

NASA Reference Publication 1013

Triple Point Determinations
of Monomethylhydrazine and
Nitrogen Tetroxide (2.2 Percent
by Weight Nitric Oxide)

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and Space Administration

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TRIPLE POINT DETERMINATIONS OF MONOMETHYLHYDRAZINE
AND NITROGEN TETROXIDE (2.2 PERCENT BY WEIGHT NITRIC OXIDE)

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SUMMARY

During the winter of 1975-76, a series of tests was performed at the NASA Lyndon B. Johnson Space Center White Sands Test Facility to ascertain the triple point of monomethylhydrazine and nitrogen tetroxide. The triple point of a material is the set of temperature and pressure conditions at which that material will exist simultaneously under equilibrium conditions in the liquid, vapor, and solid phases. Two methods were used to establish the triple point. The laboratory method using a closed system indicated the triple point of monomethylhydrazine is 219.5 K (-64.7° F) at 11.7 pascals (0.0017 psia). The laboratory method is the technique normally used to measure the triple point of fluids. In the second method, the fluid was exposed to a specific pressure in a very large chamber and allowed to cool by evaporation to the equilibrium temperature for the fluid at the pressure exerted. This method simulated a spacelike environment to more properly evaluate the behavior of monomethylhydrazine when exposed to the near vacuum of space. The results obtained using the second method indicate that a true triple point situation was not achieved because of an observed pronounced tendency of the monomethylhydrazine to supercool. Once solid-phase material is obtained in combination with liquid

material, the liquid material over a period of time converts to the solid phase. In recognition of these phenomena, the data obtained under spacelike conditions should more appropriately be called the effective freezing point rather than the triple point of the material. Using this technique, the effective freezing point under spacelike conditions of monomethylhydrazine (with agitation) was found to be 211.5 K (-79.0° F) at 3.72 pascals (0.00054 psia). Without agitation, supercooling was observed to temperatures as low as 207.6 K (-86.0° F).

As a result of the attempt to determine the triple point of monomethylhydrazine under spacelike conditions, new experimental values for the vapor pressure of the liquid phase were determined at temperatures between 275.2 K (35.60° F) and 207.6 K (-86.0° F). The new vapor pressure data were combined with existing literature data to permit the generation of equations for the vapor pressure of liquid monomethylhydrazine from the normal boiling point to below the normal freezing point and into the supercooled temperature range for the fluid.

A laboratory determination of the triple point of nitrogen tetroxide was not performed. Tentative values for the effective freezing point under spacelike conditions of nitrogen tetroxide containing 2.2 percent by weight nitric oxide were determined to be 259.4 K (7.2° F) at 15 444 pascals (2.24 psia).

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INTRODUCTION

Personnel at the NASA Lyndon B. Johnson Space Center (JSC) White Sands Test Facility (WSTF) performed a series of Shuttle orbital maneuvering engine cold-flow tests during the winter of 1975-76 to determine the amount of residual monomethylhydrazine (MMH) fuel remaining in the regeneratively cooled thrust chamber after various purge and vent sequences. These tests were performed at test chamber pressures of less than 6.89 pascals (0.001 psia) that were believed to be below the triple point pressure of MMH. Freezing of the MMH was not observed in any of the tests as would have been expected if the MMH had been subjected to pressures below the MMH triple point. An Atlantic Research Corporation report (ref. 1) indicated that the triple point of MMH was 13.79 pascals (0.002 psia) at 220.8 K (-62.3° F); however, the derived value was not based on experimental data. A thorough review of the chemical literature also indicated that the triple point of MMH had not been experimentally determined. Hence, WSTF personnel were requested to determine the triple point of MMH to assist the Propulsion and Power Division at JSC in the interpretation of the data observed in the orbital maneuvering engine purge and vent tests.

As an aid to the reader, where necessary the original units of measure have been converted to the exact equivalent value (without regard for the number of significant digits) in the Système International d'Unités (SI). The SI units are written first, and the original units are written parenthetically thereafter.

TEST OBJECTIVES

The primary objective of the tests described in this report was the determination of the observed triple point of MMH under laboratory conditions and under a spacelike environment. The secondary objective of the tests was the acquisition of MMH vapor pressure data at pressures below 1724 pascals

(0.25 psia). A third objective of the tests was the tentative determination of the triple point of nitrogen tetroxide (N₂O₄) containing 2.2 percent by weight nitric oxide (NO) under a spacelike environment.

TEST FLUIDS

The MMH and N₂O₄ used in the tests met the applicable¹ Space Shuttle requirements. The compositions of the propellents are provided in the table on the opposite page.

