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### PHYSICAL PROPERTIES OF CONCENTRATED NITRIC ACID

By W. L. Sibbitt, C. R. St. Clair, T. R. Bump,  
P. F. Pagerey, J. P. Kern, and D. W. Fyfe

Purdue University



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## SUMMARY

A review of the data existing in the literature was completed and then experimental measurements were made in order to obtain the physical properties of white fuming nitric acid. The experimental measurements were made over the temperature range from approximately  $-35^{\circ}$  F to  $300^{\circ}$  F.

In the high-temperature range (above  $250^{\circ}$  F) the acid was in a state of thermodynamic equilibrium; consequently, these data do not apply in the case of most heat-transfer operations which usually do not allow sufficient time for thermodynamic equilibrium to be established.

With the exception of the vapor pressure (and of course the acid composition) the physical properties are known within approximately 5 percent over the temperature range to  $300^{\circ}$  F.

## INTRODUCTION

The main object of this investigation was to obtain reliable values of the thermal properties of concentrated nitric acid for use in correlating the data obtained in heat-transfer research and in fluid-friction-characteristics investigations.

Commercially available white fuming nitric acid with not more than 2 percent water content was specified as the type of acid which was to be studied. Acid solutions of the following compositions, in percent by weight, were studied in this investigation:

HNO <sub>3</sub>	NO <sub>2</sub>	H <sub>2</sub> O
97.35	1.57	1.08
94.0	5.0	1.0
99.01	.46	.53

The specifications for the commercial grade of white fuming nitric acid are as follows:

Specific gravity . . . . .	1.48 to 1.50
Weight fraction of $\text{HNO}_3$ . . . . .	0.857 to 0.945
Weight fraction of $\text{NO}_2$ . . . . .	0
Weight fraction of $\text{H}_2\text{O}$ . . . . .	0.055 to 0.143

A review of the existing literature was conducted (see refs. 1 to 32) and where data were lacking the physical constants were determined experimentally. It was considered desirable to obtain data on the thermal conductivity, thermal capacity, viscosity, density, and vapor pressure of the liquid phase over the temperature range from approximately  $-35^\circ$  to  $300^\circ$  F. The exact ranges used were as follows:

Physical property	Temperature range of investigation, $^\circ\text{F}$
Thermal conductivity	-47.2 to 122
Dynamic viscosity	-34.6 to 300
Specific heat	32 to 80
Density	-35 to 300
Vapor pressure	32 to 310

White fuming nitric acid decomposes even at  $32^\circ$  F; however, at temperatures above  $250^\circ$  F the decomposition is very rapid. It would be desirable to make all physical-property measurements within a very short time interval - of the order of a second. Thermal-property determinations usually require many minutes or even hours for accurate measurements. In these experiments only the vapor-pressure measurements were carried out in a time interval of a few minutes.

This investigation, conducted in the Mechanical Engineering Laboratories at Purdue University, was sponsored by and conducted with the financial assistance of the National Advisory Committee for Aeronautics.

#### APPARATUS AND METHODS OF MEASUREMENTS

The thermal conductivity of white fuming nitric acid was determined with a concentric-cylinder, steady-state type of apparatus (refs. 2, 9, and 14). The apparatus was placed directly in the constant-temperature bath fluid. The temperature drop across the liquid layer was measured with calibrated thermistors.

The dynamic viscosity of white fuming nitric acid was measured with a modified Oswald viscometer over the temperature range from  $-34.6^{\circ}$  to  $32^{\circ}$  F. A Lawaczeck, or falling-cylinder, viscometer was used over the temperature range from  $71.6^{\circ}$  to  $300^{\circ}$  F. These secondary instruments were calibrated with water and carbon tetrachloride (ref. 10).

The Purdue measurements of specific heat were made with a nonflow, bellows type of calorimeter which had been developed for use with volatile liquids.

A sealed-flask pycnometer was used in a liquid constant-temperature bath to determine the density of the liquid white fuming nitric acid in the temperature range from  $-35^{\circ}$  to  $100^{\circ}$  F. A pycnometer made from a selected Pyrex tube (2-mm inside diameter, 8-mm outside diameter, and 80 cm long) was used in an air bath for the temperature range from  $100^{\circ}$  to  $300^{\circ}$  F.

A static method was used for measuring the vapor pressure of white fuming nitric acid. A Smith and Menzies isoteniscope was used in the temperature range from  $32^{\circ}$  to  $190^{\circ}$  F. Vapor-pressure bombs of glass, H.S. 25 (L605) alloy, and stainless steel (AISI Type 347) were used in the temperature range from  $200^{\circ}$  to  $300^{\circ}$  F.

## RESULTS

The recommended properties of white fuming nitric acid are given in tables I and II and figures 1 to 7.

The absolute accuracy of the thermal-conductivity measurements was about 5 percent (up to  $122^{\circ}$  F). The extrapolation of these data to  $300^{\circ}$  F is probably of the same order of accuracy.

The maximum errors in the viscosity measurements were of the order of 5 percent at  $300^{\circ}$  F. The errors at room temperature were less than 1 percent.

Since most of the specific-heat values were taken from the literature the accuracy is unknown. Apparently the errors are somewhat less than 5 percent over the entire temperature range.

The density determinations were within an accuracy of 0.2 percent in the region below  $100^{\circ}$  F. At  $300^{\circ}$  F the maximum error might have been as much as 4 percent.

The vapor pressure of nitric acid below  $60^{\circ}$  C has been accurately determined. In the temperature range above  $90^{\circ}$  C the vapor pressure

may vary by more than a factor of 10 at any temperature depending upon the vapor-to-liquid volume ratio; vapor pressures greater than 1,000 lb/sq in. may readily be obtained if the vapor-to-liquid volume ratio is less than 10 percent. Higher vapor pressures were observed in glass apparatus than in metal apparatus. At 300° F the equilibrium state was attained in the order of 1 minute (depending on the vapor-to-liquid volume ratio).

