-glass apparatus at low pressure. The red fuming nitric acid (2) was prepared by absorbing gaseous commercial anhydrous nitrogen tetroxide into the absolute acid (1) at -40° F. The c.p.-grade 69.9 percent nitric acid (3) was untreated prior to blending.

Compositions of the acid blends were calculated from the weights of the stock solutions used.

RESULTS AND DISCUSSION

Freezing-Point Experiments

Effect of nitrogen tetroxide and water on equilibrium freezing point of nitric acid. - Experimental freezing-point data for nitric acids of various compositions are shown in table I. The equilibrium freezing points shown in the table are actually final melting points and are the results of at least two determinations. The equilibrium freezing temperatures for the two binary systems and the ternary system are shown also in figure 3.

A freezing curve for concentrated nitric acid - water prepared from published data is shown in figure 3(a). These data show a eutectic composition of 90 percent acid with a freezing temperature of about -88° F. Since the data for 90 to 100 percent acid are well corroborated, further experiments with this system were deemed unnecessary. The equilibrium and eutectic freezing points of an acid containing 6 percent water, determined as a check on the method, are also shown in figure 3(a).

Freezing points for the binary system concentrated nitric acid - nitrogen tetroxide (+0.4 percent water) are shown in figure 3(b). These data do not corroborate the data of reference 7, but they do agree fairly well with the data of reference 8 (indicated on plot). The existence of a eutectic composition at 19 percent nitrogen tetroxide freezing at -100° F (ref. 7) was not confirmed. On the basis of these data, the eutectic composition appears to be at 25 to 26 percent nitrogen tetroxide. The data of reference 10 show the eutectic occurring at approximately 23 percent nitrogen tetroxide for acids containing 2 percent water; the data for acids containing approximately 2 percent water in table I fall reasonably close to the curve proposed in reference 10.

A plot of the equilibrium freezing-point surface for the ternary system nitric acid - nitrogen tetroxide - water, constructed from data of table I, is presented in figure 3(c). The data indicate that a minimum freezing point of -88.5° F occurs in the region of about 17 percent nitrogen tetroxide and 5 percent water. A line of minimum freezing point extends from this region to approximately anhydrous acid containing 25 to 26 percent nitrogen tetroxide, where the freezing point is -82.5° F. The substance freezing in the lower left-hand region of the plot is nitric acid; the substance in the lower right is probably $\text{HNO}_3 \cdot \text{NO}_2$. In the upper right-hand region, the freezing substance is probably nitrogen tetroxide or possibly $\text{HNO}_3 \cdot \text{H}_2\text{O}$.

Binary eutectic freezing points. - Binary eutectic freezing points are also shown in table I. These usually represent the break in the melting curve preceding the final melting point (see fig. 2 for an

example). Some of the very low temperature data, however, may not be equilibrium values but rather pseudo eutectic freezing points.

Ignition-Delay Experiments

Ignition delays at -40° and 70° F for blends of 30 percent *o*-toluidine, 50 percent allylamine, and 50 percent ethylenimine, respectively, in triethylamine are shown in table II and some of the data are plotted in figures 4 and 5.

Effect of acid composition on ignition delay at -40° F. - Data for the *o*-toluidine blend at -40° F (fig. 4(a)) show the average delay to increase with increased water content, and the effect of water content is least when the nitrogen tetroxide content is large. The curves seem to be approximately hyperbolic in shape. Effects of both water and nitrogen tetroxide were less pronounced as the water content was decreased and the nitrogen tetroxide content increased.

Similar trends were observed for the allylamine blend at -40° F (fig. 4(b)), but the effects were less pronounced than with the *o*-toluidine blend.

The effects of acid composition on ignition delay at -40° F were least apparent when the ethylenimine blend was the fuel (fig. 4(c)). The delays were of the order of 30 milliseconds or less for all acids except the one containing 10 percent water and only a trace of nitrogen tetroxide. Increasing water content appeared to have a small effect toward increasing the delay.

Effect of acid composition on ignition delay of several fuels at 70° F. - Ignition delays at 70° F of the same three fuels as functions of acid composition are shown plotted in figure 5. The trends shown by these curves are quite similar to those at -40° F (fig. 4) except that the delays were shorter and the effects of acid composition were less pronounced. Water still had a tendency to increase ignition delay and nitrogen tetroxide to overcome this effect. All these curves indicate that 8 percent nitrogen tetroxide is sufficient to reduce the delays; in fact, a trend seems to be for the delays at 8 percent nitrogen tetroxide to be smaller than those at 25 percent. This upward swing at 25 percent nitrogen tetroxide, however, is within the variation of data sometimes obtained with the modified open-cup apparatus. All the average delays at 70° F were less than 50 milliseconds.

Coincidence of Acid Compositions Giving Low Freezing
Points and Short Ignition Delays

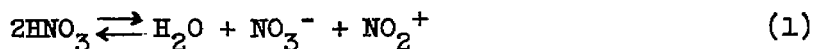
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Cross plots showing lines of constant ignition delay as functions of acid composition for the fuel blends *o*-toluidine and allylamine, respectively, in triethylamine at -40° F are shown in figure 6. These plots re-emphasize the fact that from the standpoint of short ignition delay, acids containing small amounts of water and large amounts of nitrogen tetroxide are more desirable than acids containing large amounts of water and small amounts of nitrogen tetroxide. It is also shown that at -40° F delays of 60 milliseconds or less occur for most of the respective lower right-hand regions of the plots. Low freezing temperatures also occur within this region. The coincidence of low freezing temperature and short ignition delay in acid compositions is shown by figure 7. In this figure the area of acid compositions giving freezing points of -80° F or less is shown and, also, areas of acid composition giving delays of 60 milliseconds or less at -40° F for four different fuels. The data for the *o*-toluidine and allylamine blends are the same as shown in the previous figure; data for the ethylenimine blend and for mixed alkyl thiophosphites (ref. 5) are also included. It is apparent that acids containing nitrogen tetroxide and water may be specified for low freezing point and also be in the region of short ignition delay at low temperature. This is emphasized by the data reviewed in figure 8. Ignition delays (refs. 1 and 3) obtained with low-freezing nitric acid containing approximately 3 percent water and 19 percent nitrogen tetroxide, for the same fuel blends investigated herein, are shown plotted as functions of temperature. These data show that this acid ignited the allylamine blend and the ethylenimine blend at temperatures as low as -105° F, with average delays of 50 milliseconds or less. (The acid was supercooled at -105° F.)

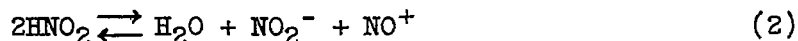
Hypotheses on the Opposing Effects of Nitrogen Tetroxide
and Water on Ignition Delay

Some hypothetical considerations may facilitate an understanding of ignition of a fuel by an acid. Reactions in both liquid and gaseous phases probably contribute toward ignition, and effects of water and nitrogen tetroxide probably occur in both phases.

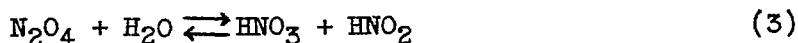
Role of oxide cations. - Published data indicate that the oxide cations, nitronium NO_2^+ and nitrosonium NO^+ , occur in oxidizer acids (ref. 9). These data show that concentrated nitric acid is in equilibrium with water, nitric ions, and nitronium ions.



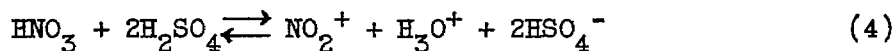
Nitrous acid, if present, would be in equilibrium with water and with nitrous and nitrosonium ions



In acids containing negligible amounts of nitrogen tetroxide, water has the effect of suppressing the formation of the oxide cations. In acids containing nitrogen tetroxide, this trend would be opposed inasmuch as the nitrogen tetroxide reacts with water to form the acids which are in equilibrium with the ions (eqs. (1) and (2)).



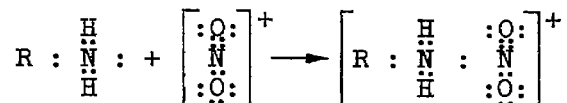
A correlation appears to exist between conditions which favor formation of oxide cations and conditions which favor short ignition delays, inasmuch as the ignition data herein show that in the absence of nitrogen tetroxide, water favors long delays, but in the presence of nitrogen tetroxide this effect is less pronounced. The hypothesis that conditions favoring oxide cation formation are criteria for short ignition delay is further supported by a consideration of mixed acid. Evidence has shown that nitronium ion formation is favored by the presence of sulfuric acid in nitric acid (ref. 9).



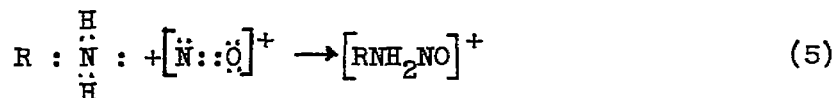
Sulfuric acid (up to about 17 percent) also promotes short ignition delays (refs. 13 and 14).

The probable role of these cations becomes evident if onium addition, neutralization in the G. N. Lewis sense (ref. 15), is assumed to be the first rapid reaction to occur between a fuel and an acid (ref. 9). Such reactions could provide activation energies for subsequent reactions and also supply substances which could undergo intramolecular oxidation. A variety of fuels ignitable by acid could conceivably undergo onium addition with these cations.

The amino group, having an unshared electron pair, is expected to add the oxide cations much as ammonia would add hydrogen cation to produce ammonium ion.



or

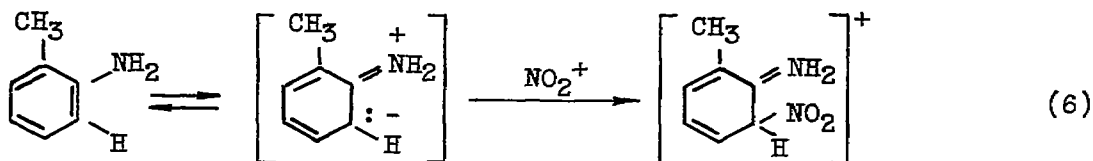


These reactions, having negligible activation energies, are expected to be quite rapid.

It has been shown in reference 16 that the salts of the amines are nonigniting with acid; this was interpreted to indicate that neutralization was not a contributing factor in ignition, because RNH_3^+ in the salts appeared to be relatively inactive. Ions of this type, admittedly, would be more likely to form in nitric acids containing large amounts of water, whereas ions of the type $\text{RNE}_2\text{NO}_2^+$ and RNH_2NO^+ would be expected in concentrated nitric acids; in either case, however, heat would be evolved. The possibility of formation of the more stable RNH_3^+ ions may be another reason why the presence of water inhibits ignition.