TEST DESCRIPTION

Laboratory System

The laboratory method used for the determination of the triple point of MMH was a modification of the system described by Colarusso and Semon (ref. 2). The principal modification consisted of the addition to the test cell of a means for measuring the pressure exerted by the fluid being tested. Figure 1 is a photograph of the test cell. The tube extending into the center of the cell contained the thermocouple (Chromel-Alumel). The fluid being tested was placed in the large-diameter tube surrounding the tube in the center of the cell. The side tube with the metal fitting was connected to the transducer used to measure the pressure exerted by the fluid vapors. The pressure was measured by a 0- to 6895 pascals (0- to 1-psia full scale) Datametrics multiple-range Barocell transducer. Adjustment of the transducer range permitted accurate measurement of pressures as low as 0.69 pascal (1 x 10⁻⁴ psia).

¹Specifications, Space Shuttle Fluid Procurement and Use Control. SE-S-0073, rev. B, Feb. 9, 1975. (These specifications have since been superseded by SE-S-0073, rev. C, Feb. 14, 1977.)

Composition parameter	Requirement	Actual
Monomethylhydrazine		
Monomethylhydrazine assay, percent by weight	98.0 (min.)	98.9
Water plus soluble impurities, percent by weight	2.0 (max.)	1.1
Nitrogen tetroxide		
Nitrogen tetroxide assay, percent by weight	97.0 (min.)	97.6
Nitric oxide assay, percent by weight	1.5 (min.) to 3.0 (max.)	2.2
N ₂ O ₄ plus NO, percent by weight	99.5 (min.)	99.8
Water equivalent, percent by weight20 (max.)	.06
Chloride content, percent by weight040 (max.)	<.04

A line at the top of the test cell connected a liquid nitrogen trap and vacuum pump to the system; the line could be isolated from the test cell at appropriate times in the test procedure by a glass vacuum stopcock.

The method used in the laboratory closely followed that described by Colarusso and Semon. The procedure consisted of the following sequence of actions after the MMH had been placed in the test cell.

1. Through use of a monochlorotrifluoromethane/dry ice bath surrounding the test cell, the MMH was frozen, and the space above the MMH was evacuated to remove dissolved gases.

2. The MMH was then allowed to melt.

3. The process of freezing and evacuation was repeated several times

(as many as six times) to thoroughly remove the gases dissolved in the fluid.

4. After the dissolved gases had been removed, the temperature and pressure in the cell were monitored as the temperature of the frozen material was slowly increased.

5. The triple point was noted by the presence of liquid around the center core of frozen fluid and by the change in the slope of the pressure curve as a portion of the frozen fluid transformed to the liquid state.

This method is very similar to that used by the National Bureau of Standards to determine the triple point of fluids, characteristically in a closed system that limits the amount of material that may become vapor. Reproducible results are obtained only when the dissolved gas content of the

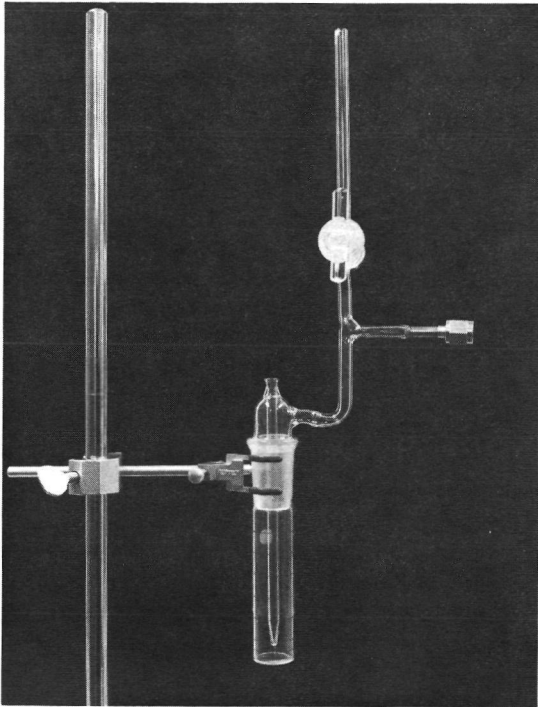


Figure 1.- Laboratory apparatus for measurement of triple point of fluids.

fluid has been removed or reduced to a minimum.