High-purity aluminum and H.S. 25 (L605) were satisfactory materials for use with nitric acid. Kel-F solids, greases, waxes, and oils; fluorolubes; and Teflon were also satisfactory materials.

#### ANALYSIS AND DISCUSSION

The variable most difficult to control in this investigation was the composition of the acid. Two liters of commercial acid were taken from a stainless-steel tank which contained about 100 gallons of acid. The 2-liter glass sample bottle was maintained at room temperature; however, the composition of the acid sample changed as the liquid volume was decreased. The commercial acid contained nickel and chromium compounds as well as the original decomposition products. The equilibrium liquid-phase composition was a function of the temperature, pressure, and liquid-vapor volume ratio.

The analytical methods were not sufficiently accurate to specify the composition of the liquid phase. As an example, the viscosity and vapor pressure were measured at 300° F and approximately 1,500 lb/sq in. Attempts to obtain representative liquid samples at 300° F and 1,500 lb/sq in. were not successful. When the acid was cooled to room temperature then the liquid-phase composition changed because of the change of gas solubilities in the liquid and the change of partial pressures in the gas phase.

Initially a Hoesppler Precision Viscosimeter (accuracy of better than 0.1 percent) was used for the viscosity measurements. Viscosity changes as great as 1 percent occurred in a 10-hour period at 100° F; however, the chemical analysis indicated no change in composition. The nitric acid showed appreciable decomposition at temperatures above 100° F; therefore, the acid samples were held at the high temperatures only for a minimum period of time. At temperatures above 250° F the liquid phase was probably in thermodynamic equilibrium; while at temperatures below 250° F the exact conditions are not known.

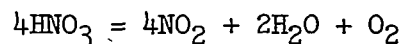
The viscosity of acid (above 200° F) with less than 2 percent water is not a sensitive function of the NO<sub>2</sub> content in the range from 1 to 5 percent NO<sub>2</sub>; consequently, the degree of completion of acid decomposition is not of great importance.

The straight line in figure 1 is considered as representing the probable value of the thermal conductivity of white fuming nitric acid with an accuracy of  $\pm 5$  percent. The maximum dispersion of the experimental measurements from the recommended values in a  $100^{\circ}$  F range was less than 2.4 percent. This dispersion was partly due to the change in acid composition. The values reported by Van der Held and Van Drunen (ref. 3) were obtained by an interesting unsteady-state method and are of the correct order of magnitude. Values reported in reference 3 for other compounds differ as much as 14 percent from the accepted values of thermal conductivity. The primary measurements of the thermal conductivity of water made at Purdue were within 1.6 percent of the accepted values. Other data on solutions of NaCl, KCl,  $MgCl_2$ , and  $CaCl_2$  show a linear temperature coefficient of thermal conductivity over a temperature range greater than  $100^{\circ}$  F; consequently, a linear extrapolation for nitric acid (constant composition) appears to be reasonable.

The specific heat of white fuming nitric acid has been measured by a number of investigators over the temperature range from  $-40^{\circ}$  to  $300^{\circ}$  F (refs. 19, 20, and 31, p. 572). The values for pure acid at  $32^{\circ}$  F (where the composition can be accurately known) differ as much as 6 percent. This disagreement is difficult to explain; however, it is probably due to different acid compositions. Acids of various compositions showed the same specific-heat value at about  $90^{\circ}$  F. For the system  $HNO_3-H_2O$  the specific heat is a linear function of the water content and amounts to over a 2 percent increase in the specific heat per weight percent of water.

The density data as reported by a number of investigators are in qualitative agreement at  $100^{\circ}$  F; however, the temperature coefficients of some of the data reported show wide variations at  $0^{\circ}$  and  $200^{\circ}$  F. Water additions decrease the density of nitric acid while  $NO_2$  increases the density.

The kinetics of the decomposition of nitric acid have not been completely established. Apparently the pure acid decomposes as follows:



These products are not the end products of the decomposition of commercial nitric acid in a metal container. The decomposition products have density effects which oppose each other; however, the  $NO_2$  and  $H_2O$  are not formed in equal amounts and their distribution between the liquid and vapor phase is unknown.

The vapor pressures of nitric-acid solutions have been measured over the temperature range from  $-30^{\circ}$  to  $300^{\circ}$  F. Excellent data are available up to  $140^{\circ}$  F. Approximate values of vapor pressure are available in the temperature range from  $140^{\circ}$  to  $200^{\circ}$  F. The vapor pressure in the temperature range above  $200^{\circ}$  F was a sensitive function of the vapor-liquid volume ratio and the material of the container.

#### CONCLUDING REMARKS

The recommended values of the physical properties of white fuming nitric acid (less than 2 percent water) are given for the temperature range from approximately  $-35^{\circ}$  to  $300^{\circ}$  F. Values are given for the thermal conductivity, dynamic viscosity, specific heat, density, and vapor pressure based on data obtained from a review of the literature and from experimental measurements.

All acid analyses were made at room temperature and are not indicative of the composition at temperatures above  $200^{\circ}$  F.

Purdue University,  
Lafayette, Ind., December 1, 1951.