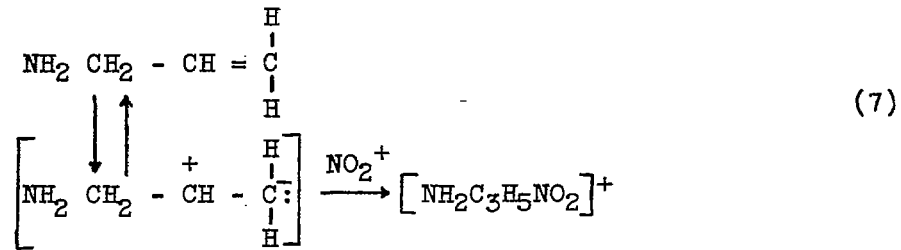
The nonigniting property of the amine salts would confirm rather than disprove the hypothesis that onium addition is a first step in ignition by acid. The amine salts have already undergone onium addition and therefore the heat of this reaction would not be available for subsequent reactions during the early phases of ignition. Rapid formation of unstable fuel-oxide ions would also be improbable, inasmuch as an exchange rather than an addition reaction would be required.

A similar addition may take place on a benzene ring

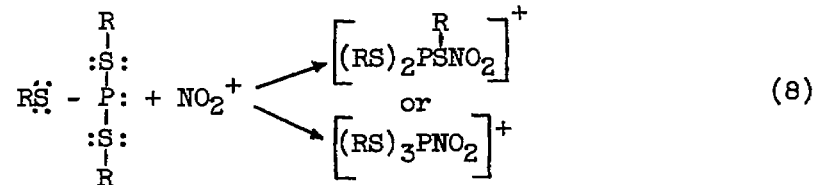


This reaction is closely analogous to the first step in nitration; the resulting product is unstable. In ignition this addition probably progresses more rapidly than under conditions of controlled nitration. In an aromatic amine, for example *o*-toluidine, the acid may therefore attack either the ring or the amino group.

An olefinic group, for example allyl, may act as a base in the G. N. Lewis sense (ref. 9). Thus allylamine may be attacked at the side chain as well as the amino group.



The trialkyl trithiophosphite molecule has seven unshared electron pairs and presumably would be very vulnerable to onium attack at a sulfur, or possibly a phosphorus atom. This may account in part for its extremely short ignition delay.



Evidence exists, therefore, for the hypothesis that in ignition of a fuel by an acid the first reaction because of its negligible activation energy is neutralization, in the G. N. Lewis sense, and that oxidation may follow because of: (1) the heat evolved from the neutralization reaction and (2) the resulting fuel-oxide cations which can undergo intramolecular reactions. Pyrolysis of the fuel and acid probably also results.

The probable importance of the oxide cations during ignition has also recently been recognized in reference 16, wherein other possible reactions between the fuel and cation are proposed. Some of these reactions, possibly, could occur within the fuel-oxide cation after neutralization.

Other chemical evidence. - Other evidence also may be cited to rationalize how water inhibits and nitrogen tetroxide (or dioxide) promotes ignition. One obvious effect of water is simple molecular dilution of the acid. An acid, for example, containing 10 percent water by weight is more than 1/4 water on the molecular basis. Large fractions of water presumably would slow the reactions by dilution of the reactants and by absorption of heat.

Another possibility in gas-phase reactions is that nitrogen dioxide is thought to oxidize carbon monoxide directly in a homogeneous reaction (ref. 17). Mixtures of nitrogen dioxide - carbon monoxide - oxygen, furthermore, are known to explode when water and hydrogen are present. The role of such an explosion in fuel-acid ignition is difficult to appraise. It may be beneficial in that it causes adiabatic compression which may promote ignition. Ignition in the modified open-cup apparatus, for example, is frequently accompanied by a strong pressure pulse.

An increase in vapor pressure of the acid probably would promote gaseous reactions. In the absence of nitrogen tetroxide, water up to 30 percent somewhat decreases the vapor pressure of nitric acid. This effect, however, is soon overcome when nitrogen tetroxide is added to the acid, and in red fuming nitric acid the combined effect of both nitrogen tetroxide and water is to increase vapor pressure (refs. 9 and 18).

SUMMARY OF RESULTS

The interrelated effects of water, from 0 to 10 percent, and nitrogen tetroxide, from 0 to 25 percent by weight, in fuming nitric acid were investigated with respect to the freezing points of the acids and the ignition delays at -40° and 70° F with fuel blends of 30 percent *o*-toluidine, 50 percent allylamine, and 50 percent ethylenimine, respectively, in triethylamine. The following results were obtained:

1. The minimum equilibrium freezing point for the composition range studied was -88.5° F for a red fuming nitric acid containing approximately 5 percent water and 17 percent nitrogen tetroxide. A line of minimum freezing point extended from acids of this approximate composition to nearly anhydrous red fuming nitric acid containing 25 to 26 percent nitrogen tetroxide, having a freezing point of -82.5° F.
2. With respect to ignition delay, the fuel blends varied in their sensitivity to the amount of water and nitrogen tetroxide in the acid, and this effect was more pronounced at -40° F. At this temperature, the *o*-toluidine blend was most sensitive while the ethylenimine blend was least sensitive to acid composition.
3. In the absence of nitrogen tetroxide, the ignition delays increased as the water in the nitric acid was increased. This effect, however, was counteracted by the presence of nitrogen tetroxide in the acid. This trend was found at both 70° and -40° F, but was more pronounced at -40° F.
4. At -40° F most of the acids studied gave average delays less than 60 milliseconds; the shortest delays occurred for acids containing small amounts of water and large amounts of nitrogen tetroxide. The effect on ignition delay of varying either water or nitrogen tetroxide content also was small for such acids.
5. At 70° F all the acids studied gave average ignition delays less than 50 milliseconds, with the three fuels.
6. An acid composition region of low freezing temperatures was within the region of short ignition delay.

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CONCLUSION

The equilibrium freezing point of fuming nitric acid may be controlled by varying the amount of water and nitrogen tetroxide in the acid. Acids may be specified which would freeze at low temperatures and also give short ignition delays at low temperatures with suitable fuels.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, August 6, 1953

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TABLE I. - FREEZING POINTS OF NITRIC ACIDS CONTAINING VARIOUS
AMOUNTS OF NITROGEN TETROXIDE AND WATER

Acid composition, percent by weight			Freezing point, °F	
H ₂ O	N ₂ O ₄	HNO ₃	^a Equilibrium	^b Binary Eutectic
0	0	100	^c -42.9	-----
.4	8.4	91.2	-48.5	-----
.4	14.5	85.1	-56.5	-82.5
.4	22.3	77.3	-74.0	-82.5
.3	31.9	67.8	-59.0	-78±2
.4	42.1	57.5	-41.5	-53
2	0	98	^c -45.5	-----
1.7	8.7	89.6	-52.5	-----
1.4	17.3	81.3	-64.0	-83
.8	25.9	73.3	-77.5	-88
4	0	96	^c -52.0	-----
3.7	8.6	87.7	-61.5	-94±1.5
3.4	17.2	79.4	-81.0	-88±1
2.8	25.8	71.4	-69±2	-----
6	0	94	^c -63.0	-----
6.3	.1	93.6	-62.5	-88.5
5.7	8.6	85.7	-77.5	-92
6.4	13.9	79.7	-80.0	-----
5.3	17.2	77.5	-88.5	-88.5
4.8	25.8	69.4	-70.0	-----
8	0	92	^c -74.5	-----
7.7	8.6	83.7	-77.5	-----
7.8	8.8	83.4	-77.5	-----
7.3	17.3	75.4	-75±1	-92.0
6.7	25.9	67.4	-70.0	-----
10	0	90	^c -88.0	-----
9.6	8.7	81.7	-72.5	-96.5
9.2	17.4	73.4	-62.0	-----
8.6	26.1	65.3	-60.0	-----

^aFinal melting point.

^bBreak in melting curve prior to final melting point.

^cData from fig. 3.



TABLE II. - IGNITION DELAYS OF NITRIC ACIDS CONTAINING VARIOUS AMOUNTS OF NITROGEN TETROXIDE AND WATER

(a) Temperature, -40° F

Acid composition, percent by weight			Fuel composition, percent by volume											
			30 o-toluidine - 70 triethylamine				50 allylamine - 50 triethylamine			50 ethylenimine - 50 triethylamine				
H ₂ O	N ₂ O ₄	HNO ₃	Number of ignition experiments	Ignition delay, millisec			Number of ignition experiments	Ignition delay, millisec			Number of ignition experiments	Ignition delay, millisec		
				Min	Max	Av		Min	Max	Av		Min	Max	Av
0.4	0.1	99.5	4	25	35	30	4	27	48	38	4	17	23	20
.4	2.1	97.5	6	25	28	26	-	---	---	---	-	---	---	---
.4	3.7	95.9	25	16	28	21	-	---	---	---	-	---	---	---
.4	7.4	92.2	25	18	23	20	-	---	---	---	-	---	---	---
2.8	0.1	97.1	3	29	48	40	^a 4	22	40	35	4	18	30	23
1.8	8.0	90.1	4	19	30	25	6	24	41	29	4	16	21	18
1.7	16.1	82.2	4	25	33	28	4	25	39	35	4	17	20	18
1.3	24.6	74.1	4	25	30	28	4	26	44	33	4	15	18	17
4.4	0.1	95.5	2	42	97	69	4	48	57	52	3	19	36	27
3.9	8.0	88.1	4	25	36	30	3	24	50	34	4	22	35	26
3.7	16.0	80.3	4	26	41	34	4	30	41	34	4	18	27	23
3.3	24.6	72.1	4	30	36	34	4	30	36	34	4	20	25	22
6.3	0.1	93.6	4	78	164	129	4	60	77	69	4	25	48	36
5.9	8.0	86.1	4	39	43	40	4	39	46	42	4	29	35	32
5.8	15.8	78.5	4	30	42	34	4	47	58	52	4	23	27	25
5.3	24.7	70.0	4	30	47	33	4	37	50	42	4	20	24	22
8.2	0.1	91.7	5	140	212	179	5	80	123	97	4	35	41	37
7.7	8.1	84.2	4	57	91	68	4	35	50	43	2	17	24	21
7.7	15.9	78.4	4	30	58	42	4	41	60	46	4	25	35	32
7.2	24.7	68.1	4	47	70	57	4	35	56	42	4	25	35	29
10.1	0.1	89.8	^b 4				3	83	210	135	^c 6			
9.7	8.1	82.2	4	100	172	129	4	61	91	69	4	20	36	28
9.8	15.8	74.5	4	51	92	65	4	46	60	55	4	30	50	40
9.3	24.4	66.3	4	33	44	39	4	44	62	55	4	36	42	40

(b) Temperature, 70° F

2.8	0.1	97.1	4	20	29	24	4	30	40	37	4	11	17	13
2.1	8.1	89.8	3	13	21	16	4	21	40	28	4	7	10	8
1.3	24.6	74.1	4	20	25	23	3	30	45	37	4	11	19	15
6.1	0.1	93.8	4	18	27	21	4	25	45	36	4	6	13	10
5.9	8.0	86.1	4	12	24	18	4	13	26	22	4	8	10	9
5.3	24.7	70.0	3	18	32	24	4	29	42	35	3	18	26	20
10.2	0.1	89.7	2	30	49	40	4	40	54	48	2	28	38	33
10.0	8.2	81.8	4	19	29	23	4	20	27	24	4	10	15	13
9.1	24.6	66.3	4	20	27	24	4	27	33	31	4	14	30	21

^aData from counter.

