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Supercooling of Hydrazine

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ABSTRACT

The supercooling of hydrazine in thin-walled capillaries and as droplets suspended in silicone oil has been investigated by observing the freezing points of samples held in the cold stage of a microscope. A wide range in capillary diameters was employed, but a smooth correlation between capillary size and degree of supercooling was not obtained due to heterogeneous nucleation at the glass surface.

Suspension of hydrazine droplets in silicone oil permitted the study of much smaller samples, while eliminating the nucleating effect of solid surfaces. Also, by this procedure, foreign nuclei present in the original sample were isolated in a certain few droplets, while the majority, having been freed of foreign nuclei, froze by homogeneous nucleation. Under these conditions, the maximum degree of supercooling of hydrazine was 120°C.

Using data from these experiments together with estimated values for the heat of fusion and for the free energy of activation for self-diffusion, the solid-liquid interfacial free energy for hydrazine was calculated from the theory of homogeneous nucleation to be 39.5 ergs/cm². Thus the supercooled state is a normal one that can be dealt with thermodynamically.

The high degree of supercooling of small droplets of hydrazine would not be feasible with bulk hydrazine. At present, it is felt that in order to keep hydrazine in the liquid state at low temperatures the depression of its freezing point by blending with other fuels would be the most reliable method.

PROBLEM STATUS

This is the final report on this phase of the problem; work is continuing on other phases.

AUTHORIZATION

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SUPERCOOLING OF HYDRAZINE

INTRODUCTION

During the past thirty years, there has been considerable interest in hydrazine not only because of its potential as a liquid rocket propellant but also because of its unusual chemical reactivity. However, limitations have been placed on the more widespread use of this compound as a rocket propellant because certain of its properties do not meet military requirements. For example, the freezing point of hydrazine, 2°C, is considered too high for most rocket fuel applications. To overcome this problem, investigations have been carried out at this Laboratory and elsewhere on the use of freezing point depressants with hydrazine (1,2). During the course of these studies, it was observed that hydrazine exhibits a tendency to undergo extensive supercooling, but no attempt was made at that time to pursue this point. So, the present investigation was initiated to investigate the phenomenon of supercooling and to determine the lowest temperature at which hydrazine can be preserved in the metastable liquid state before spontaneous crystallization occurs.

The phenomenon of supercooling can be explained by either of two theories, depending on the circumstances under which nucleation takes place (3-7). In the majority of cases, the sample is in contact with foreign particles which can initiate freezing as described by the theory of heterogeneous nucleation. Under these conditions, only limited supercooling is obtained. However, in some cases such particles are absent, and liquids can be supercooled to a much greater extent as revealed by the theory of homogeneous nucleation. According to this theory, since there are no particles present to attract and orient molecules of the liquid, nuclei must form as the result of chance collisions among molecules of the melt. As the temperature of the liquid is taken below its thermodynamic melting point, these nuclei continue to grow until finally they reach a critical size at which they can initiate freezing of the melt. Whether or not a supercooled liquid will freeze at a particular temperature depends on the probability that a nucleus of critical size can form at that temperature within the time of the experiment. The radius of a critical nucleus at a given temperature can be calculated from the following equation (8):

$$r = \frac{2\sigma T_0}{\rho_s \ell_f (T_0 - T)} \quad (1)$$

where

r = radius, cm

σ = solid-liquid interfacial free energy, ergs/cm²

T_0 = melting point, °K

ρ_s = density of the crystal, g/cm³

ℓ_f = heat of fusion, ergs/g

T = temperature of supercooled liquid, °K.

Where considerable supercooling is encountered, for example 40° for water, the following form should be used (6):

$$r = \frac{2\sigma}{\rho_s \lambda_f \ln T_0/T} \quad (2)$$

The rate of formation of critical nuclei in a homogeneous system can be obtained from the following expression derived by Turnbull and Fisher (9):

$$\log I = \log \frac{nkT}{h} - \frac{\Delta F_A}{2.3 kT} - \frac{\Delta F_c}{2.3 kT} \quad (3)$$

where

I = number of nuclei produced/sec/cm³

n = number of molecules/cm³

k = Boltzmann's constant

T = temperature of supercooled liquid, °K

h = Planck's constant

ΔF_A = free energy of activation for the short range diffusion of atoms or molecules moving a fraction of an atomic distance across an interface to join a new lattice

ΔF_c = free energy of formation of a nucleus of critical size.