Test Stand System

A very large test stand (401) at the WSTF was used to acquire triple point data under spacelike conditions. This test stand has an internal volume of approximately 935 cubic meters (33 000 cubic feet), which may be maintained at a desired vacuum through the use of mechanical vacuum pumps. Figure 2 shows two identical test setups used to ascertain the triple point of MMH under spacelike conditions. Approximately 40 cubic centimeters of MMH were loaded into the 1.27-centimeter-diameter (0.5 inch) tubing assembly mounted above the 6.35-millimeter (0.25 inch) solenoid valves before closing of the test chamber. As shown in the photograph, a 5.08-centimeter-long (2 inch) section of 6.35-millimeter (0.25 inch) tubing extended below the valve into the

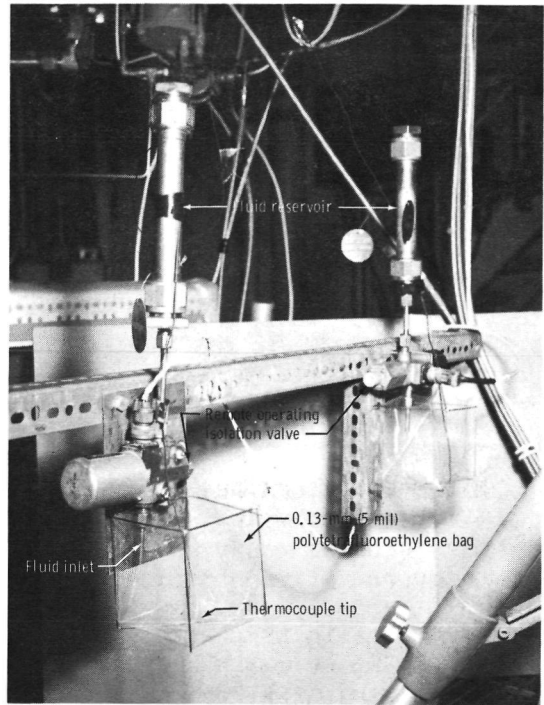


Figure 2.- Test stand apparatus for measurement of triple point fluids under spacelike conditions.

10.16-centimeter-square (4 inch), 10.16-centimeter-high (4 inch), 0.13-millimeter-thick (5 mil) polytetrafluoroethylene bag. The bag was supported by a wire frame to minimize the conduction of heat into the MMH contained in the bag. A bare-tip Chromel-Alumel thermocouple was mounted with the tip on the bottom of the bag. The pressure in the test stand was measured by a Barocell transducer identical to that used in the laboratory tests described in the preceding section.

For each test, the pressure in the test chamber was reduced to the desired value by the mechanical vacuum pumps, and then the MMH was introduced into the bag by opening the solenoid valve. The MMH in the bag was monitored (by television) for the presence of a solid phase while the temperature and pressure were continuously recorded. The triple point in these tests was defined as the set of temperature and pressure conditions

at which the MMH was present in the bag in both the liquid and solid phases.

A similar test setup was placed adjacent to a window in the test stand as shown in figure 3. This view of the setup taken from inside the test stand shows the placement of a solenoid-actuated "arm" covered with foam insulation; the arm was used to softly strike the bottom of the bag to provide some agitation to the MMH in the bag. This setup permitted visual observation of the MMH in the bag during several tests.

The test results obtained by this method provide data that more realistically relate to the behavior of the fluid in a vacuum of unlimited volume, because of the large ratio of test-stand volume to test-liquid volume. This spacelike condition requires that the fluid being tested cool itself (while in the open) by evaporation of

a portion of the fluid. These triple point test conditions more closely resemble those that might occur in space and differ significantly from the laboratory test conditions for the closely controlled measurement of the triple point.

MMH TRIPLE POINT TEST RESULTS

Laboratory Results

Before the MMH triple point test, the test system and procedure were performance-checked using reagent-grade carbon tetrachloride (CCl_4) as the test fluid. The literature values for the triple point of CCl_4 calculated from data cited by Moelwyn-Hughes (ref. 3) are 250.2 K (-9.4°F) at 1082 pascals (0.157 psia). Two laboratory tests yielded identical values of 250.2 K (-9.4°F) at 1069 pascals (0.155 psia). The nearly perfect agreement with the literature data confirmed that the test system and procedure were satisfactory for measuring the triple point of MMH.

The triple point pressure and temperature data obtained using the laboratory test system and procedure are provided in table I. The data, obtained on two samples of MMH, indicate that the average values for the laboratory (closed system) triple point are 219.4 K (-64.7°F) at 11.72 pascals (0.0017 psia). Some variation in the observed pressure may be due to leakage of air into the test system. In any event, the variation is not considered significant because of the limited accuracy in measuring the relatively low pressures involved.

The observed laboratory values for the triple point of MMH are reasonably close to the values of 13.79 pascals (0.002 psia) at 220.8 K (-62.3°F) indicated in the literature (but not experimentally determined) by Atlantic Research Corporation personnel.