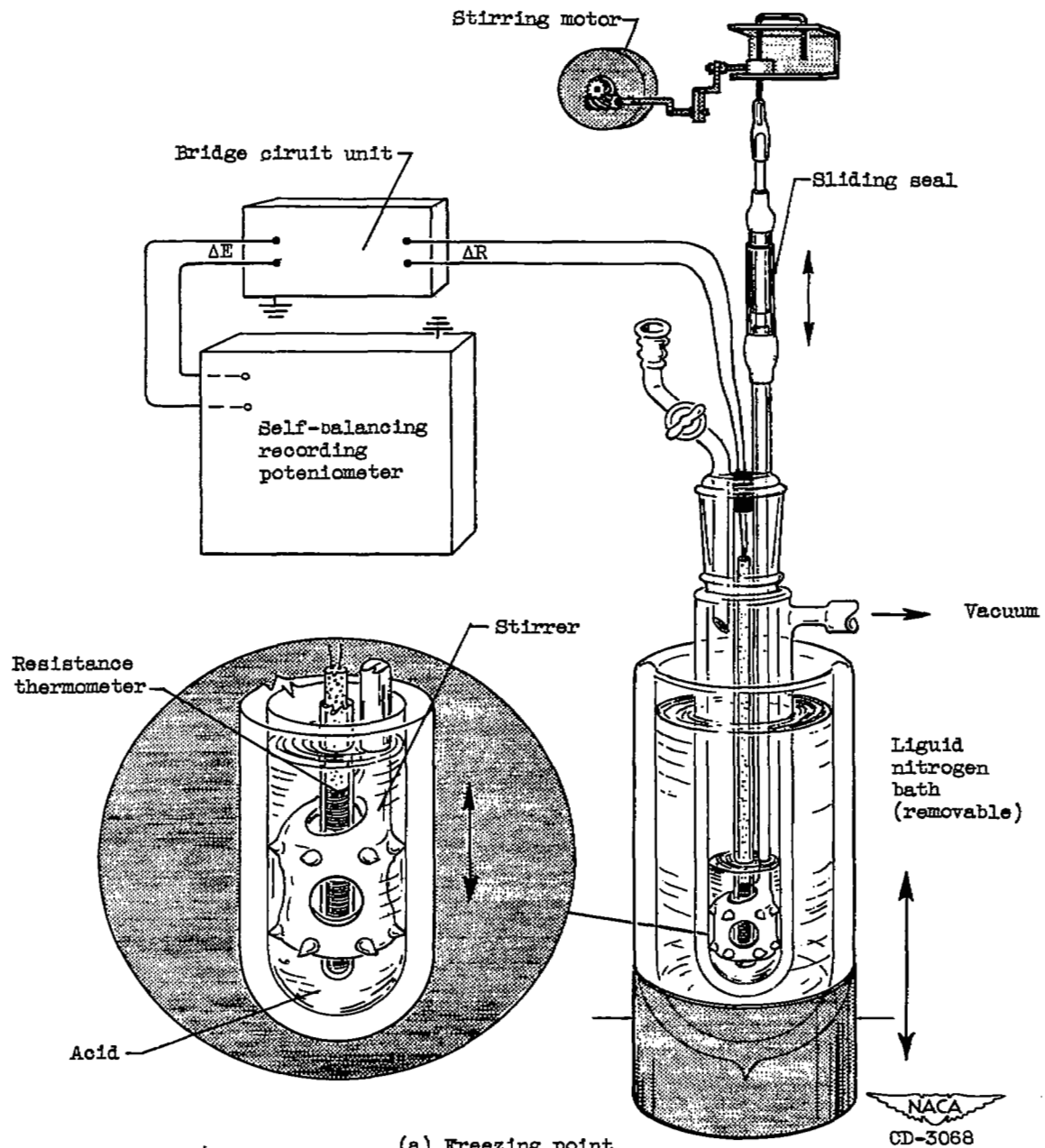
^bNo ignition.

^cSporadic ignition.



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(a) Freezing point.

Figure 1. - Experimental apparatus.

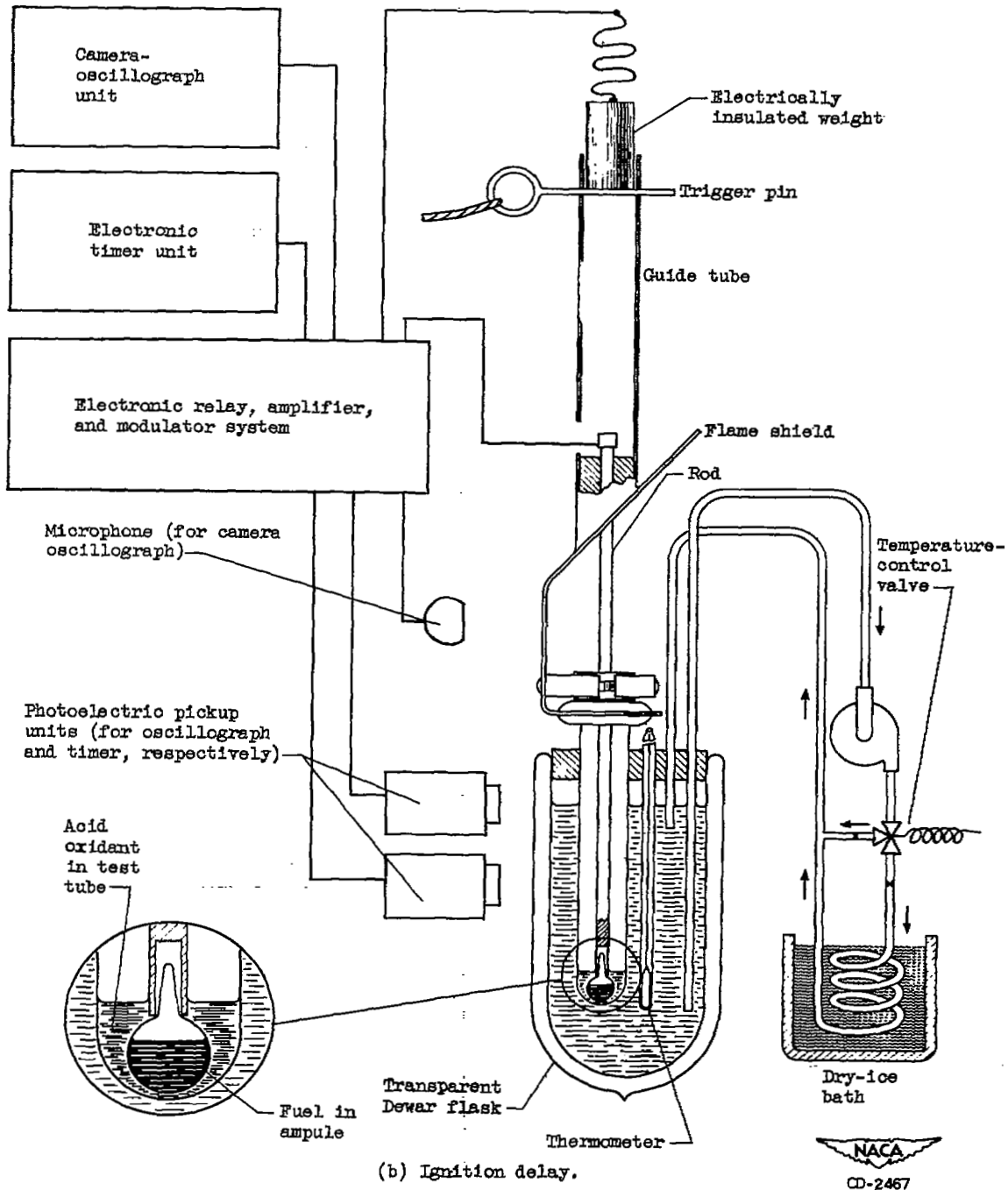


Figure 1. - Concluded. Experimental apparatus.