The term ΔF_A is considered to be of the same magnitude as E , the activation energy for viscous flow (10), since the processes involved, i.e., the transfer of a molecule across the interface, is analogous to the movement of a molecule from one equilibrium position to another as described by the theory of viscosity. The activation energy appears in the viscosity equation as

$$\eta = A e^{E/kT} \quad (4)$$

The value of E and consequently ΔF_A may be obtained from viscosity data (11) or may be estimated from the heat of vaporization (12) since the following relationships exist:

$E \approx \Delta H_{vap}/3$ for molecules having symmetrical force fields

$E \approx \Delta H_{vap}/4$ for unsymmetrical molecules

$E \approx \Delta H_{vap}/3$ plus 1/3 of the energy of H-bonds that must be broken when the liquid flows.

Some workers (13-15) who have reported on the supercooling of molecular liquids have followed the lead of Turnbull (10) in assigning a negligible role to the term $-\Delta F_A/2.3kT$ in Eq. (3). However, Turnbull was concerned with the supercooling of metals where E (and consequently ΔF_A) is approximately equal to $\Delta H_{vap}/8$ to $\Delta H_{vap}/25$ (12). Thus, for metals, the contribution of this term to Eq. (3) would be small. On the other hand, McDonald (6) has shown that this term $-\Delta F_A/2.3kT$ is an important quantity in the case of water, and Barrer's (11) values for E indicate that it is significant for other molecular liquids as well.

The final term in Eq. (3), the free energy of formation of a nucleus of critical size, can be calculated from the following expression (4-6):

$$\Delta F_c = \frac{1}{3} S \sigma \quad (5)$$

where

S = surface area

σ = solid-liquid interfacial free energy.

Assuming spherical nuclei and using the expression in Eq. (2) for r ,

$$S = \frac{16\pi\sigma^2}{\rho_s^2 \ell_f^2 (\ln T_0/T)^2} \quad (6)$$

Therefore,

$$\begin{aligned} \frac{\Delta F_c}{2.3 kT} &= \frac{16\pi\sigma^3}{2.3 kT 3\rho_s^2 \ell_f^2 (\ln T_0/T)^2} \\ &= \frac{5.28 \times 10^{16} \sigma^3}{\rho_s^2 \ell_f^2 T \ln (T_0/T)^2} \end{aligned} \quad (7)$$

Thomas and Staveley (14) have used some of Turnbull's (10,16,17) data on the supercooling of liquid metals to solve for the first three terms in Eq. (3) and have arrived at the expression

$$\frac{\Delta F_c}{2.3 kT} = \frac{16\pi\sigma^3 T_0^2}{2.3 kT 3\rho_s^2 \ell_f^2 (\Delta T)^2} = 27 \quad (8)$$

where

$\Delta T = T_0 - T$, which is the extent of supercooling.

This equation provides a means for calculating the maximum degree of supercooling for a liquid, provided that σ , the solid-liquid interfacial free energy, is known. The latter term may be calculated by use of the following relationship (10,14):

$$\sigma = \frac{\sigma_g}{N^{1/3} v^{2/3}} \quad (9)$$

where

σ_g = gram atomic surface free energy $\approx L_f / 3$ (16)

L_f = molar heat of fusion

N = Avogadro's number

v = molar volume.

Since the values that Thomas and Staveley report for the maximum degree of supercooling for H_2O ($\Delta T_{max} = 40.5^\circ$) and for C_6H_6 ($\Delta T_{max} = 70.2^\circ$) correspond to the maximum values found in the literature for H_2O (4,5,18-21) and C_6H_6 (14,22), Eqs. (8) and (9) were

used to estimate ΔT_{max} for hydrazine. By solving Eq. (9) at the limits $\sigma_g/L_f = 0.30$ and 0.35 (which are the limits of the range found for several liquids (14)) and by substitution in Eq. (8), it was calculated that hydrazine should supercool to the extent 64 to 85° .

Since preliminary tests on large samples (up to a few cc) only yielded about 10 to 15° of supercooling for hydrazine, experiments were designed to determine whether the calculated degree of supercooling could be attained by another procedure. The following objectives were set forth for this study:

1. To develop a technique for determining the maximum degree of supercooling of hydrazine which would also take into consideration the hygroscopicity and reactivity of that compound.
2. To test this procedure on both water and benzene. If the maximum values for the supercooling of these compounds could be achieved by the adopted procedure, then the value obtained for hydrazine under the same conditions should correspond to ΔT_{max} for that compound.

EXPERIMENTAL PROCEDURE

The liquid samples used in this study were freshly distilled in an inert, particle-free atmosphere and their purity checked by observation of the melting point. Subsequent storage and handling of the samples took place in a dry box which was also under an inert, particle-free atmosphere.

In order to achieve maximum supercooling, it was necessary to employ very small samples and to insure that these samples were completely free of foreign particles which could serve as heterogeneous nuclei. Two methods of handling samples were selected in the present study in an effort to satisfy these conditions: samples held in very small capillaries, and droplets suspended in silicone oil.