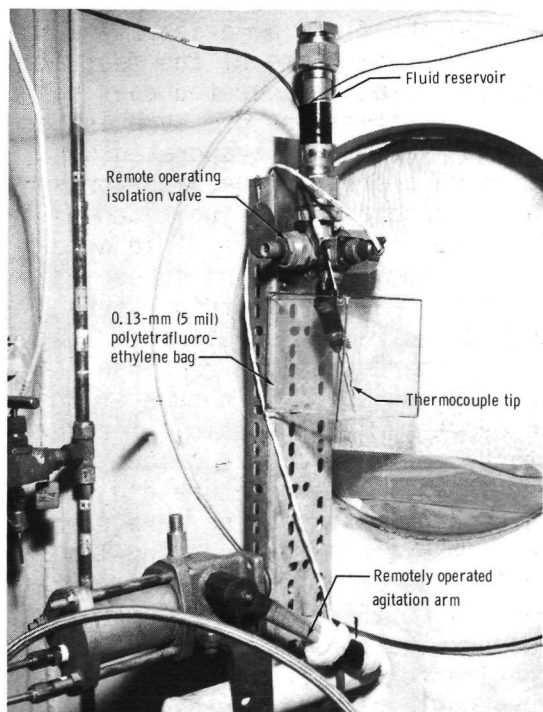


Figure 3.- Test stand apparatus equipped with remotely operated agitation arm.

TABLE I.- TRIPLE POINT OF MMH USING LABORATORY METHOD

Sample no.	Temperature, K (°F)	Pressure, Pa (psia)
1	219.7 (-64.3)	12.41 (0.0018)
1	219.2 (-65.2)	10.34 (.0015)
1	219.2 (-65.2)	9.65 (.0014)
1	219.2 (-65.2)	13.79 (.0020)
1	219.2 (-65.2)	15.17 (.0022)
1	219.2 (-65.2)	13.79 (.0020)
1	218.2 (-67.0)	8.96 (.0013)
1	219.7 (-64.3)	10.34 (.0015)
2	220.2 (-63.4)	10.34 (.0015)
2	220.2 (-63.4)	11.72 (.0017)
2	220.2 (-63.4)	9.65 (.0014)
Average	219.4 (-64.7)	11.47 (0.0017 ± 1.73 ± 0.0003)
σ	0.6 1.1	1.96 0.0003

Test Stand Results

The test system and procedure used in the test stand triple point tests conducted under spacelike conditions were also evaluated using CCl₄ as a reference material. Two tests yielded the following results.

Observed temperature, K (° F)	Observed pressure, Pa (psia)
248.8 (-11.9)	1048 (0.152)
248.4 (-12.6)	1000 (.145)

In both tests, the CCl₄ began to freeze less than 2 minutes after being released into the polytetrafluoroethylene bag.

It should be noted that, in this method, cooling of the fluid to the triple point is accomplished by removal

of heat from the fluid by evaporation into the very large volume of the test stand. The amount of fluid evaporated does not significantly affect the pressure in the test stand. The amount evaporated was sufficient to approach true vapor pressure equilibrium conditions as indicated by the constant temperature of the fluid after the initial vaporization and subsequent fluid cooling. The fluid temperature was observed to remain constant as long as the test stand pressure remained constant. Because of the nature of the cooling process, it is possible for the fluid to become supercooled below the triple point. The temperature and pressure values in the preceding paragraph are lower than the literature and laboratory test values of 250.2 K (-9.4° F) at 1082 pascals (0.157 psia). However, the differences were considered minor, leading the experimentors to believe that the procedure would effectively ascertain the triple point of MMH under spacelike conditions.

Before the MMH triple point tests were conducted using the test stand,

the literature value for the melting point of MMH was checked in the laboratory and found to be approximately 220.6 K (-62.6° F). Because the melting point of a material is near the triple point, this temperature datum was used to guide the triple point tests conducted under spacelike conditions through comparison of observed temperatures with the melting point.

Numerous attempts to observe the triple point of MMH were made. Most trials failed to produce solid MMH in combination with liquid MMH but did yield values of temperature and pressure, which are used in a later section of this report to construct a new curve for the vapor pressure of liquid-phase MMH. On the basis of these tests, it was concluded that liquid MMH will supercool rather than freeze when exposed to a pressure below the vapor pressure (12.4 pascals (0.0018 psia)) at the normal freezing point (220.7 K (-62.5° F)). In an attempt to counter this tendency to supercool, some tests were performed using the test setup (fig. 3) in which the liquid MMH in the bag could be agitated during the cooling process.