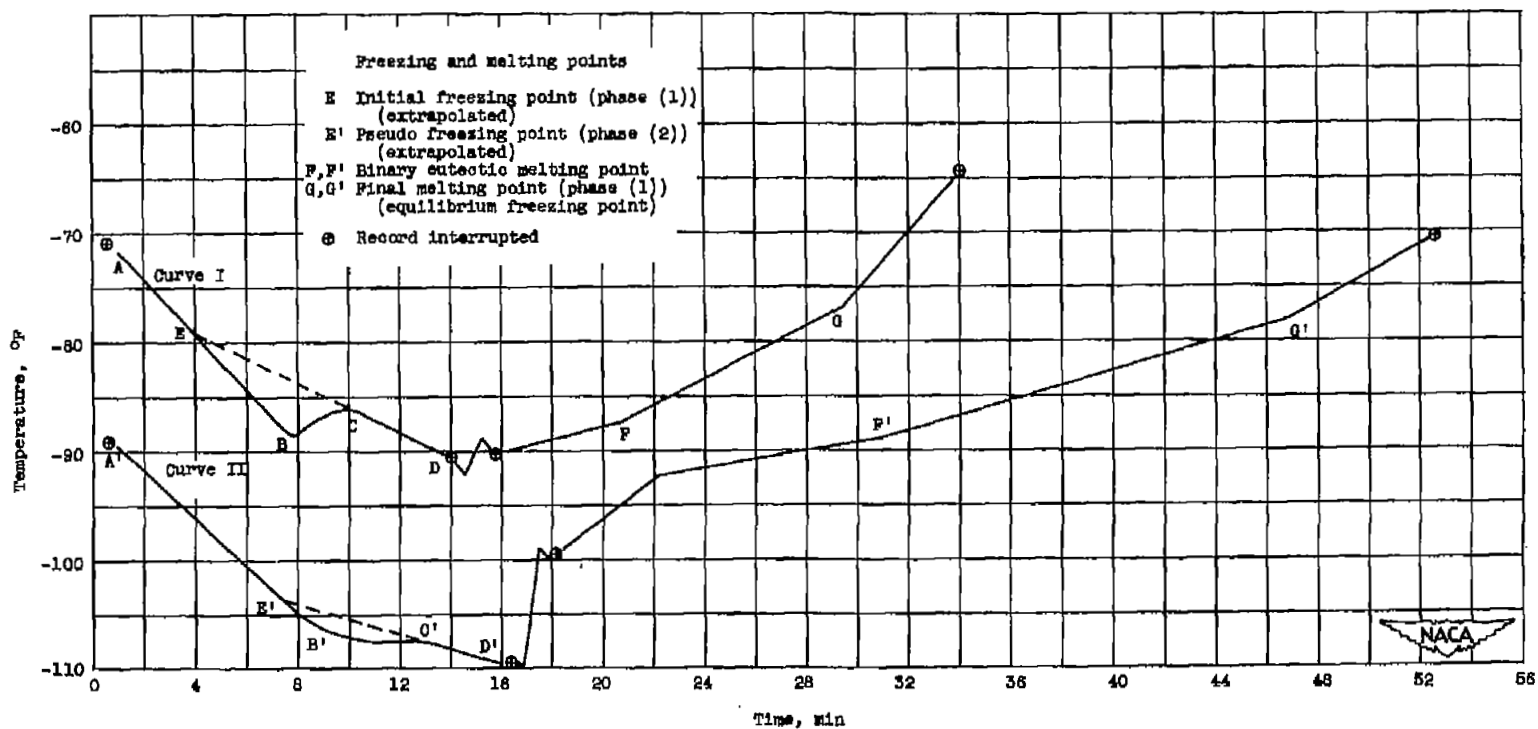
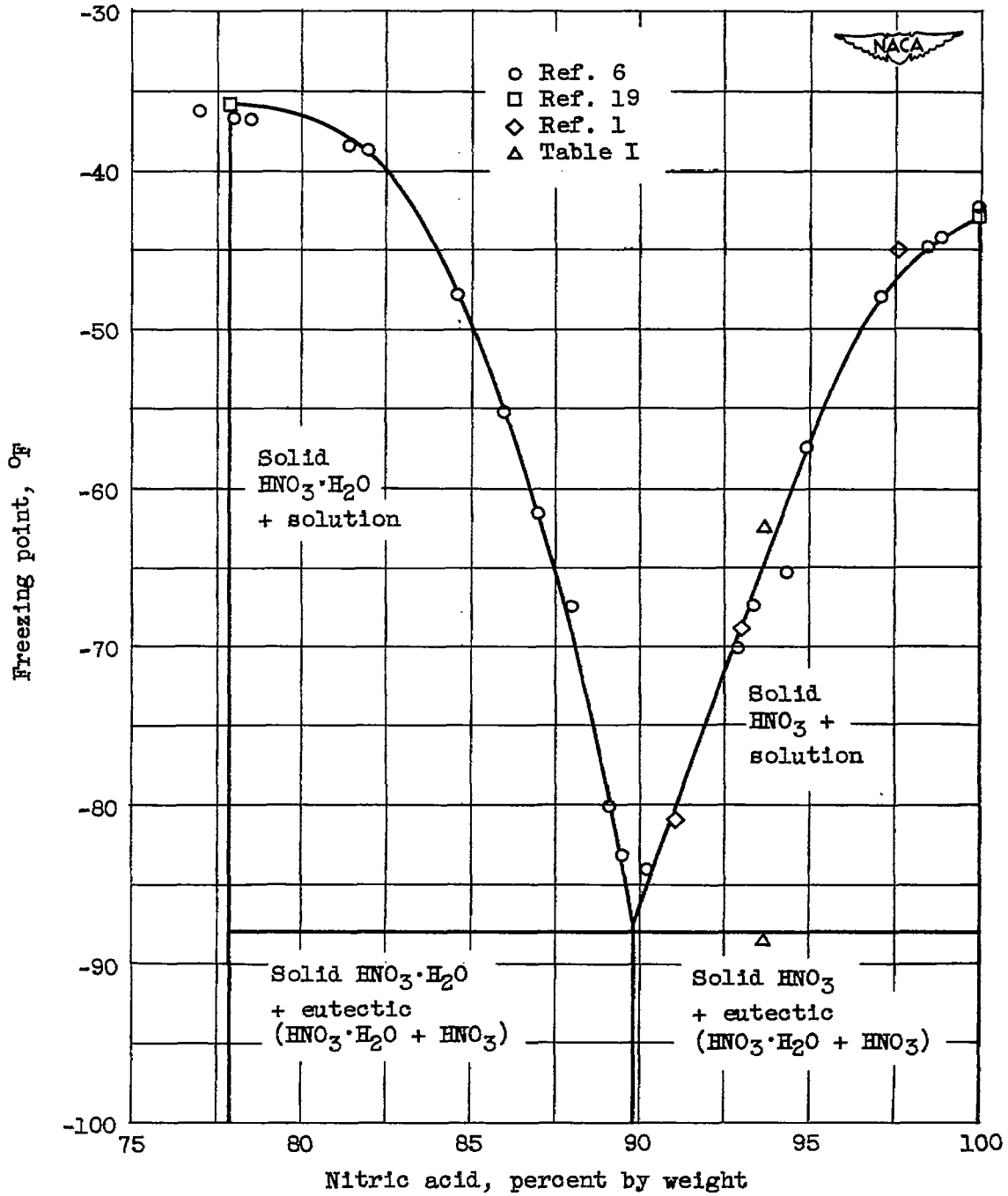
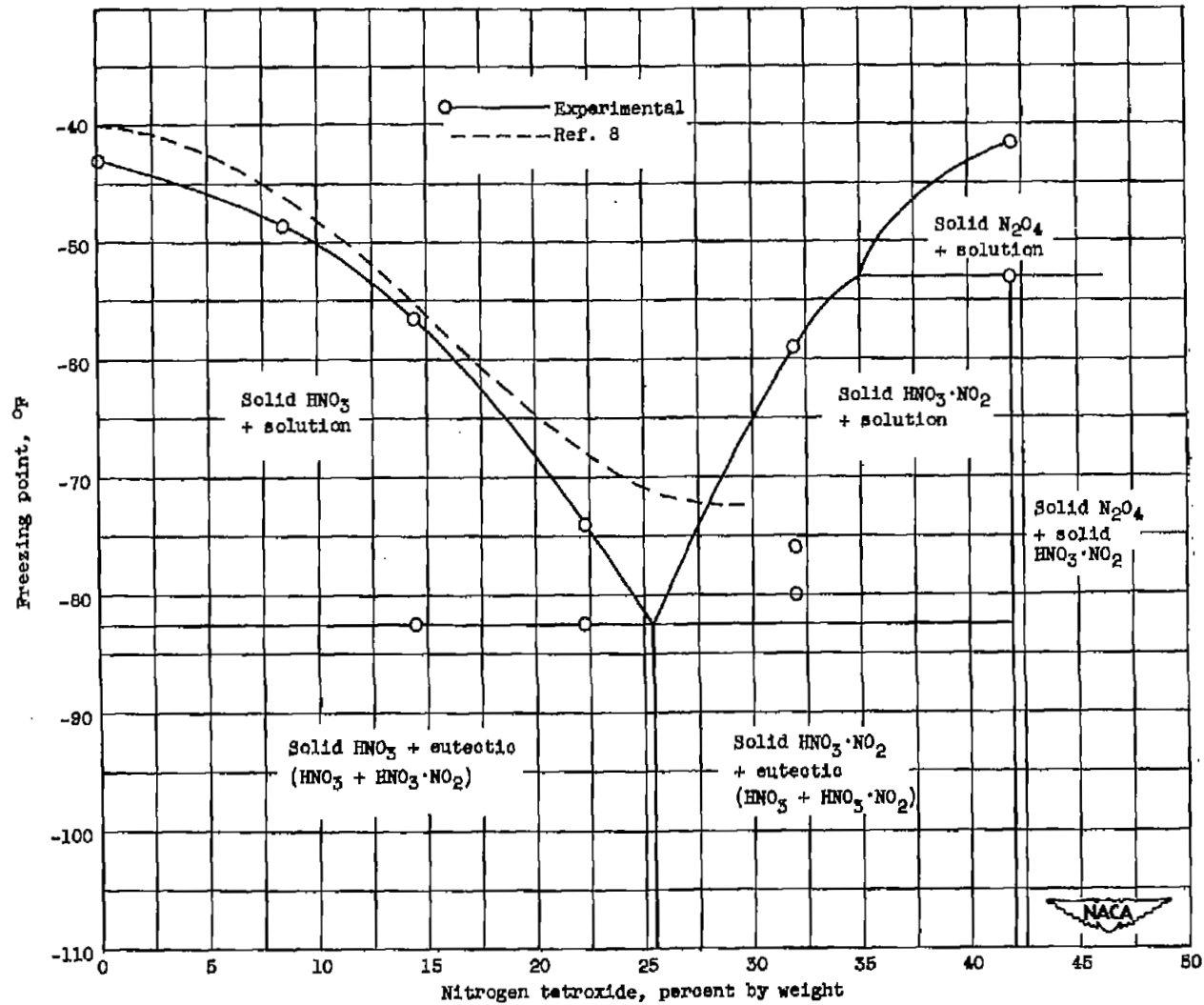


Figure 2. - Examples of cooling and warming curves from freezing-point apparatus. Composition of acid: 0.8 percent H_2O ; 25.9 percent N_2O_4 ; 73.3 percent HNO_3 .