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TABLE I  
RECOMMENDED PROPERTIES OF NITRIC ACID<sup>a</sup>

Temperature, °F	Thermal conductivity, Btu/(hr)(sq ft)(°F/ft)	Viscosity, centipoises	Specific heat, Btu/(lb)(°F)	Density, g/cc	Kinematic viscosity, sq ft/hr	Prandtl modulus	Temperature, °C
-30	0.145	2.46	0.423	1.617	0.0590	17.35	-34.3
0	.150	1.73	.423	1.587	.0423	11.81	-17.8
50	.157	1.08	.423	1.537	.0273	7.05	10
100	.166	.726	.423	1.488	.0189	4.45	37.8
150	.175	.525	.423	1.437	.0142	3.07	65.6
200	.183	.397	.424	1.388	.0111	2.23	93.3
250	.191	.314	.429	1.337	.00908	1.71	121.1
300	.199	.254	.436	1.290	.00763	1.35	148.9

<sup>a</sup>Contains 95 to 97.5 percent by weight of HNO<sub>3</sub> and less than 2 percent by weight of H<sub>2</sub>O.

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TABLE II  
VAPOR PRESSURE OF NITRIC ACID<sup>a</sup>

Temperature, °F	Vapor pressure, mm of Hg, of -		Temperature, °C
	100 percent HNO <sub>3</sub> (b)	90 percent HNO <sub>3</sub> (c)	
32	14.4	5.5	0
50	26.6	11	10
68	47.9	20	20
86	81.3	37.3	30
104	133	64.4	40
122	208	107	50
158	<sup>d</sup> 467	242	70
176	<sup>d</sup> 670	354	80
194	<sup>d</sup> 937	504	90
212	<sup>d</sup> 1,282	710	100

<sup>a</sup>Order of 50 to 100 percent relative vapor volume.

<sup>b</sup>Data taken from reference 28.

<sup>c</sup>Data taken from reference 22.

<sup>d</sup>Extrapolated values.



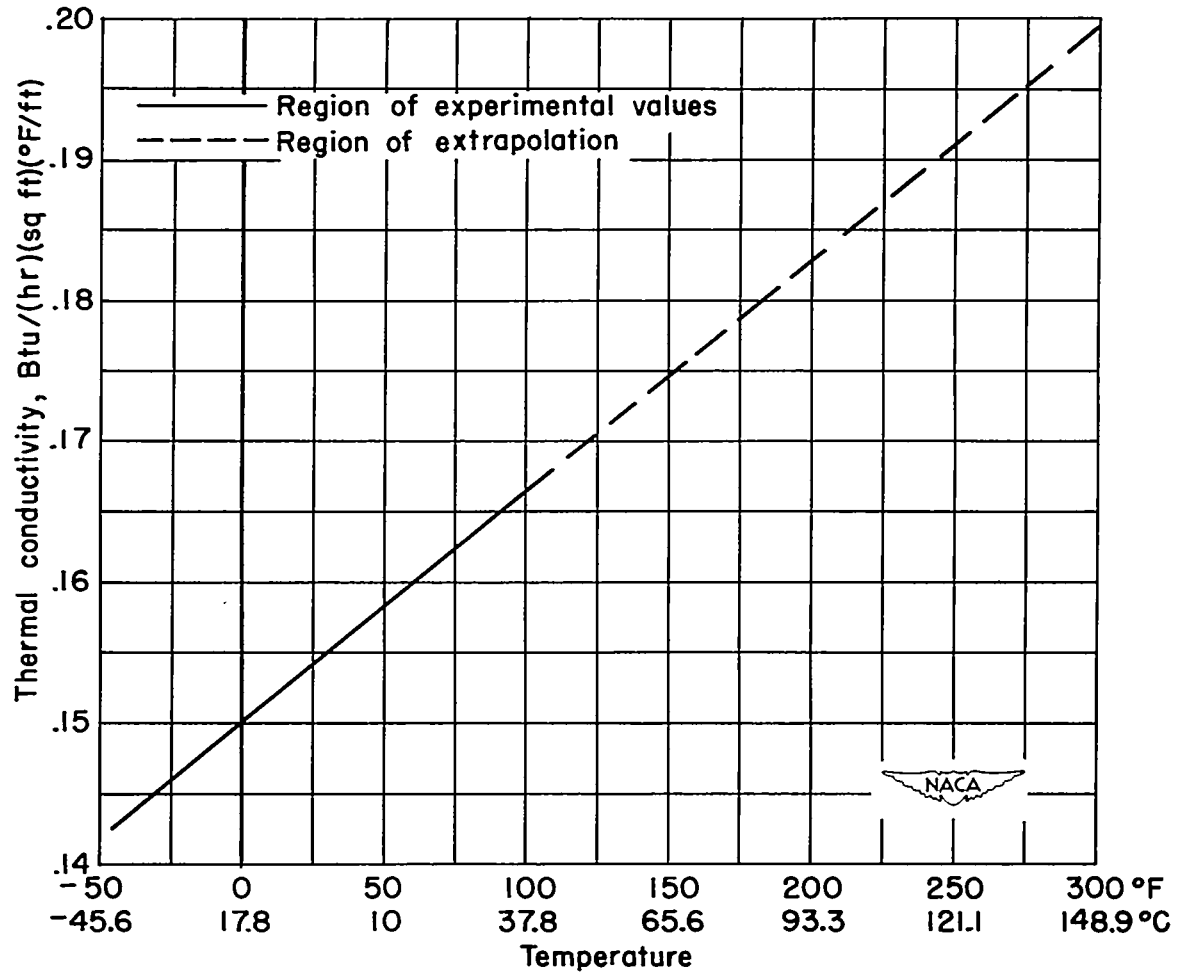


Figure 1.- Recommended values of thermal conductivity of nitric acid.  
 Data taken from reference 2 for white fuming nitric acid with composition (in percent by weight) of:  $\text{HNO}_3$ , 99.01;  $\text{NO}_2$ , 0.46;  $\text{H}_2\text{O}$ , 0.53.