Capillary Method

Thin-walled capillaries were prepared from 6-mm-O. D. soft glass or 7-mm-O. D. Pyrex tubing. The tubing was cut in 10-cm lengths, cleaned in chromic acid, and then rinsed thoroughly with hot water, with distilled water, and finally with triply distilled water. It was found that the final rinsing with triply distilled water had a profound influence on the degree of supercooling of hydrazine. Apparently the residue from ordinary distilled water was sufficient to initiate freezing at higher temperatures.

The cleaned tubes were dried at 240°C for 2 hours and then drawn to the required diameters by using a small flame. The elongated tube, which at this stage had the configuration of an exaggerated hour glass, was cut into two 1-foot lengths with a portion of the original tubing remaining attached to the capillary to serve as a funnel for filling the capillary.

The preparation of all samples was carried out in a dry box under an atmosphere of dry, particle-free nitrogen. Sulfuric acid was used inside the dry box as a desiccant and to absorb hydrazine vapors. The capillary tube was clamped into a vertical position by its wider end and the sample introduced by means of a hypodermic syringe. The appearance of a droplet at the capillary end of the tube indicated that the tube was filled and could safely be removed from the dry box. This method of filling the capillaries was preferred to filling by capillary action since the latter method would have necessitated handling of the capillaries inside the dry box with rubber gloves. The capillaries used in certain of these experiments had diameters as small as 0.025 mm and consequently were too delicate to withstand such treatment.

The capillary was removed from the dry box, cut into short (18-mm) lengths which were cemented to a 15-mm-sq microscope slide, care being taken not to allow the capillaries to touch one another. Since the diameters of these capillaries were so small, it was possible to observe the freezing points of as many as four samples in one experiment.

Suspension of Droplets in Silicone Oil

In order to observe the supercooling of smaller volumes of sample, droplets were suspended in silicone oil. A technique described by Pound et al. (21) was modified for these experiments. Pound passed a stream of particle-free nitrogen over warm (not boiling) distilled water and condensed droplets from the gas stream in silicone oil. In the present study, preliminary experiments were performed using emulsions prepared in this manner. Later it was found that equally good results could be obtained from emulsions prepared by mechanical dispersion. For this purpose, 1 ml of the sample was injected under the surface of 10 ml of silicone oil in a 25-ml Erlenmeyer flask which was then covered and the contents stirred magnetically. The entire sample preparation took place inside a dry box under an atmosphere of dry, particle-free nitrogen. A drop of the emulsion thus formed was placed on a 15-mm-sq microscope slide, and an aluminum washer was added to prevent the cover slip from coming in contact with the emulsion. The sample was then transferred to the cold stage for the freezing point determination.

Dow-Corning 710 Fluid (viscosity: 500 centistokes) was used to prepare the emulsions of triply distilled water and also in the initial experiments with hydrazine. However, it was found that 710 Fluid, which has a nominal freezing point of -22°C , crystallizes around -80°C . In order to make observations in the region below -80°C , Dow-Corning 510 Fluid was used to prepare the emulsions. Although this fluid has a reported freezing point of -74°C , crystallization was not observed even as low as -140°C . Therefore it was considered satisfactory for this study.

General

The slide holding the sample (either in capillaries or as an emulsion) was placed in a Thomas-McCrone cold stage, Fig. 1, which was used in conjunction with a Spencer binocular microscope. The cold stage was modified for these experiments by completely covering its base with a 1/4-inch Lucite plate to prevent the ambient air from coming into contact with the bottom cover glass of the cold stage. Without such protection, this cover glass acquired a coating of ice when the cold stage was operated at very low temperatures and when the relative humidity of the ambient air was high. Another modification of the cold stage was the substitution of an iron-constantan thermocouple for the thermometer which was supplied with the apparatus.

The temperature of the cold stage was lowered by passing a stream of nitrogen through a copper coil immersed in liquid nitrogen and then through the cold stage. The cooling gas entered the lower part of the cold stage, passed under the electrically conducting (E. C.) slide, passed over the sample, and exited around the objective lens of the microscope. The continuous passage of cold, dry nitrogen over the objective lens prevented fogging of this lens. The E. C. slide is coated with an electrically conducting film and may be heated as a further means of regulating the temperature. The rate of cooling was controlled by drawing lines on the recorder chart paper corresponding to the desired cooling rate, e.g., $1^{\circ}/\text{min}$, before the run and then by adjusting the flow of nitrogen during the run so that the chart pen followed the prescribed course. It was found that very close temperature patterns could be achieved in this way.