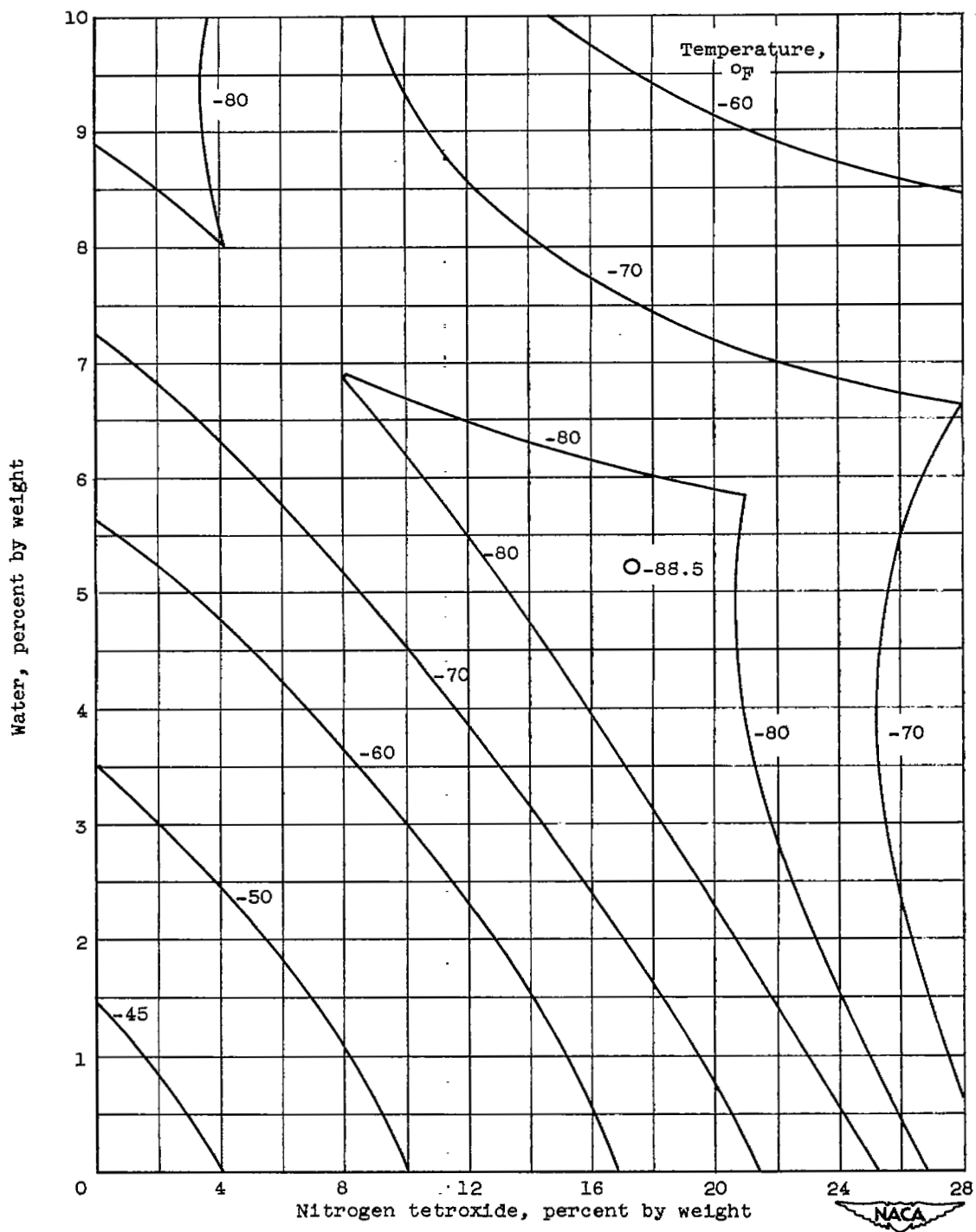
(a) Nitric acid - water.

Figure 3. - Freezing-point curves.

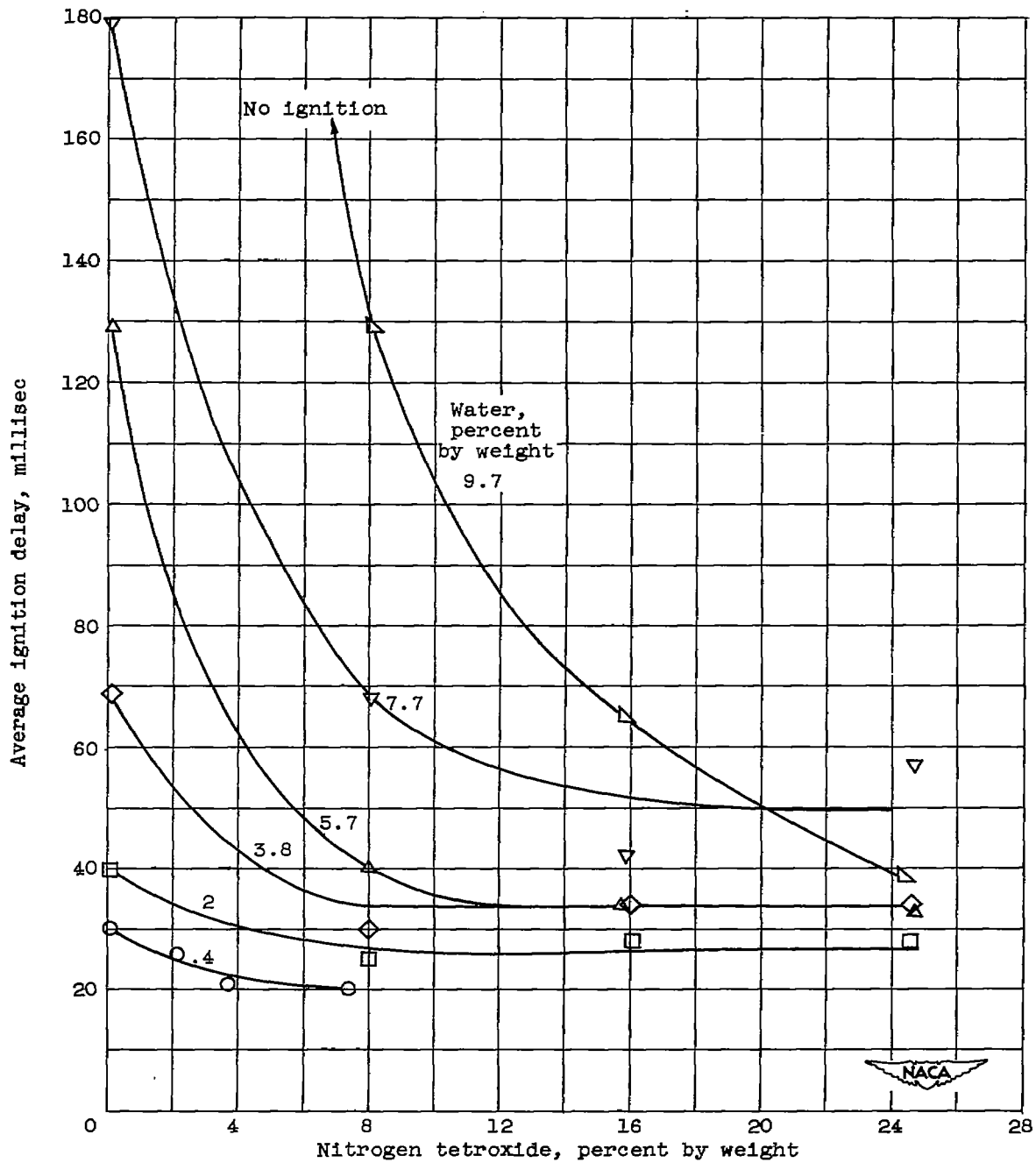


(b) Nitric acid - nitrogen tetroxide (+ 0.4 percent water).

Figure 3. - Continued. Freezing-point curves.

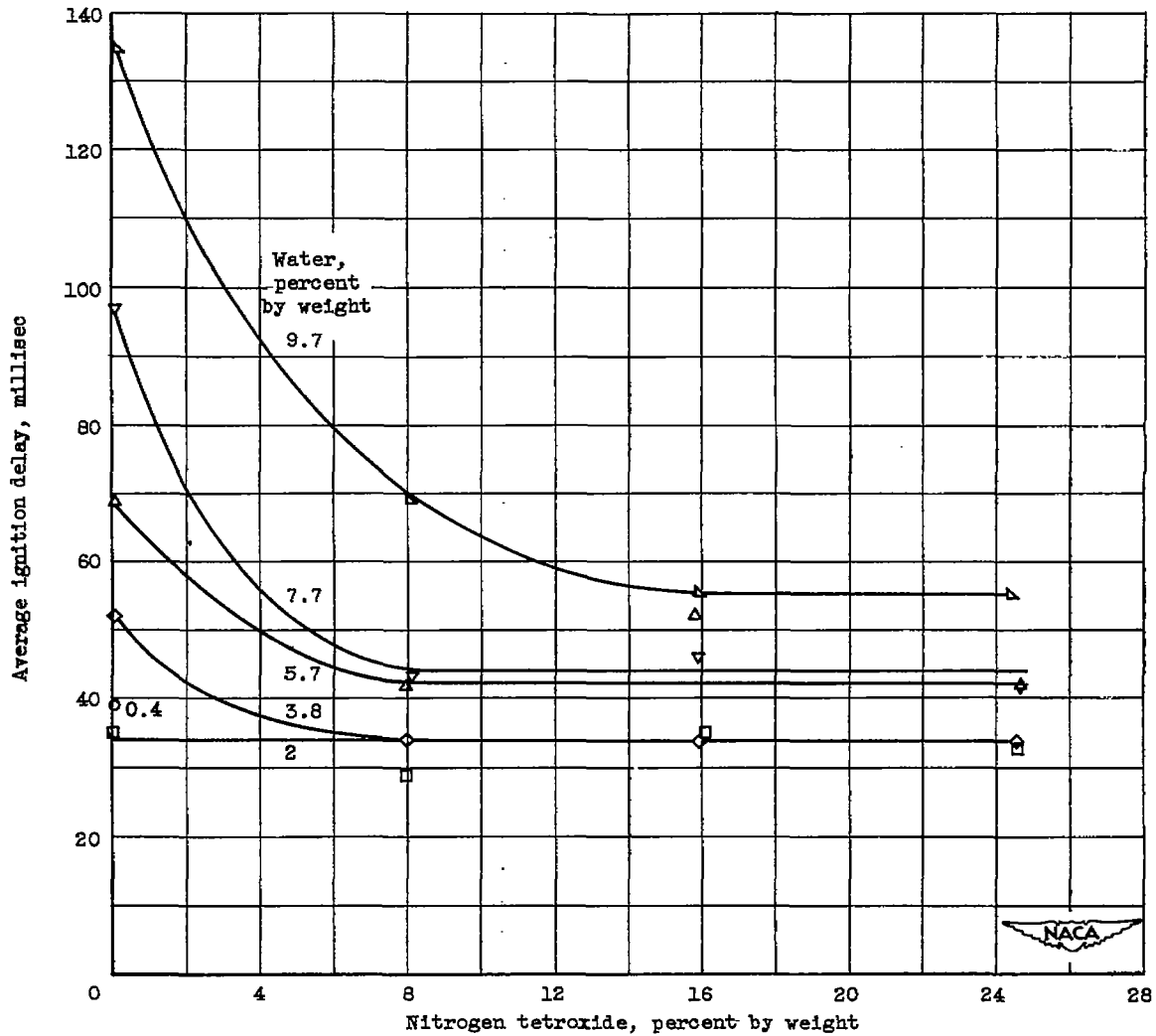


(c) Nitric acid - nitrogen tetroxide - water.
Figure 3. - Concluded. Freezing-point curves.