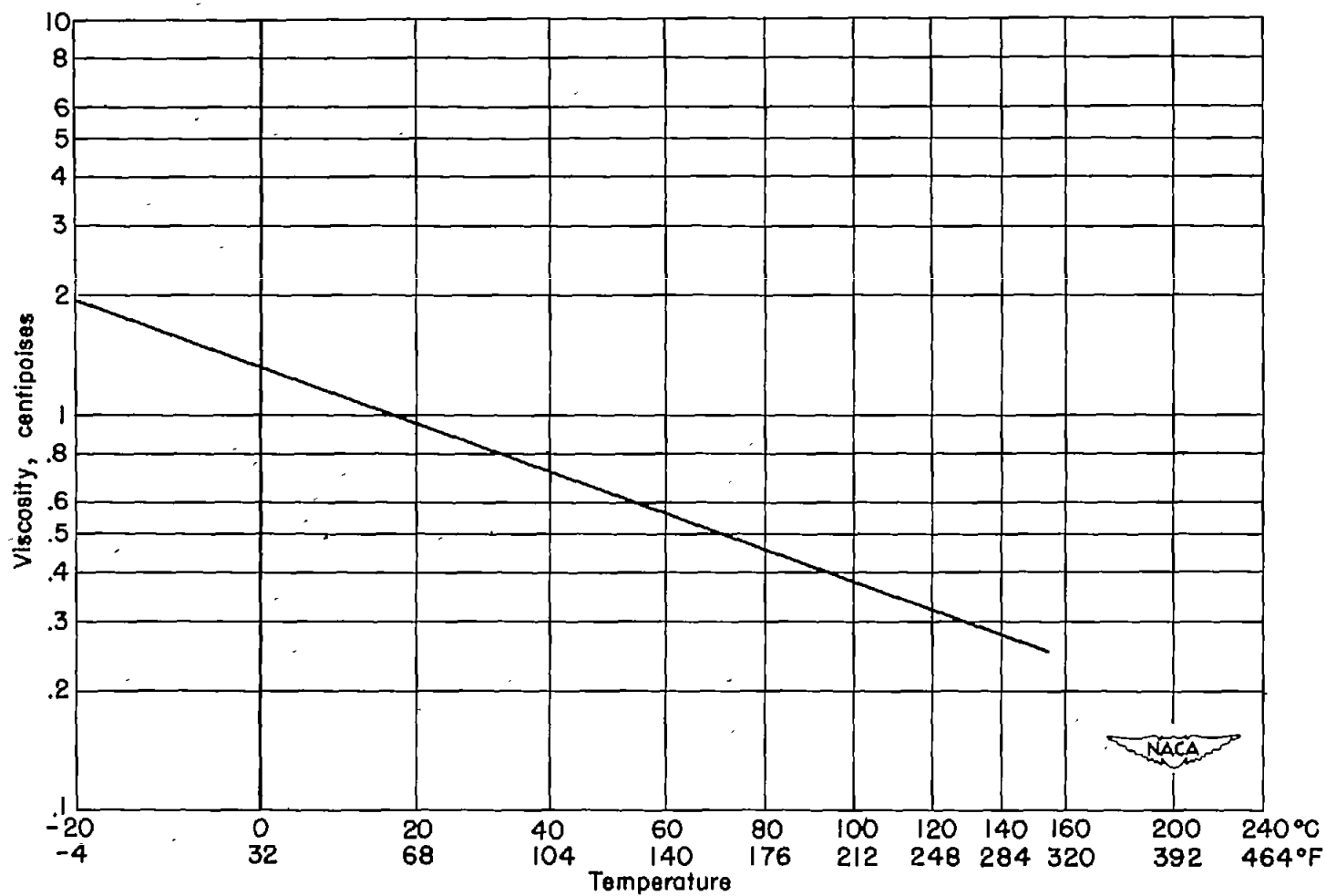


Figure 2.- Recommended values of viscosity of nitric acid. Data taken from reference 10 for white fuming nitric acid with composition (in percent by weight) of:  $\text{HNO}_3$ , 97.35;  $\text{NO}_2$ , 1.57;  $\text{H}_2\text{O}$ , 1.08. Density at  $0^\circ\text{C}$ , 1.5796 grams per cubic centimeter.