A set of Polaroid filters was installed in the microscope to facilitate detection of the freezing point. In many cases it was impossible to determine when samples in capillary tubes had frozen without the aid of polarized light.

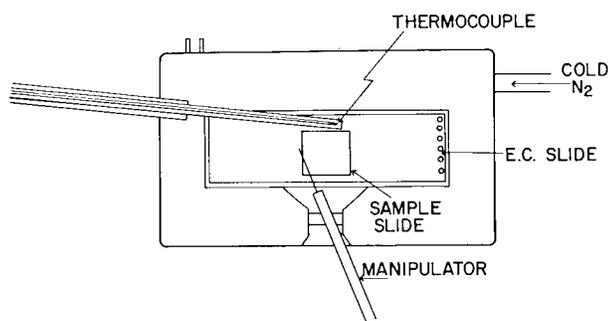


Fig. 1 - Top view of the cold stage with the top removed

When emulsions were observed under the microscope, approximately 10 to 20 droplets appeared in the field. In an ideal situation, only about 10 droplets were present and the freezing points were readily detected by the sudden appearance of cracks and by the distortion of the spherical profile of the droplet. These effects were more pronounced in polarized light.

After the freezing points had been determined, the temperature in the cold stage was raised at a rate of $1^\circ/\text{min}$ until the melting point was reached.

The thermocouple was calibrated in the cold stage by determining the melting points of benzene (5.5°C), water (0°C), carbon tetrachloride (-22.6°C), pyridine (-42°C), chloroform (-63.5°C), and ethyl alcohol (-114.5°C). These samples were cooled at a rate of $1^\circ/\text{min}$ until the temperature was about 10° below the freezing point. Then the sample was made to freeze by rapidly lowering the temperature. After the cold stage was allowed to equilibrate, the temperature was raised at a rate of $1^\circ/\text{min}$ to the melting point.

RESULTS AND DISCUSSION

Supercooling in Capillaries

The distribution in the freezing points of 115 hydrazine samples in capillaries is given in Fig. 2. These results show that while the majority of samples froze between -35° and -45°C , a small percentage did freeze in the range -62° to -75°C , which is within the limits calculated from Thomas and Staveley's equation. As a further check on the reliability of these results and to determine how effectively heterogeneous nuclei were removed from the capillary walls by the cleaning procedure, the freezing points of samples of water and of benzene were also determined by this procedure.

The results obtained from supercooling 106 samples of triply distilled water in capillaries are shown in Fig. 3. The majority of these samples froze above -30°C , while only two samples were found to freeze below -35°C , indicating that heterogeneous nuclei had not been eliminated. Since some of these samples had been filtered through $10\text{-m}\mu$ Millipore filters immediately before loading the capillaries, it appears that the nuclei involved are either very small or are located on the walls of the capillary, or both.

The distribution in the freezing points of benzene samples in capillaries is given in Fig. 4. Only 8% of these samples froze between -45° and -50°C , and at best these results are 15° short of the calculated maximum degree of supercooling. The lowest freezing points were obtained with samples that had been distilled in a particle-free atmosphere and filtered through a $10\text{-m}\mu$ filter, indicating that at least some heterogeneous nuclei were