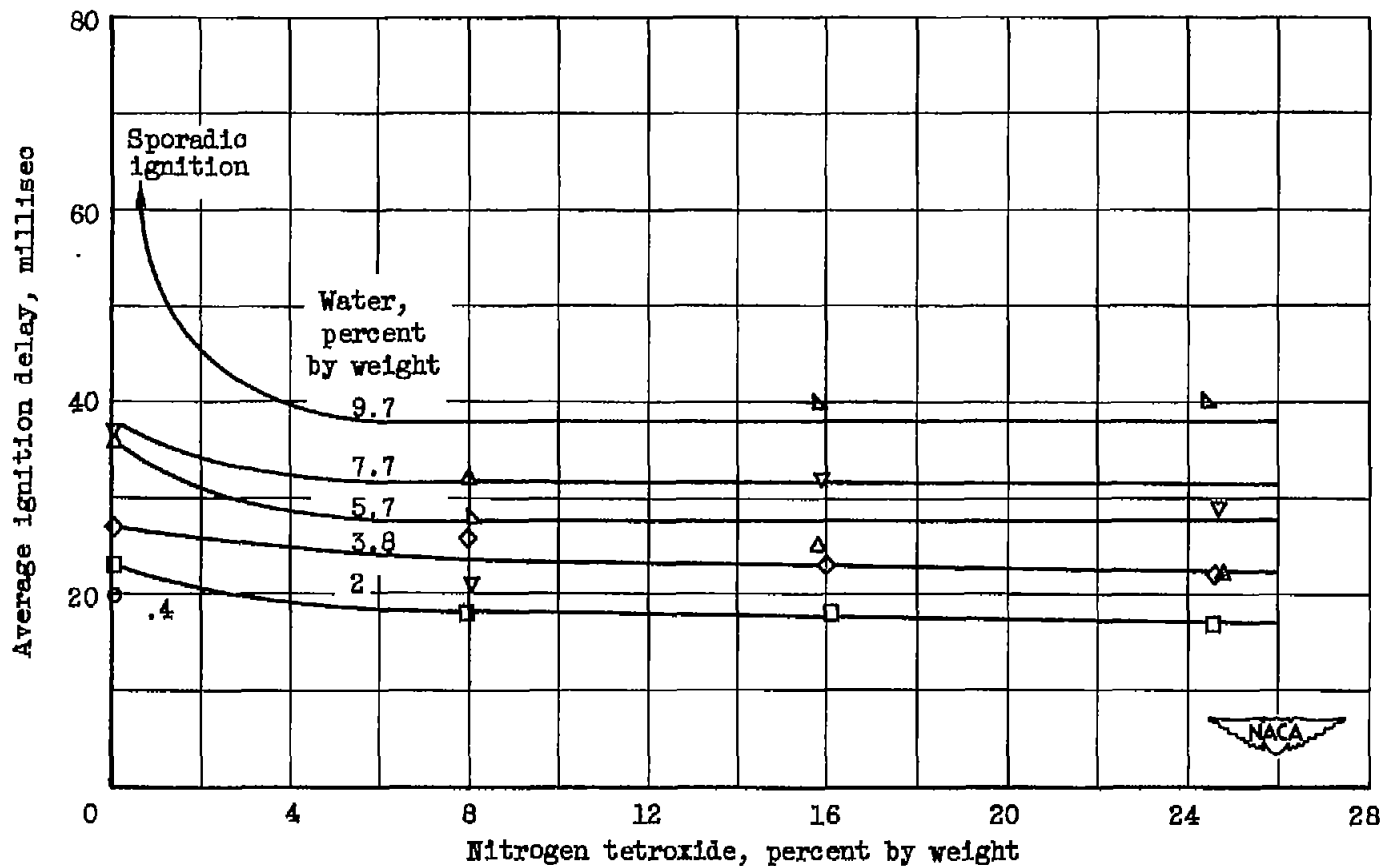
(a) Fuel, 30 percent o-toluidine - 70 percent triethylamine (by volume).

Figure 4. - Ignition delay as function of nitrogen tetroxide and water in nitric acid at -40° F.



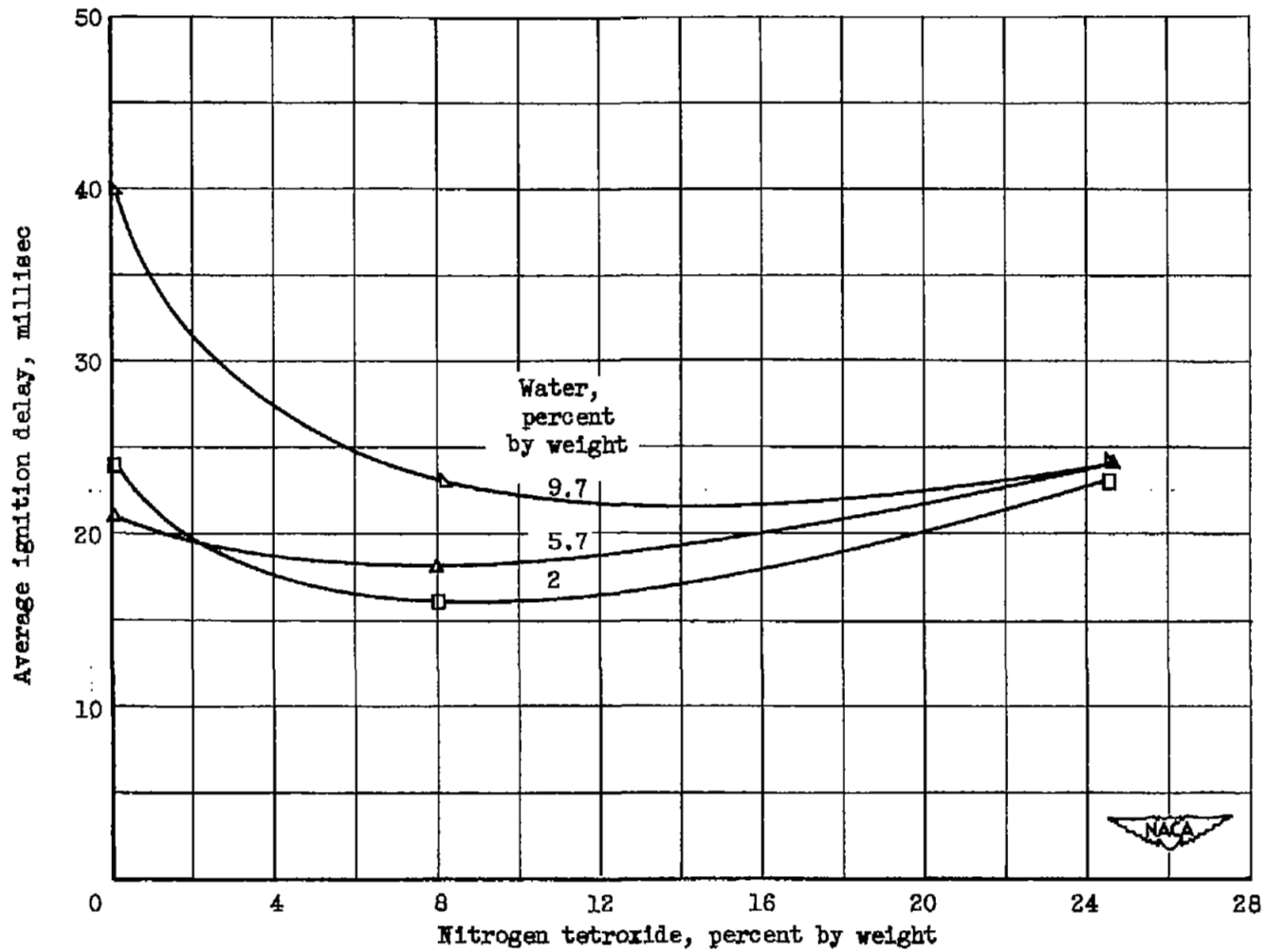
(b) Fuel, 50 percent allylamine - 50 percent ethylenimine (by volume).

Figure 4. - Continued. Ignition delay as function of nitrogen tetroxide and water in nitric acid at -40° F.



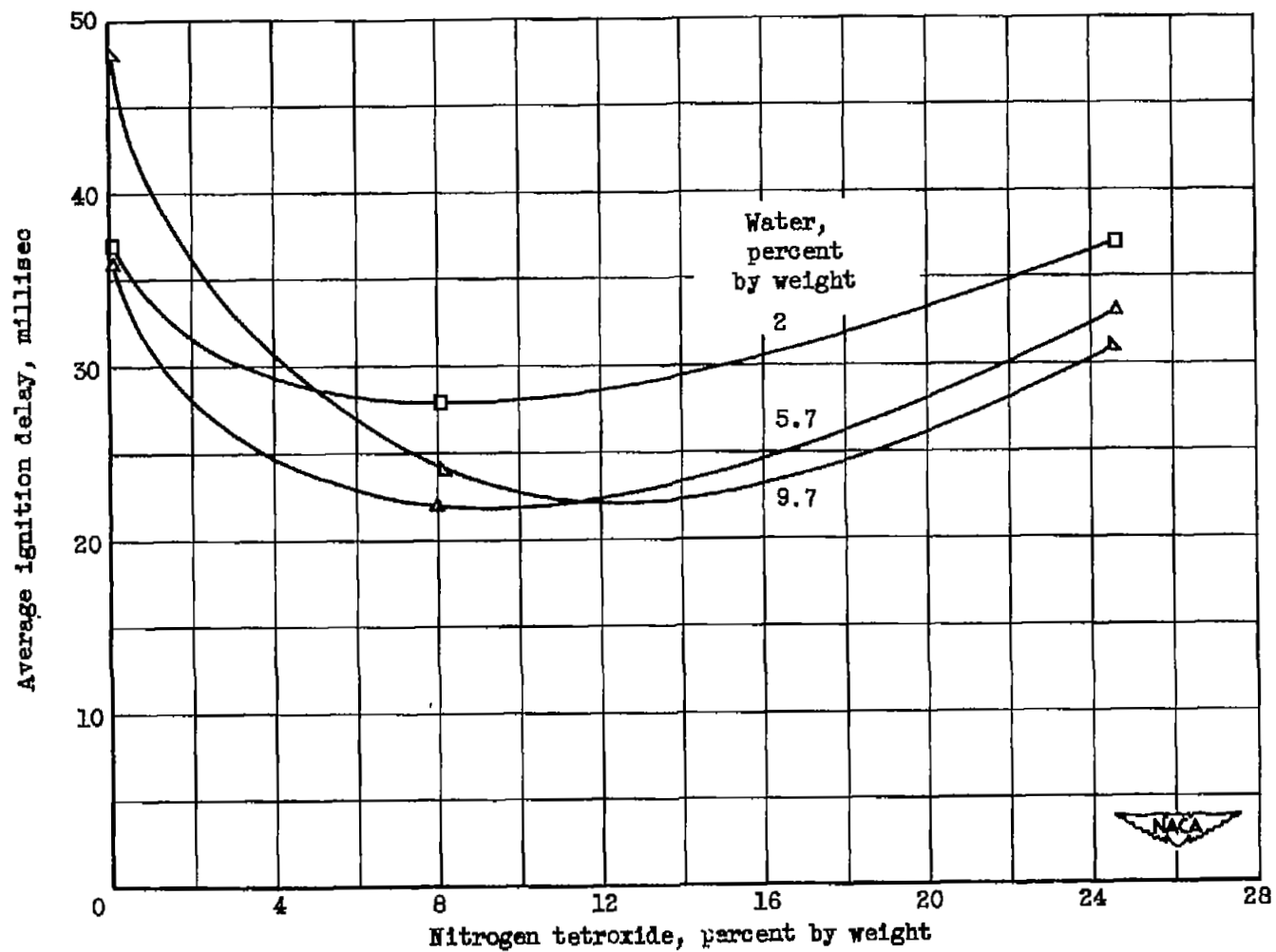
(c) Fuel, 50 percent ethylenimine - 50 percent triethylamine (by volume).