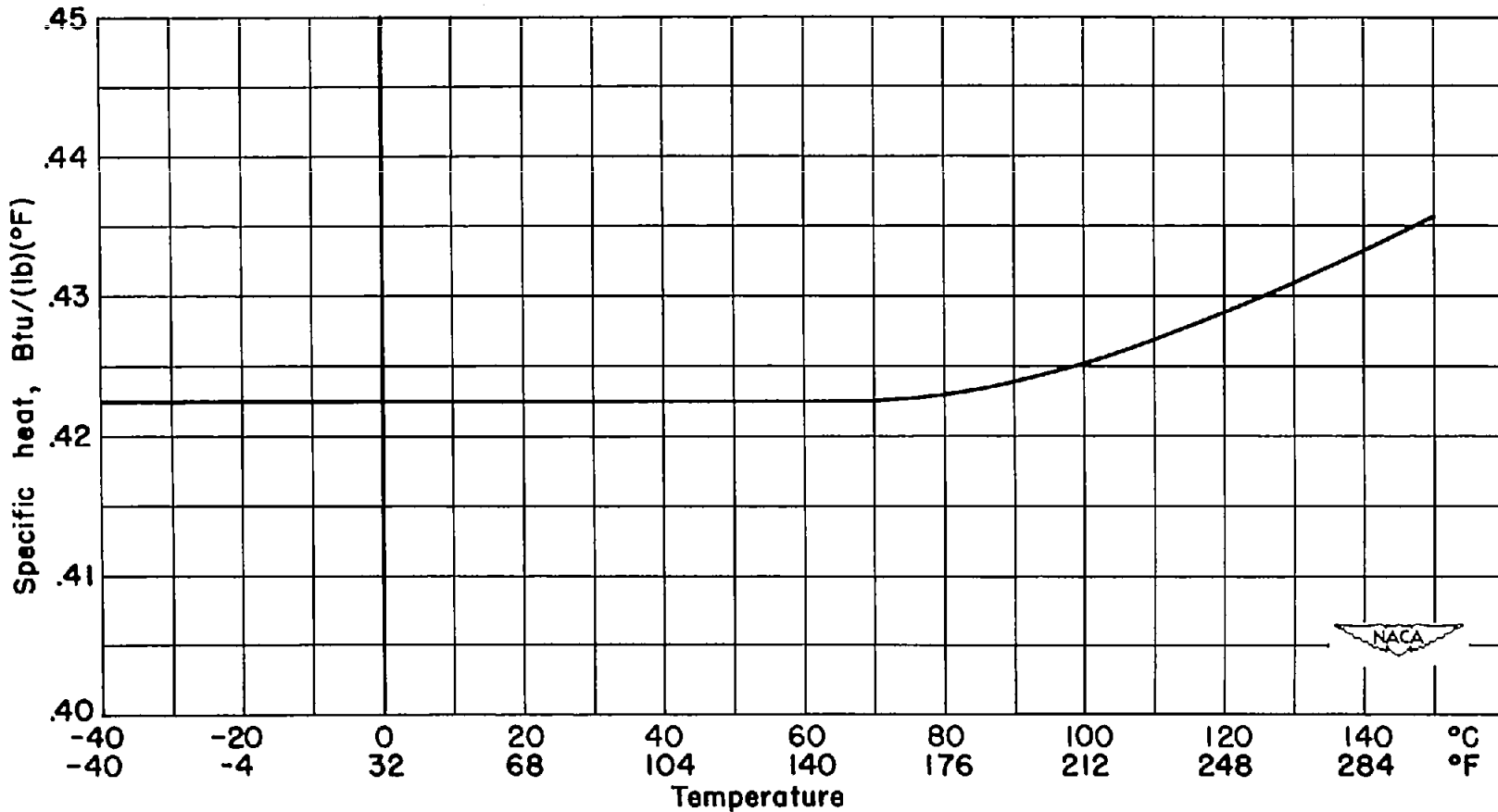


Figure 3.- Recommended values of specific heat of white fuming nitric acid containing 95 to 97.5 percent HNO<sub>3</sub>. (Data from refs. 19, 20, and 31.)