Using that test setup, frozen MMH was observed in combination with liquid material approximately 3 minutes after the MMH was released into the bag. During this period, the liquid MMH was agitated several times. When the frozen MMH appeared, the fluid temperature was 211.5 K (-79.0° F) and the pressure in the test stand was 3.72 pascals (0.00054 psia). The quantity of frozen MMH increased with test time, indicating a nonequilibrium condition; the frozen MMH was present in conjunction with liquid MMH for several minutes. After 10 minutes, all the MMH remaining in the bag had frozen, as shown in figure 4.

As previously noted, once solid-phase material had been obtained in combination with liquid-phase material, the liquid-phase material over a period of time converted to the solid phase. In recognition of this phenomenon, the data obtained under spacelike conditions

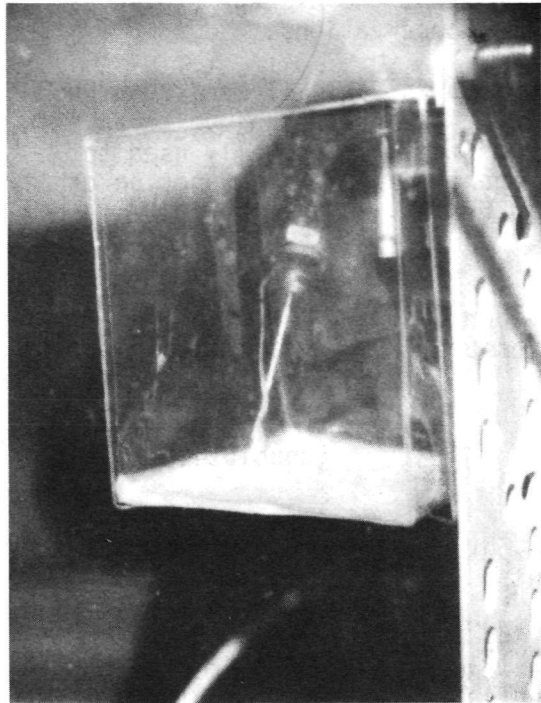


Figure 4.- Frozen MMH at conditions approaching the triple point.

should more appropriately be called the effective freezing point rather than the triple point of the material. Therefore, the test stand tests indicated that the effective freezing point of MMH under spacelike conditions was 211.5 K (-79.0° F) at 3.72 pascals (0.00054 psia).

MMH VAPOR PRESSURE TEST RESULTS

The numerous tests conducted in the attempt to find the triple point of MMH under spacelike conditions resulted in the derivation of data on the temperature of liquid-phase MMH at the test stand pressure under near-equilibrium conditions. These results, therefore, represent the vapor pressure data of the MMH under stable temperature conditions. The 15 vapor pressure data points given in the literature and the 31 points observed during the test stand triple point tests are listed in table II. It should be noted that the vapor pressure

values at several of the 31 temperature points represent the average of two or more actual observations.

The data in table II were smoothed by the least-squares technique to an equation of the form normally used to relate vapor pressure as a function of temperature.

$$\log \left(\frac{\text{vapor}}{\text{pressure}} \right) = a + \frac{b}{(\text{absolute temp.})} + \frac{c}{(\text{absolute temp.})^2}$$

where a, b, and c are derived coefficients.

During the least-squares process, the data were slightly weighted as indicated in table II at the high-temperature end to compensate for the large number of low-temperature points. All the data points were found to fit the following equations within less than 3σ variation.

$$\log (\text{Pa}) = 9.181\ 621 - \frac{1065.025\ 088}{K} - \frac{158\ 905.5445}{K^2}; \sigma = 170$$

$$\log (\text{psia}) = 5.476\ 093 - \frac{2058.727\ 760}{^{\circ}\text{R}} - \frac{477\ 730.2677}{^{\circ}\text{R}^2}; \sigma = 0.0779$$

The derived equations were used to provide the smooth calculated values of vapor pressure at each temperature listed in table II.