Figure 4. - Concluded. Ignition delay as function of nitrogen tetroxide and water in nitric acid at -40° F.



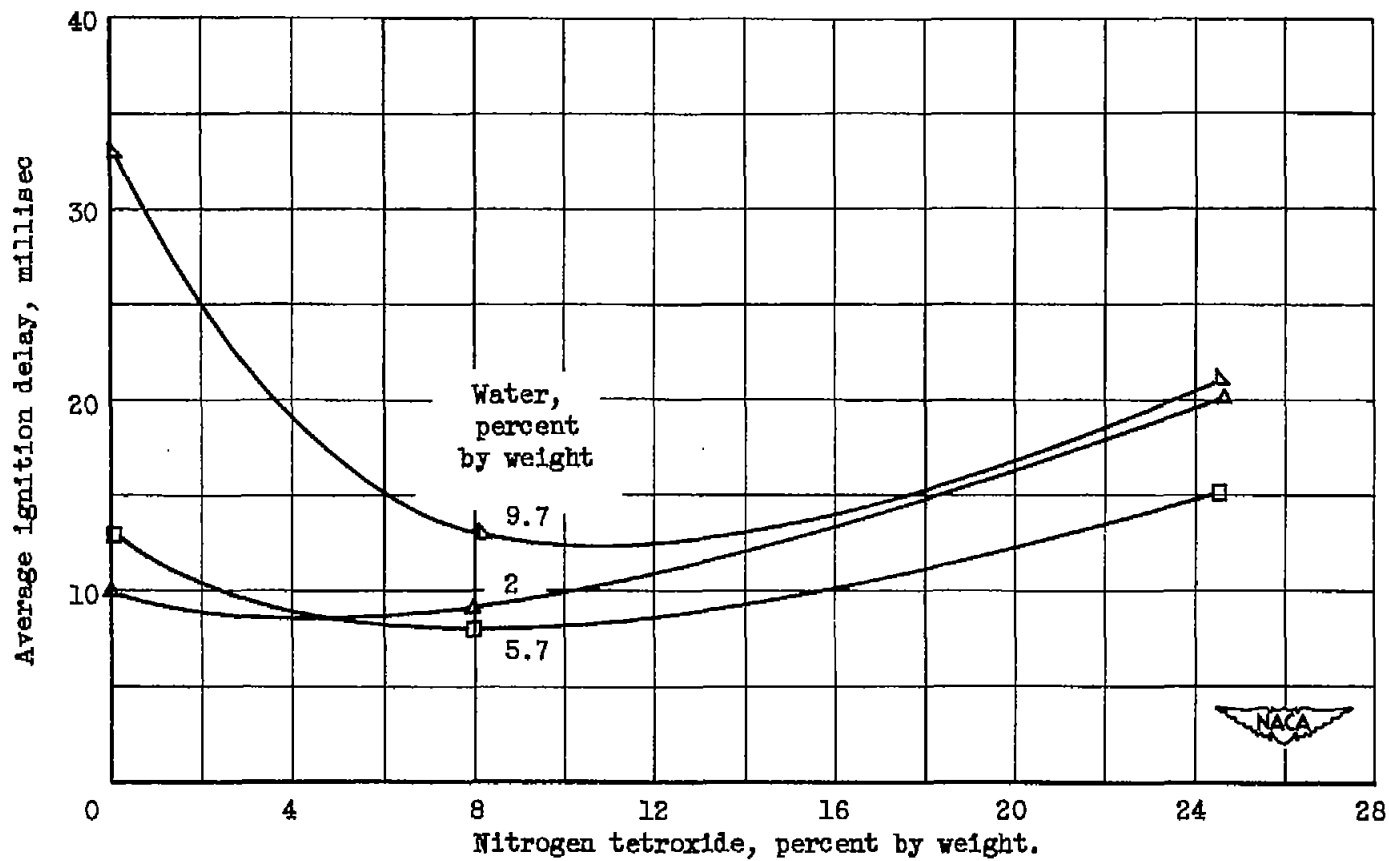
(a) Fuel, 30 percent o-toluidine - 70 percent triethylamine (by volume).

Figure 5. - Ignition delay as function of nitrogen tetroxide and water in nitric acid at 70° F.



(b) Fuel, 50 percent allylamine - 50 percent triethylamine (by volume).

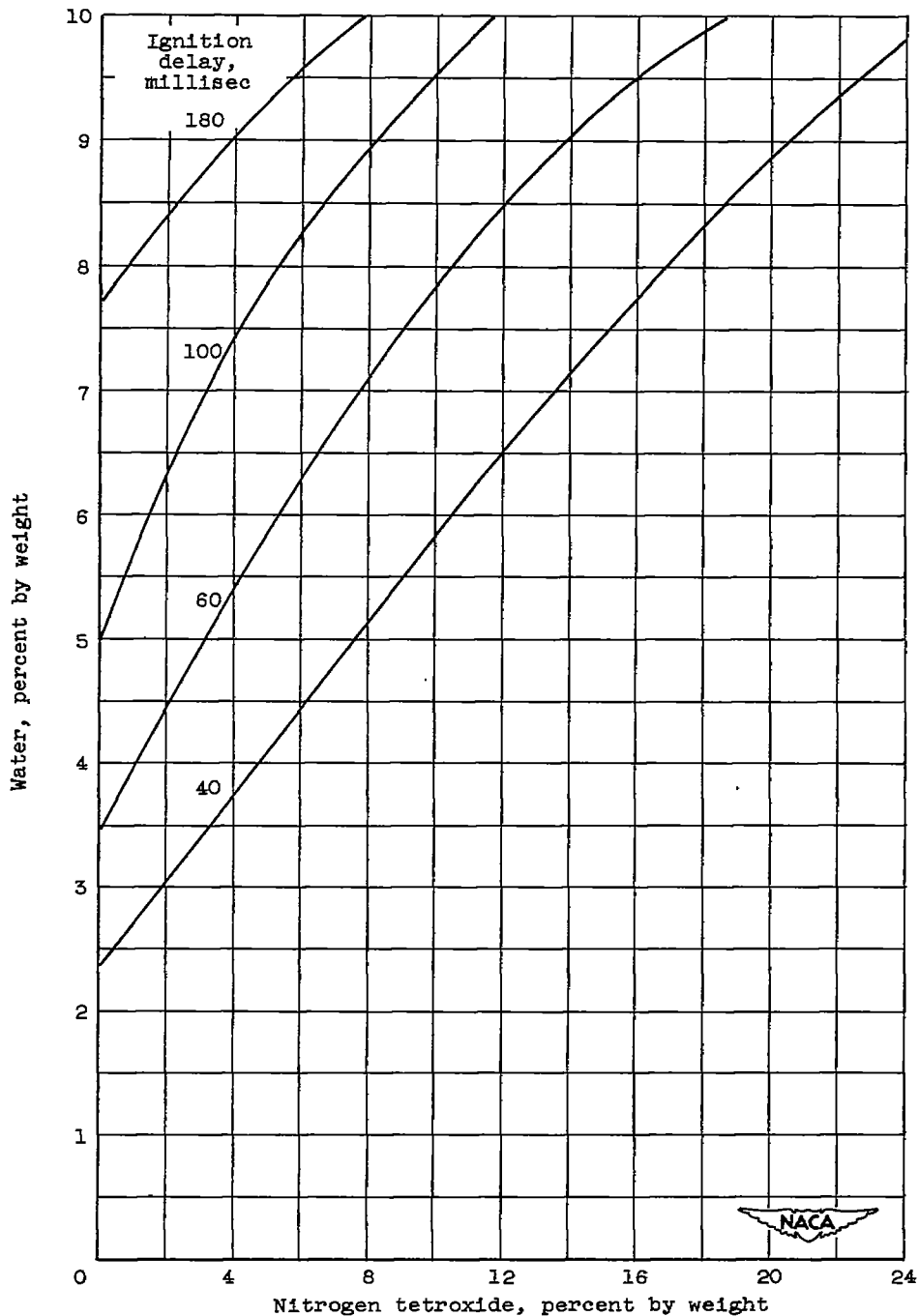
Figure 5. - Continued. Ignition delay as function of nitrogen tetroxide and water in nitric acid at 70° F.



(c) Fuel, 50 percent ethylenimine - 50 percent triethylamine (by volume).