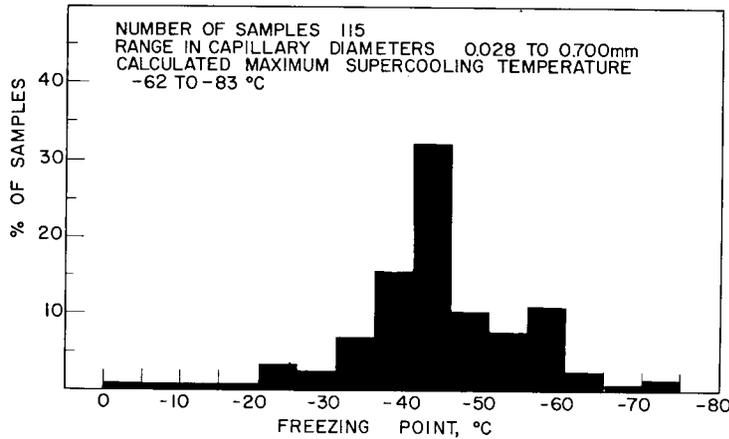


Fig. 2 - Distribution in the freezing points of hydrazine in capillaries

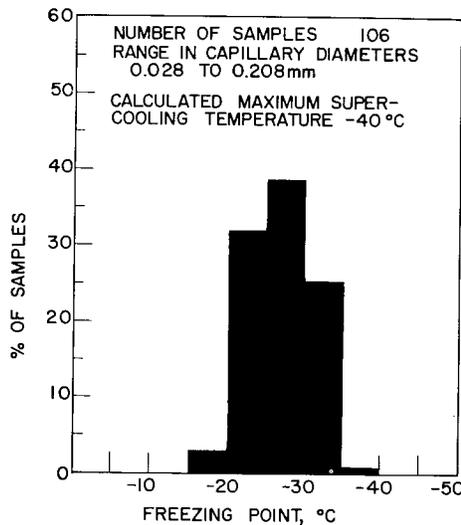


Fig. 3 - Distribution in the freezing points of water in capillaries

removed in this way. However, the walls of the capillaries remained a potential source of heterogeneous nucleation, and no further attempt was made to render them inactive.

Although the maximum values obtained for hydrazine by this procedure were within the estimated limits, the fact that maximum supercooling of water or of benzene was not achieved made the results for hydrazine suspect. Accordingly, the silicone oil suspension procedure was employed in an attempt to eliminate heterogeneous nucleation.

Supercooling of Droplets in Silicone Oil

The technique of supercooling droplets suspended in silicone oil has three advantages over the capillary method:

1. Smaller sample volumes can be observed.

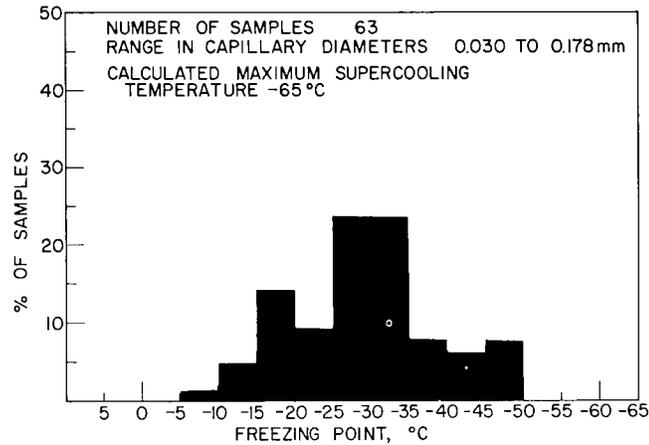


Fig. 4 - Distribution in the freezing points of benzene in capillaries

2. The sample is not in contact with solid supporting surfaces that can harbor heterogeneous nuclei.

3. If the original sample contains relatively few foreign particles, then by dividing this sample into a number of small noncommunicating droplets, the impurities become isolated in a certain few droplets, while the majority are freed of particles and become susceptible to freezing by homogeneous nucleation.

The data obtained from supercooling triply distilled water in silicone oil are given in Fig. 5. The fact that only 27% of the samples froze above -35°C indicates how effectively foreign nuclei were isolated in certain droplets, causing them to freeze at higher temperatures. The majority of droplets froze between -35°C and -40°C , while 7.4% froze below -40°C .

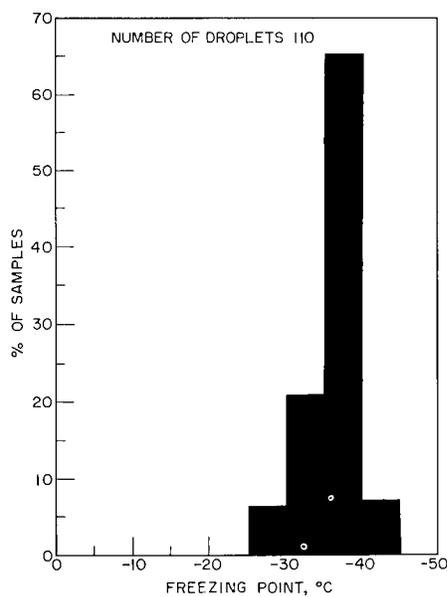


Fig. 5 - Distribution in the freezing points of water droplets in silicone oil

The data for droplets which froze below -35°C are presented again in Fig. 6, together with the data for those samples in capillaries that froze below -30°C . Also shown in this figure is the curve for homogeneous nucleation as calculated by Mason (5). If it is assumed that the data points lie sufficiently close to the curve so as to be representative of homogeneous nucleation, then it appears that 80% of the droplets in silicone oil froze by homogeneous nucleation and 26% of the samples in capillaries froze by this mechanism.