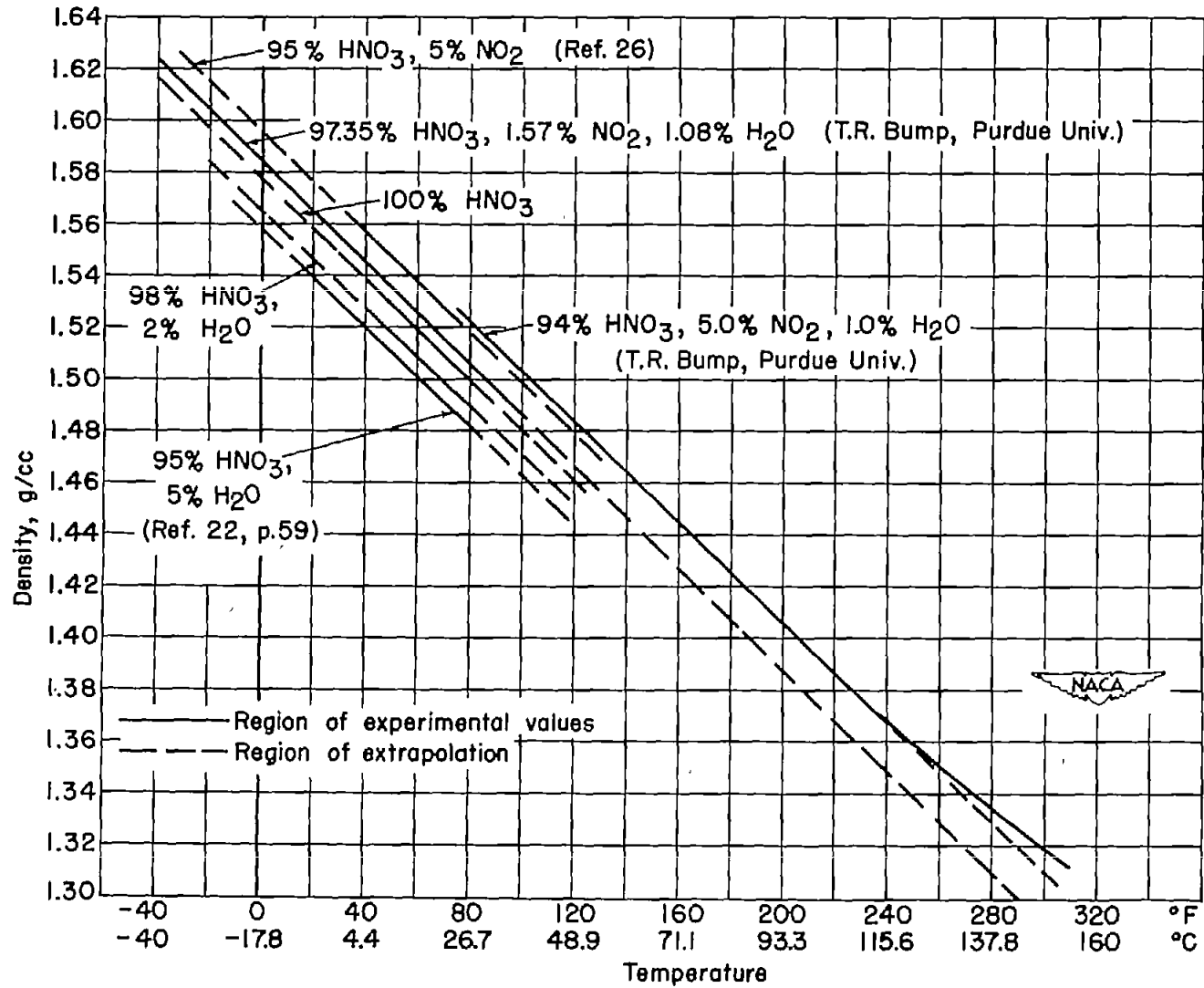
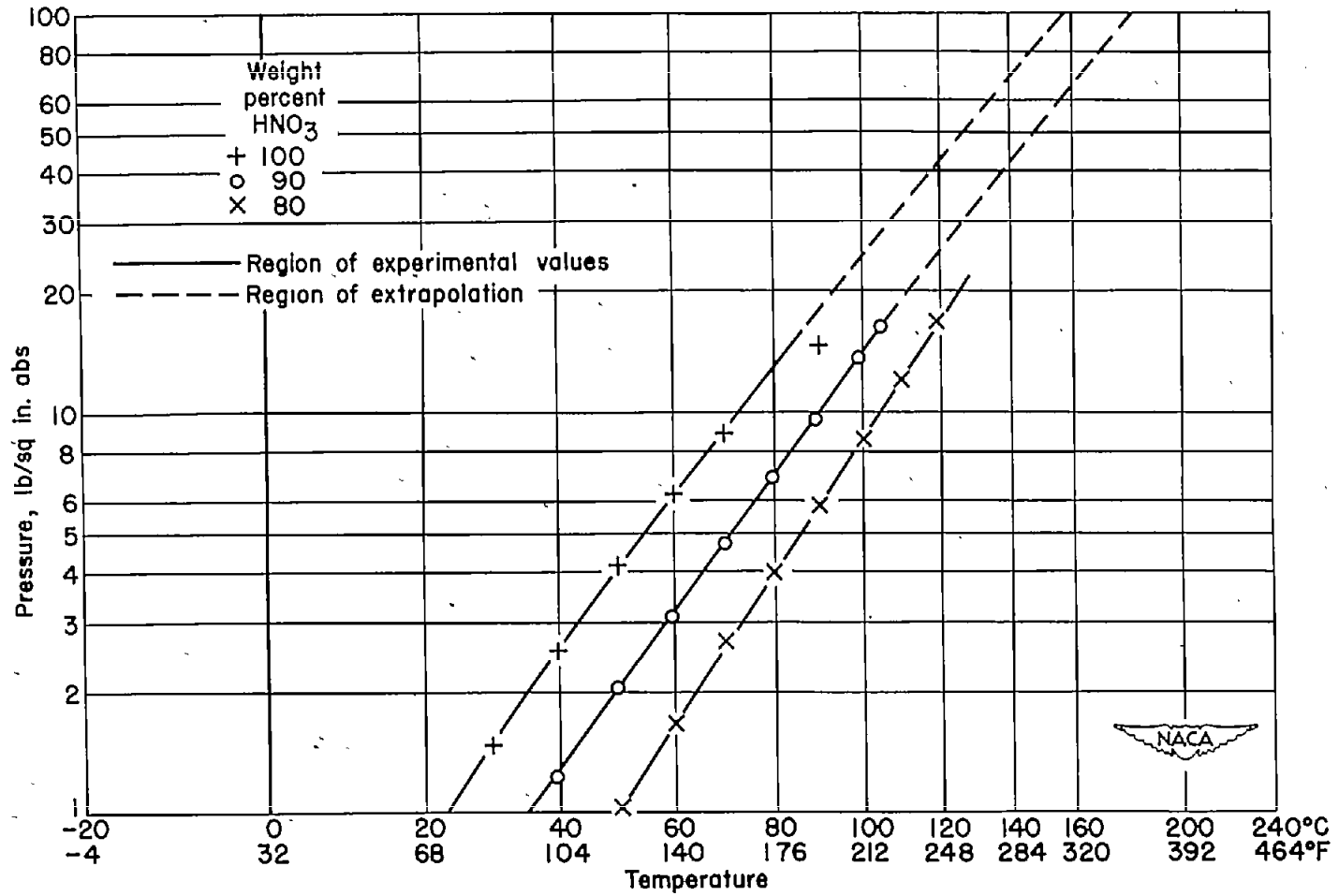