The existing literature values ranged from 360.1 K (188.52° F) - the normal MMH boiling point - to 275.2 K (35.60° F). The new data extend the vapor pressure data to 207.6 K

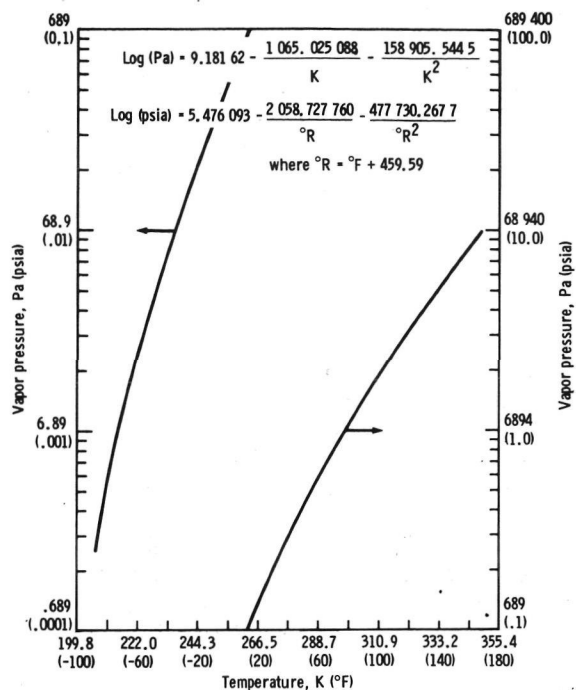


Figure 5.- Calculated vapor pressure of MMH. (The Système International units correspond closely but not exactly to this line because of variation in significant figures. The original measurements were taken in customary units.)

(-86.0° F), which is below the normal freezing point of 220.7 K (-62.5° F); therefore, these data include some vapor pressure data for supercooled MMH. The smoothed data listed in the tables are graphed in figure 5.

N₂O₄ TRIPLE POINT TEST RESULTS

The test setup described earlier was used to evaluate the behavior of N₂O₄ containing 2.2 percent by weight NO under spacelike conditions. For these tests, the small reservoir previously used for MMH was replaced with a 1-liter bottle containing N₂O₄. The test procedure was similar to that used for the MMH test, except the solenoid valve was opened for 2 seconds to deliver approximately 40 cubic centimeters of oxidizer from the N₂O₄ reservoir bottle under its own vapor

TABLE II.- VAPOR PRESSURE OF MMH

Observed temperature, ^a K (°F)	Observed vapor pressure, Pa (psia)	Calculated vapor pressure, ^b Pa (psia)	Deviation, observed vs. calculated, Pa (psia)	
Literature data ^c				
360.11 (188.52)	99 154 (14.381)	100 181 (14.530)	-1027	(-0.149)
354.67 (178.74)	81 551 (11.828)	82 599 (11.980)	-1048	(-.152)
351.07 (172.25)	71 423 (10.359)	72 388 (10.499)	-965	(-.140)
343.34 (158.35)	53 331 (7.735)	53 938 (7.823)	-607	(-.088)
337.81 (148.38)	42 582 (6.176)	43 244 (6.272)	-662	(-.096)
331.68 (137.36)	33 157 (4.809)	33 515 (4.861)	-359	(-.052)
325.77 (126.71)	25 959 (3.765)	25 910 (3.758)	48	(.007)
319.72 (115.82)	19 650 (2.850)	19 671 (2.853)	-21	(-.003)
313.07 (103.86)	14 052 (2.038)	14 320 (2.077)	-269	(-.039)
309.47 (97.38)	11 942 (1.732)	11 976 (1.737)	-34	(-.005)
298.36 (77.38)	6 666 (.9668)	6 665 (.9667)	.7	(.0001)
293.73 (69.04)	5 162 (.7487)	5 136 (.7449)	26	(.0038)
290.33 (62.92)	4 234 (.6141)	4 214 (.6112)	20	(.0029)
284.93 (53.21)	3 046 (.4418)	3 043 (.4413)	3.4	(.0005)
284.26 (52.00)	3 551 (.515)	2 916 (.423)	634	(.092)
Test stand data ^d				
282.04 (48.00)	3 489 (0.506)	2 537 (0.368)	951	(0.138)
275.15 (35.60)	1 615 (.2342)	1 618 (.2346)	-2.8	(-.0004)
274.26 (34.00)	1 717 (.249)	1 524 (.221)	193	(.028)
269.26 (25.00)	1 027 (.149)	1 076 (.156)	-48	(-.007)
267.59 (22.0)	1 014 (.147)	951 (.138)	62	(.009)
267.04 (21.00)	1 014 (.147)	917 (.133)	96	(.014)
263.71 (15.00)	682 (.0989)	717 (.1040)	-35	(-.0051)
263.15 (14.0)	696 (.101)	688 (.0998)	8.3	(.0012)
255.37 (.0)	352 (.0511)	374 (.0543)	-22	(-.0032)
254.82 (-1.0)	347 (.0504)	358 (.0519)	-10.3	(-.0015)
247.59 (-14.0)	177 (.0256)	194 (.0282)	-17.9	(-.0026)
246.48 (-16.0)	177 (.0256)	176 (.0255)	.7	(.0001)
245.93 (-17.0)	152 (.0221)	168 (.0243)	-15	(-.0022)
244.82 (-19.0)	134 (.0194)	152 (.0220)	-18	(-.0026)
243.15 (-22.0)	125 (.0182)	130 (.0189)	-4.8	(-.0007)
238.71 (-30.0)	84.8 (.0123)	85.5 (.0124)	-.69	(-.0001)
238.15 (-31.0)	81.4 (.0118)	81.4 (.0118)	.0	(.0000)
234.82 (-37.0)	60.0 (.0087)	58.6 (.0085)	1.38	(.0002)
234.26 (-38.0)	55.2 (.0080)	55.2 (.0080)	.0	(.0000)
230.37 (-45.0)	36.5 (.0053)	37.2 (.0054)	-.69	(-.0001)
229.26 (-47.0)	34.5 (.0050)	33.1 (.0048)	1.38	(.0002)
226.48 (-52.0)	27.6 (.0040)	24.1 (.0035)	3.4	(.0005)
225.37 (-54.0)	17.9 (.0026)	21.4 (.0031)	-3.4	(-.0005)
223.15 (-58.0)	13.8 (.0020)	16.5 (.0024)	-2.8	(-.0004)
221.48 (-61.0)	11.0 (.0016)	13.8 (.0020)	-2.8	(-.0004)
218.71 (-66.0)	11.0 (.0016)	10.3 (.0015)	.69	(.0001)
217.59 (-68.0)	7.58 (.0011)	8.96 (.0013)	-1.38	(-.0002)
214.82 (-73.0)	6.21 (.0009)	6.21 (.0009)	.0	(.0000)
210.93 (-80.0)	4.14 (.0006)	3.45 (.0005)	.69	(.0001)
208.71 (-84.0)	3.45 (.0005)	2.76 (.0004)	.69	(.0001)
207.59 (-86.0)	2.76 (.0004)	2.07 (.0003)	.69	(.0001)