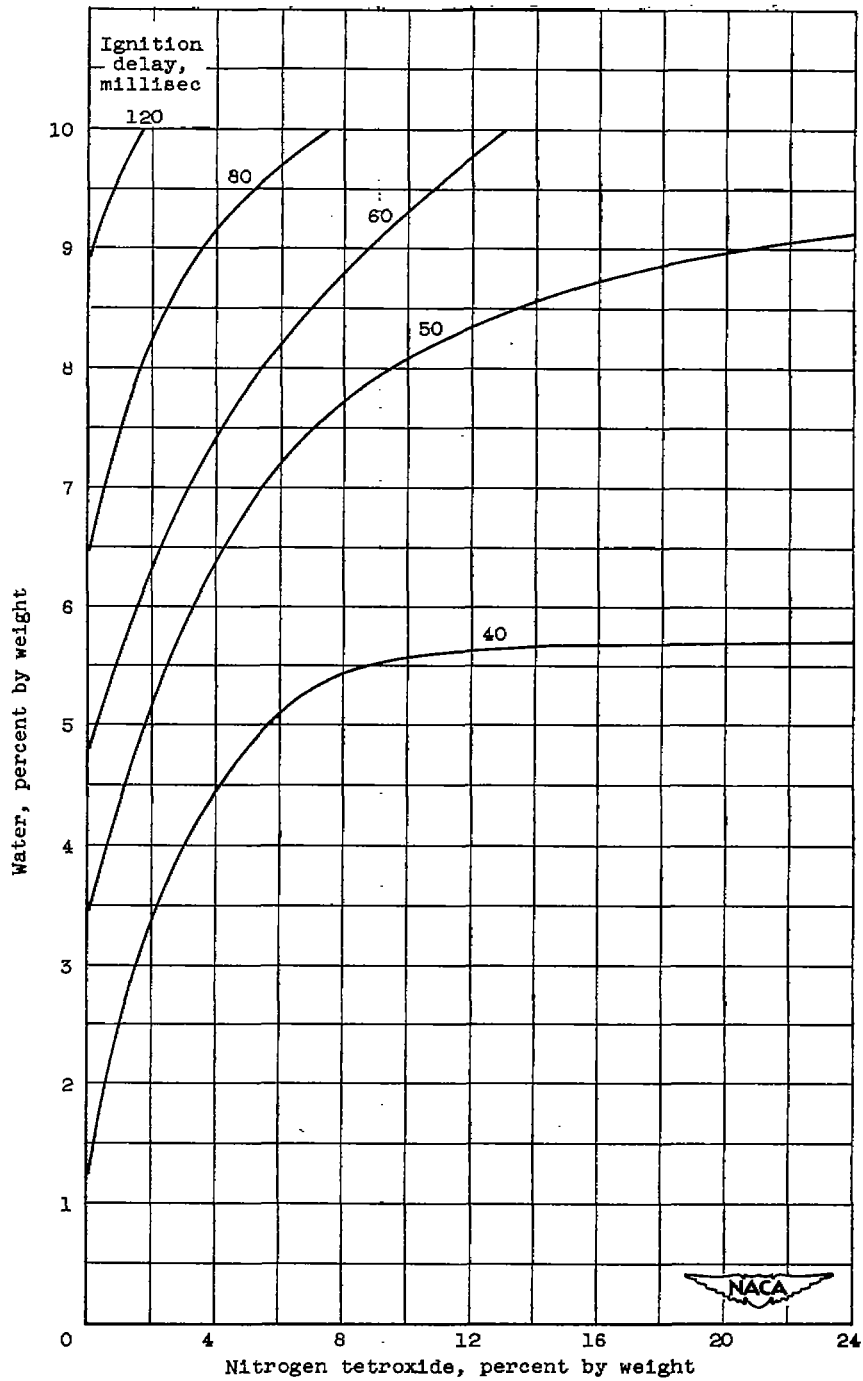
Figure 5. - Concluded. Ignition delay as function of nitrogen tetroxide and water in nitric acid at 70° F.

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(a) Fuel, 30 percent o-toluidine - 70 percent triethylamine (by volume).

Figure 6. - Ignition-delay surface of system concentrated nitric acid - nitrogen tetroxide - water at -40° F.



(b) Fuel, 50 percent allylamine - 50 percent triethylamine (by volume).

Figure 6. - Concluded. Ignition-delay surface of system concentrated nitric acid - nitrogen tetroxide - water at -40° F.

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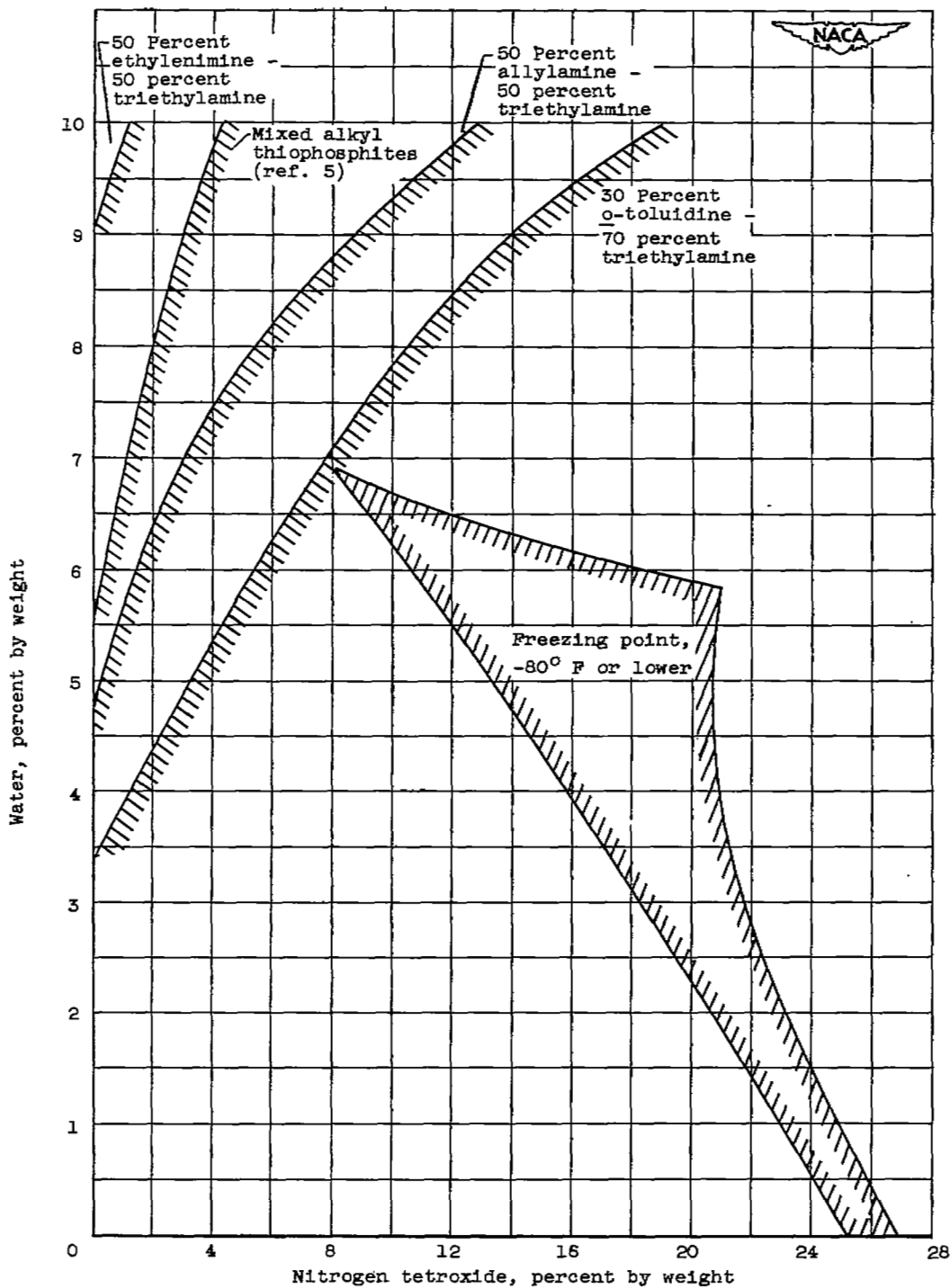


Figure 7. - Comparison of acid composition regions giving delays of 60 milliseconds or less at -40° F and region with freezing points of -80° F or lower.

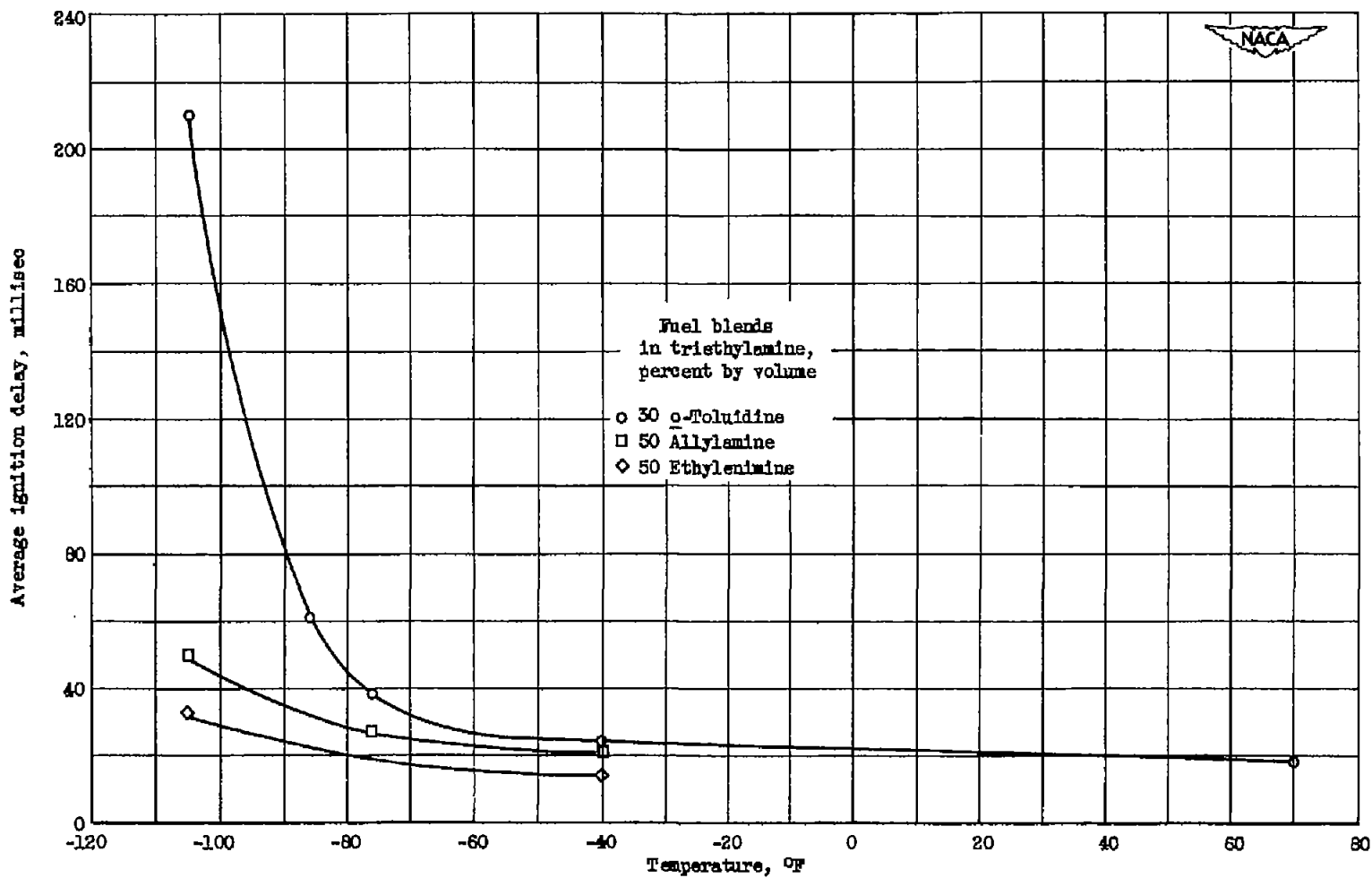


Figure 8. - Ignition delays of several fuel blends with low-freezing red fuming nitric acid (3 percent H_2O - 19 percent H_2O_4) as functions of temperature (refs. 1 and 3). (Acid supercooled at $-105^\circ F.$)

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