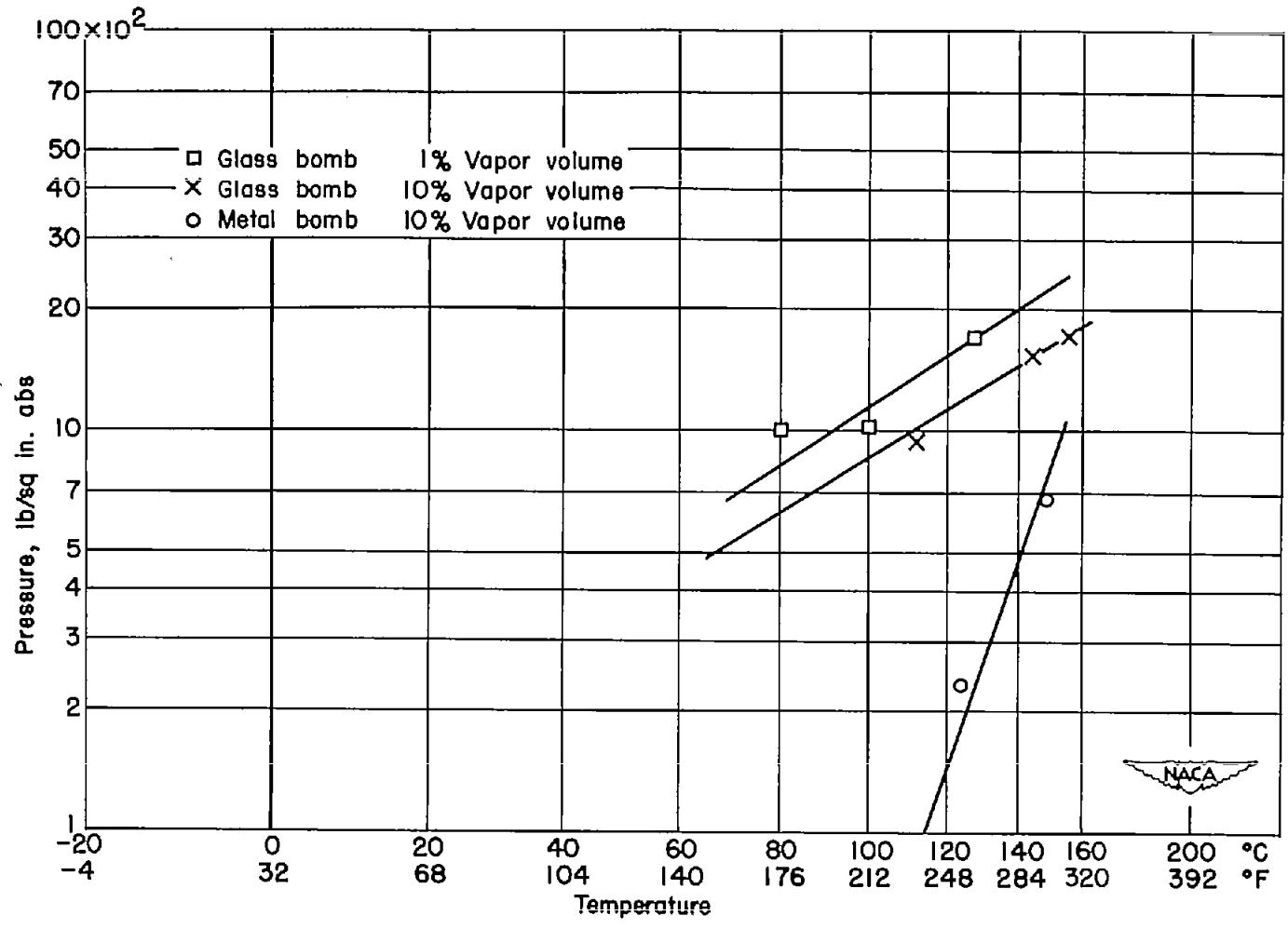
Figure 4.- Recommended values of density of nitric-acid solutions.





(a) Data from reference 21, page 304.

Figure 5.- Vapor pressure of concentrated nitric acid.



(b) Purdue data. Composition of acid (in percent by weight): HNO<sub>3</sub>, 97.35; NO<sub>2</sub>, 1.57.

Figure 5.- Concluded.