^aTo compensate for the large number of low-temperature data points, the three high-temperature points were weighted in the least-squares process by the following factors.

360.11 K (188.52° F) - 5

354.67 K (178.74° F) - 4

351.07 K (172.25° F) - 3

Additional weighting of the data was restricted by the least-squares program.

$$b \log (\text{Pa}) = 9.181\ 621 - \frac{1.065.025\ 088}{K} - \frac{158\ 905.544\ 5}{K^2}; \sigma = 1700$$

$$(\log (\text{psia}) = 5.476\ 093 - \frac{2\ 058.727\ 760}{OR} - \frac{477\ 730.267\ 7}{(OR)^2}; \sigma = 0.0779.)$$

^cRef. 4.

^dRef. 5.

pressure (approximately 137 895 pascals (20 psia)). As discussed earlier, in this technique, the effective freezing point of the fluid under spacelike conditions is actually determined rather than the triple point. Accordingly, the effective freezing point of N_2O_4 containing 2 percent by weight NO was determined to be approximately 259.4 K (7.2° F) at 15 444 pascals (2.24 psia). Figures 6 and 7 show the N_2O_4 in the bag when the temperature was near the triple point. Figure 6 was taken approximately 15 seconds after the oxidizer was introduced into the bag. The dark (green) liquid-phase oxidizer can be seen on the bottom of the bag, and some light-colored (light blue-green) frozen oxidizer can be seen on the sides of the bag. Figure 7, taken

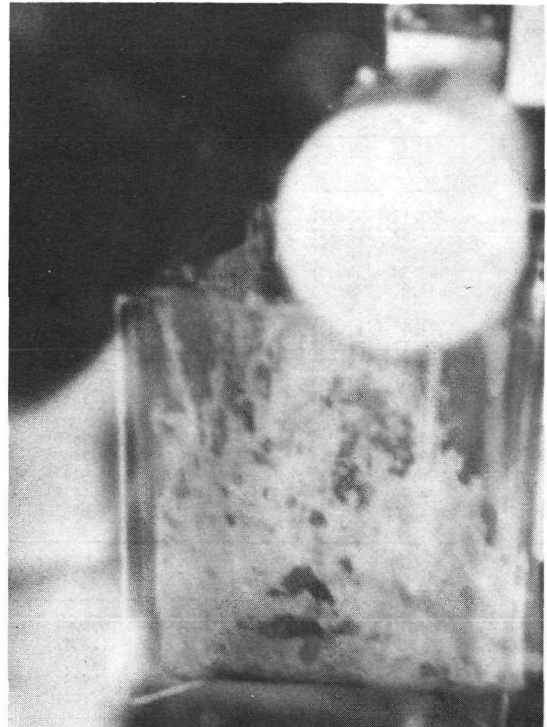


Figure 7.- Photograph taken a few seconds after that shown in figure 6, showing frozen N_2O_4 on sides of bag. Some dark liquid-state N_2O_4 is still present on bottom of bag.