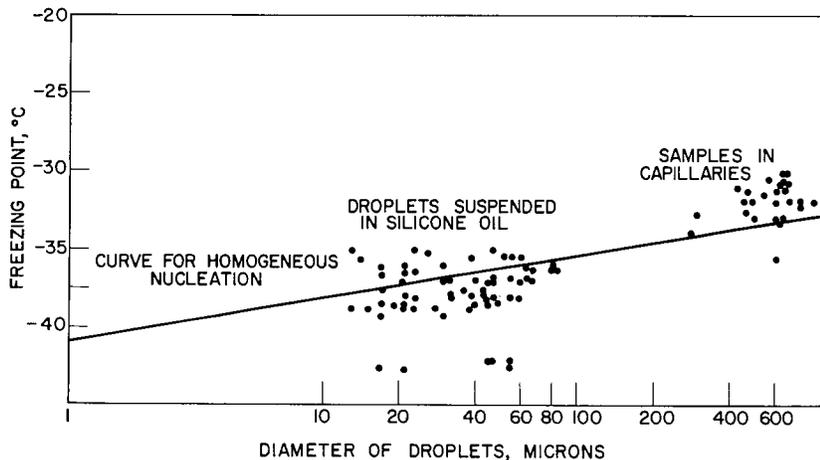


Fig. 6 - Freezing points of triply distilled water as a function of droplet size or capillary diameter

Another important conclusion can be drawn from the data in Fig. 6. If the degree of supercooling of water is truly volume-dependent as indicated by the curve for homogeneous nucleation, then in order to achieve ΔT_{max} of 40° in capillaries, it would be necessary to reduce the diameter of the capillary by a factor of 10 to 100. The smallest capillary used in the present study was 0.025 mm, and this was considered to be about the minimum size that could be handled conveniently by this procedure. A reduction in the diameter by a factor of 10 seemed impractical. Hence it appears that 35 to 36° of supercooling is the maximum value that can be obtained for water in capillaries by the procedure used in these studies.

Since the emulsion technique yielded the maximum degree of supercooling for water ($\Delta T_{\text{max}} = 40^{\circ}$), this procedure was attempted with other compounds of interest. Unfortunately, silicone oil is miscible in benzene, and so further studies with that compound were abandoned. However, the supercooling of hydrazine was amenable to study by this technique.

Preliminary experiments were performed on emulsions of hydrazine in Dow-Corning 710 Fluid. The data from these studies as given in Fig. 7(a) show that hydrazine can be supercooled considerably below -70°C , which was the lowest value obtained in the capillaries. Although some droplets did freeze above -50°C , data were not taken in this region since it was apparent that such samples froze by heterogeneous nucleation. A small percentage of the samples were found to freeze below -100°C , but further experiments could not be carried out in this region with the 710 Fluid due to crystallization of the oil. In some cases the oil crystallized as high as -80°C . However, the experiments in 710 Fluid were useful in that they established that hydrazine could be supercooled below -100°C .

In order to make more reliable determinations in the region below -80° , hydrazine droplets were suspended in Dow-Corning 510 Fluid. Although this oil has a nominal

freezing point of -74°C , it was never observed to crystallize at temperatures as low as -140°C and hence caused no interference with these experiments.

The data obtained from supercooling hydrazine droplets in 510 Fluid are shown in Fig. 7(b). For the initial experiments, this oil was filtered through a $0.49\text{-}\mu$ Millipore filter as was the 710 Fluid used in all the previous experiments. However, the 510 Fluid appeared to contain some active nuclei which were not removed by filtration as evidenced by the large number of samples which froze above -70°C . (The same sample of hydrazine was used in both cases.) Filtration of the 510 Fluid through a $0.10\text{-}\mu$ Millipore filter did not alter the results.

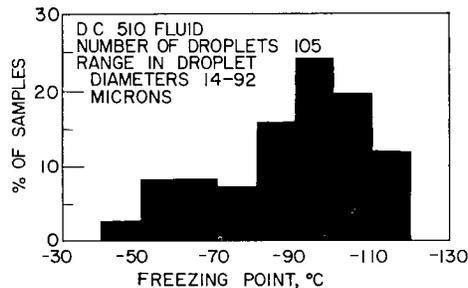
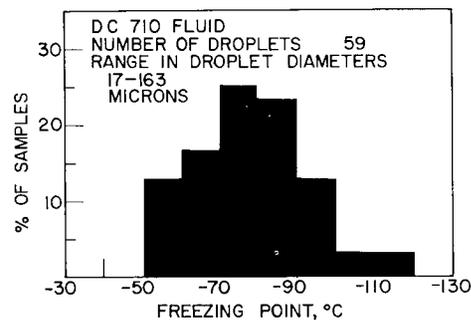


Fig. 7(a) - Distribution in the freezing points of hydrazine droplets in silicone oil (Dow-Corning 710 Fluid)

Fig. 7(b) - Distribution in the freezing points of hydrazine droplets in silicone oil (Dow-Corning 510 Fluid)