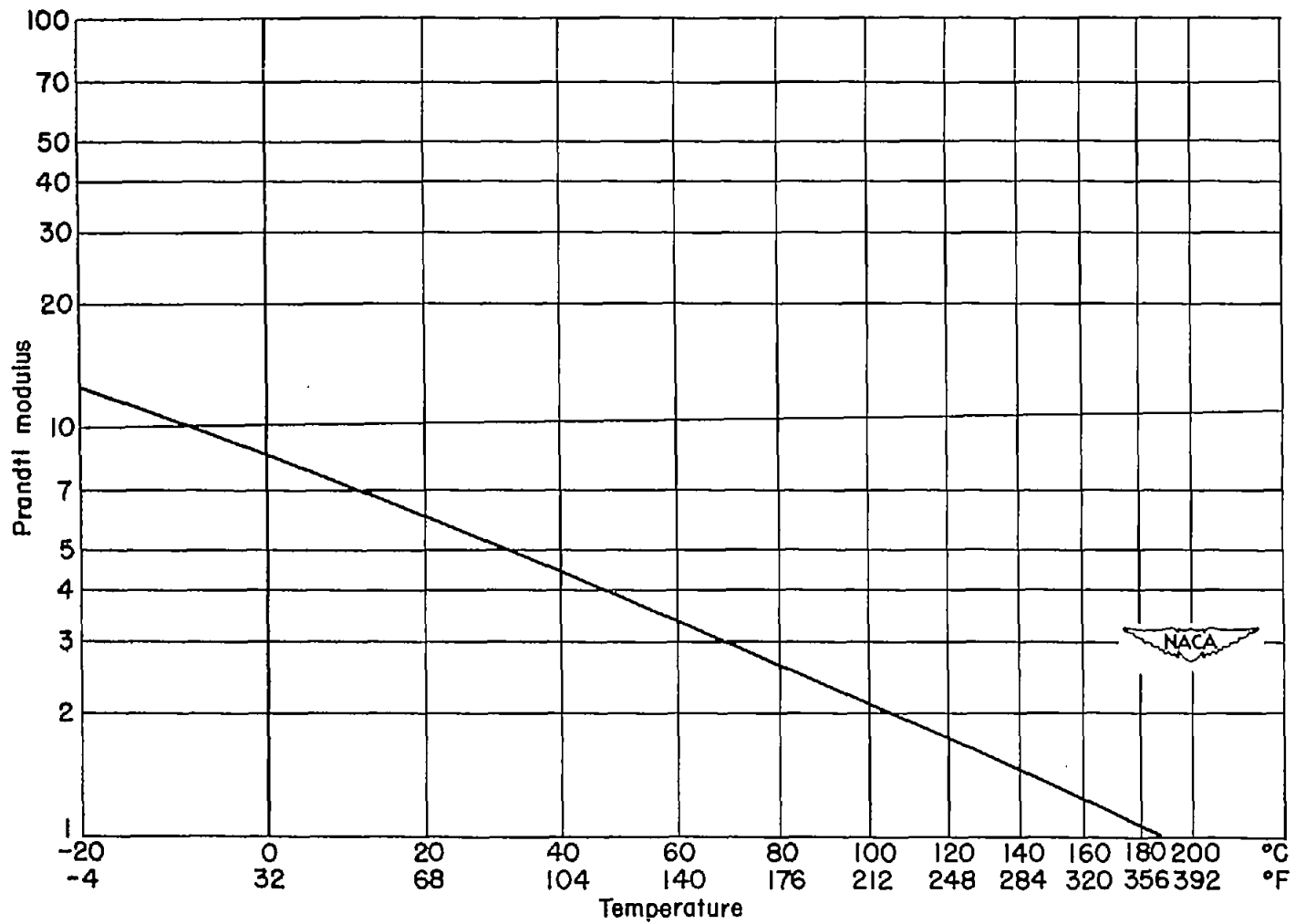


Figure 6.- Recommended values of Prandtl modulus of nitric acid. Composition of acid (in percent by weight):  $\text{HNO}_3$ , 97.35;  $\text{NO}_2$ , 1.57;  $\text{H}_2\text{O}$ , 1.08.

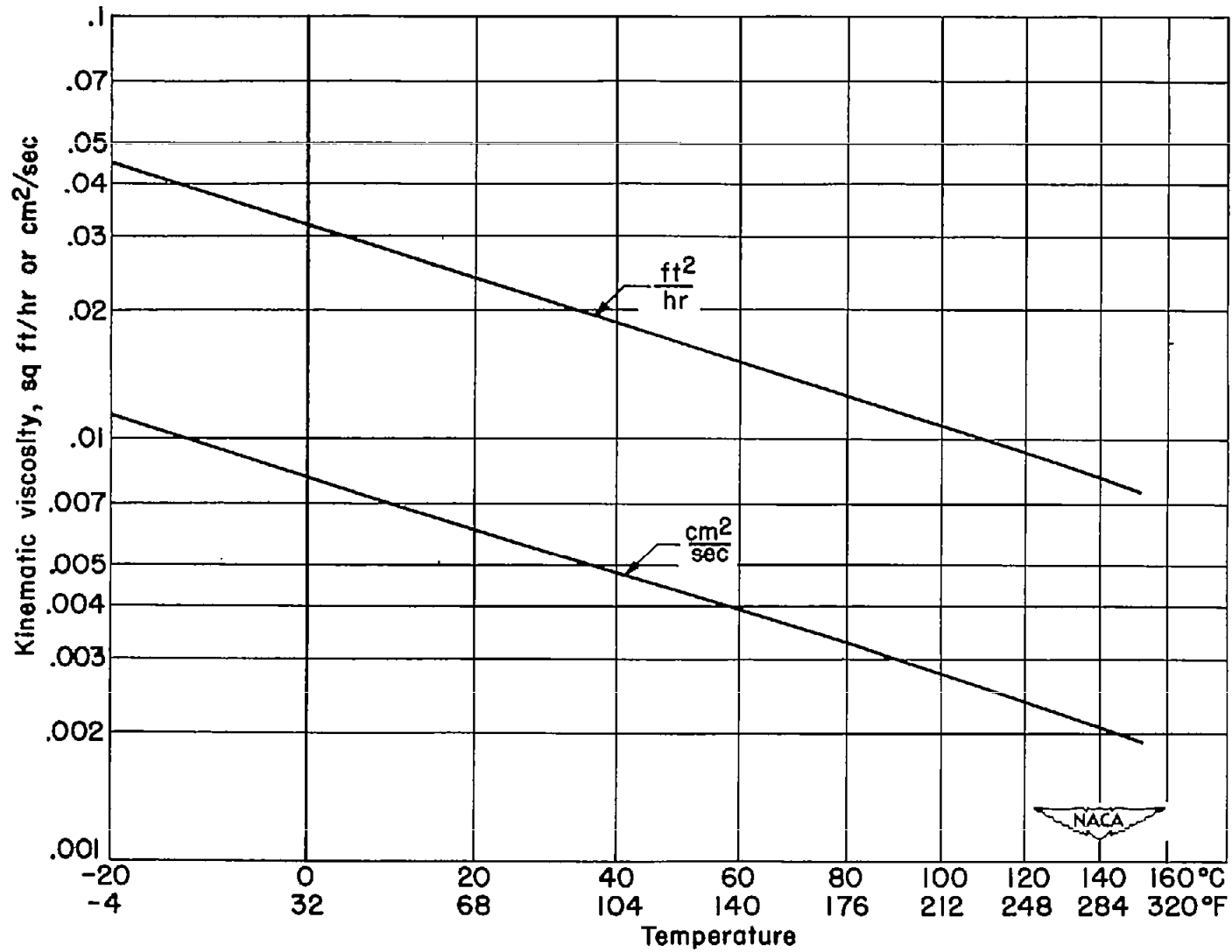


Figure 7.- Recommended values of kinematic viscosity of nitric acid.