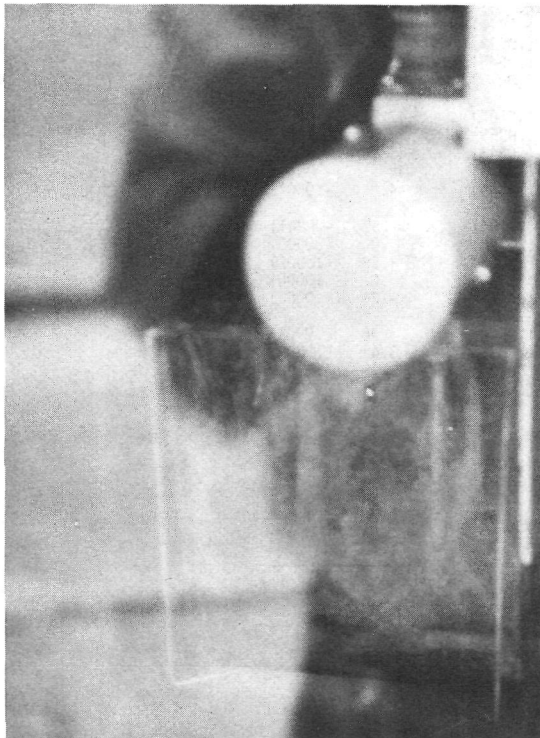


Figure 6.- Photograph showing some dark liquid-state N_2O_4 present in bottom of bag 15 seconds after introduction of the N_2O_4 .

shortly after figure 6, shows that the freezing process had progressed further, but some dark (green) liquid-phase oxidizer was still present on the bottom of the bag.

Because of limited test time, this experiment was not repeated at a slightly higher test stand pressure to verify the values reported in the preceding paragraph. In several tests conducted at lower pressures, the oxidizer froze immediately when released into the bag. The literature value for the triple point of pure N_2O_4 containing little or no NO was determined in 1938 by Giaque and Kemp (ref. 6) to be 261.9 K (11.73° F) at 18 637 pascals (2.703 psia).

CONCLUDING REMARKS

The tests conducted at the White Sands Test Facility indicate that the laboratory (closed system) value for the triple point of monomethylhydrazine (MMH) is 219.4 K (-64.7° F) at 11.74 pascals (0.0017 psia). These values were found to be reasonably close to the derived values reported in the literature. It was concluded that a true triple point determination could not be made under spacelike conditions, in which the fluid is permitted to self-cool by evaporation. It was observed in tests conducted under spacelike conditions that, once solid-phase material was obtained in combination with liquid-phase material, the liquid-phase material over a period of time converted to the solid phase. In recognition of this phenomenon, the data obtained under spacelike conditions should more appropriately be called the effective freezing point rather than the triple point.

Accordingly, the effective freezing point of MMH with agitation under spacelike conditions was experimentally determined to be approximately 211.5 K (-79° F) at 3.72 pascals (0.00054 psia). It should be noted (1) that the effective freezing point of MMH under spacelike conditions was very difficult to observe because of the tendency of MMH to supercool below the normal freezing point as a result of the evaporation of the liquid phase, and (2) that the effective freezing point may indeed be even lower than 207.6 K (-86.0° F) in the absence of agitation.

A side benefit of the various MMH triple point tests was the acquisition of new vapor pressure data at temperatures below 275.2 K (35.60° F). Literature data for vapor pressure of MMH did not exist below this temperature.

The new data were combined with the previously published data for the generation of equations yielding the vapor pressure of MMH in both International System and conventional units.

The temperature range of the data is from the normal boiling point to 207.6 K (-86.0° F). This temperature is below the normal freezing point of 220.7 K (-62.5° F); therefore, some of the data represent information obtained on supercooled MMH. All the data were found to fit the equation satisfactorily.

An approximate value for the effective freezing point of nitrogen tetroxide containing 2.2 percent by weight nitric oxide was also determined under spacelike conditions. The value was found to be approximately 259.4 K (7.2° F) at 15 444 pascals (2.24 psia). This value differs considerably from the triple point values of 261.9 K (11.73° F) at 18 637 pascals (2.703 psia) determined using the 1938 laboratory triple point technique on nitrogen tetroxide containing little or no nitric oxide.

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