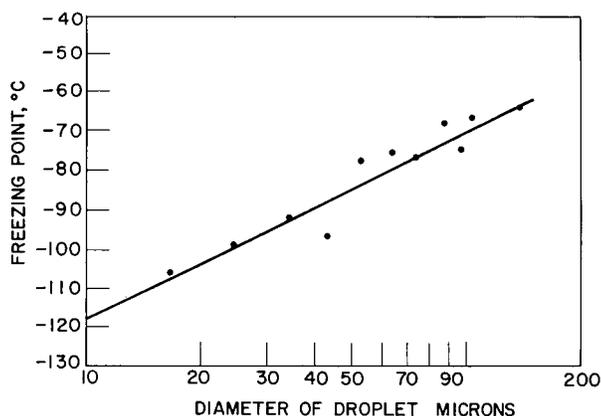


Despite the apparent shortcoming of this procedure, very significant information regarding the supercooling of hydrazine was obtained. As shown in Fig. 7(b), a number of hydrazine droplets could be preserved in the metastable liquid state below -100°C . The lowest freezing point obtained was -118°C , which corresponds to 120° of supercooling.

The data from Figs. 7(a) and 7(b) were arranged in order of increasing droplet diameter, and the freezing points of these droplets, averaged over $10\text{-}\mu$ intervals, are shown in Fig. 8. In a few cases, data were not included where the freezing points were considerably higher than the others in the group, since these samples obviously froze by heterogeneous nucleation. However, the total number of droplets excluded by this procedure was insignificant. The data in Fig. 8 indicate that $10\text{-}\mu$ droplets of hydrazine should freeze at -118°C , which is the lowest value obtained in these experiments. Since this amount of supercooling is considerably in excess of the 64 to 85° calculated from the expression of Thomas and Staveley, Eq. (8) was re-examined in the light of this new experimental evidence and several interesting points were uncovered.

At first glance, Eq. (8) appears to contain only two unknowns: σ , the solid-liquid interfacial free energy, and T , the freezing point, from which ΔT is calculated. When ΔT_{max} is

Fig. 8 - Freezing points of hydrazine droplets in silicone as a function of droplet size



determined from supercooling studies, σ may then be obtained from their equation. Alternately, σ may be calculated from the molar heat of fusion, by using Eq. (9) and the σ value thus obtained substituted in Eq. (8) to solve for ΔT . However, in order to obtain the σ value for water which Thomas and Staveley present ($\sigma = 30.8$ ergs/cm²), it is necessary to use a value of $\ell_f = 87$ cal/g. This value for the heat of fusion is considerably greater than the accepted value of 79.7 cal/g at 0°C. Actually, neither of these values can properly be used in Eq. (8), since the freezing of supercooled water takes place at -40°C and ℓ_f should have a lower, not higher, value at this temperature than at 0°C. McDonald (6) has shown that the heat of fusion of water decreases from 79.7 cal/g at 0°C to about 58 cal/g at -40°C. If the latter value were substituted into Eq. (8), the result would be that $\sigma = 23.5$ ergs/cm². Because this σ value, obtained by using the corrected value for ℓ_f is considerably less than Thomas and Staveley's value of 30.8 ergs/cm², doubt must be cast on the reliability of their value.

Since it was established that Eq. (8) did not predict the maximum degree of supercooling for hydrazine correctly nor provide a reliable estimate for σ , an attempt was made to derive a more pertinent expression for hydrazine from the equation for homogeneous nucleation, Eq. (3). A similar equation was also derived for water. In both derivations, it is assumed that the critical nuclei are spherical and that at the temperature of maximum supercooling, 10- μ droplets freeze in 1 sec. In the case of water, McDonald's values for ΔF_A (4.8×10^{-13} ergs) and ℓ_f (58 cal/g) were used. For the hydrazine equation, the following assumptions were also made:

1. $\Delta T_{\max} = 120^\circ$, based on the freezing points of hydrazine droplets in silicone oil.
2. $\Delta F_A = 5.7 \times 10^{-13}$ ergs/molecule, as estimated from viscosity data and by assuming that the value for ΔF_A changes with temperature at the same rate as that of water does.
3. ΔH_f at 155°K is 1820 cal/mol, as extrapolated from the equation expressing the dependence of ΔH_f on temperature (23).

Under these conditions the values for the different factors in Eq. (3) are as follows:

	<u>Log I</u>	<u>Log (nkT/h)</u>	<u>$\Delta F_A / 2.3 kT$</u>
H ₂ O	0	25.9	6.5*
N ₂ H ₄	0	25.5	11.8*

*Thomas and Staveley's values of E/RT for hydrogen bonded liquids fall between 4 and 15 at temperatures near the melting point, and E increases rapidly as the temperature is lowered because of increasing structure of the liquid.

Therefore:

	$\Delta F_c / 2.3 kT$
H ₂ O	19.4
N ₂ H ₄	13.7

By substituting the appropriate values into Eq. (7), the σ value for H₂O is calculated to be 22.3 ergs/cm². This value is higher than that of 17.2 ergs/cm² obtained by Mason (4). In making his calculations, Mason assumed that the critical nucleus was an isometric hexagonal prism instead of a sphere as in the above derivation. If Mason's equation is adapted to a spherical nucleus, a value of $\sigma = 20.1$ ergs/cm² is obtained. This value is in fair agreement with that of 22.3 ergs/cm² calculated above when one considers that the σ values for water at -40°C reported in the literature vary from 7.7 to 38 ergs/cm² depending on the method of calculation employed (6). McDonald (6) gives a "corrected" σ value for water at -40°C of 12 ergs/cm² which he admits is low since the degree of supercooling estimated from this figure is 26°. Unfortunately, there does not appear to be any independent experimental method of determining σ .

The value obtained for the solid-liquid interfacial free energy of hydrazine at 155°K using the above derivation is 39.2 ergs/cm². The accuracy of this value depends on the validity of the assumptions used in making the derivation and principally on the adopted values for ΔF_A and ℓ_f at 155°K. Since ΔF_A to the 1/3 power and ℓ_f to the 2/3 power are used in the final expression to solve for σ , small errors in the chosen values of these parameters will not affect the value of σ significantly.

SUMMARY AND CONCLUSION

The supercooling of hydrazine in thin-walled capillaries (O. D.: 0.028 to 0.282 mm) and also in the form of droplets (14 to 163 μ) has been studied. The samples were placed in a cold stage of a microscope and cooled at a controlled rate, with the freezing points being detected by the aid of polarized light. The purpose of this investigation was to determine the lowest temperature at which hydrazine can be maintained in the metastable liquid state before spontaneous crystallization occurs. Companion studies were also made on water and benzene in capillaries and also on water droplets in silicone oil in order to test the efficacy of the two methods, since the maximum degree of supercooling (ΔT_{max}) of both of these compounds has already been established.

In the present investigation it was found that hydrazine could be supercooled 70° in capillaries, while, under these same conditions, water was supercooled 35.5° ($\Delta T_{max} = 40^\circ$) and benzene 54.5° ($\Delta T_{max} = 70^\circ$). The inability to supercool either of these compounds to their respective maxima by this procedure was ascribed partly to the influence of heterogeneous nuclei and also to the dependence of the degree of supercooling on the volume of the sample. There is evidence that perhaps 26% of the water samples froze by homogeneous nucleation, but due to the volume limitations of the capillaries ΔT_{max} could not be achieved in this manner. The inference drawn from this experience was that the value obtained from supercooling hydrazine in capillaries (70°) did not necessarily correspond to ΔT_{max} for that compound even though it was within the estimated limits.

The supercooling of water droplets suspended in silicone oil yielded ΔT_{max} for that compound and established that this technique was suitable for studying hydrazine. It was found that hydrazine could be supercooled 120° by this procedure. With the assumption that 120° corresponds to ΔT_{max} for hydrazine, an expression was derived from the theory of homogeneous nucleation which permitted the calculation of a value of 39.5 ergs/cm² for σ , the solid-liquid interfacial free energy. Because of the necessity of making certain assumptions in solving for σ , this value must be regarded as tentative until confirmation is made by an independent method.

Thus, the supercooled state is a normal one and can be dealt with thermodynamically provided that the values for certain physical constants are known.

That hydrazine was found to supercool to a much greater extent than either water or benzene is due to its relatively high solid-liquid interfacial free energy. Consequently, a molecule of hydrazine does not move from a position in the supercooled liquid to the solid lattice with the ease that a molecule of water does.

The utilization of hydrazine in the supercooled state does not appear feasible in a system involving large amounts of the liquid. This is because (a) extremely high purity hydrazine would be required in conjunction with an ultraclean container and (b) the extent of supercooling of the pure liquid is very sensitive to droplet size and would not be appreciable for volumes greater than a few milliliters. The present work has shown that the freezing of supercooled hydrazine is triggered by foreign matter by the heterogeneous nucleation process, which is somewhat random. Therefore, exact figures of merit on the reliability of supercooling as a means of keeping bulk hydrazine in the liquid state at various temperatures below its freezing point and under various conditions of handling cannot be given. At present, however, it is felt that in order to keep hydrazine in the liquid state at low temperatures, the depression of its freezing point by blending with other fuels would be more reliable than supercooling.

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