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KINETICS OF SOLIDIFICATION OF SUPERCOOLED
LIQUID MERCURY DROPLETS

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The solidification rate of supercooled liquid mercury droplets is strongly dependent upon the nature of foreign substances on their surface or suspended in them. Droplets (2-8 microns diameter) coated with mercury laurate solidify at rates that are proportional to droplet volume and satisfactorily described by the theory of homogeneous nucleation of crystals. Droplets coated with mercury acetate solidify with frequencies that are proportional to droplet area and in good agreement with the theory of heterogeneous nucleation.

The results on Hg_2I_2 -coated droplets are interpreted on the hypothesis that nucleation is effected by suspended crystallites of one kind. For some droplet dispersions the kinetic results are apparently best described by a multiplicity of solidification frequencies/area or volume. Various hypotheses for this multiplicity are considered.

BECKER and Döring¹ have developed the theory for the rate of homogeneous nucleation² of liquid droplets in supersaturated one-component vapors. This theory predicts values of the supersaturation ratios required to nucleate liquid droplets rapidly in several one-component systems in excellent agreement with the measured values of Volmer and Flood,³ with the exception of that for methyl alcohol.

By following the basic assumptions of the Becker-Döring theory, Turnbull and Fisher⁴ have developed a theory for the rate of homogeneous nucleation in condensed systems according to which the frequency of formation, I , of crystal nuclei/volume of supercooled liquid is:

$$I = K_v \exp[-a\sigma^2/(\Delta F_v)^2 kT], \quad (1)$$

where

$$K_v = n^*(A/9\pi)^{1/3} n_s (kT/h) \exp[-\Delta F_A/kT], \quad (2)$$

σ = interfacial energy/area between crystal nuclei and the liquid,

ΔF_v = the free energy change/volume for the transition liquid $\rightarrow$ crystal,

n^* = number of atoms in the surface of a nucleus of critical size,

n = number of atoms/volume of liquid,⁵
 ΔF_A = free energy of activation/atom for transport across the liquid-crystal interface, and
 a = constant determined by the nucleus shape.
 A is defined by the equation

$$\Delta F/kT = Ai^3 + Bi, \quad (3)$$

where ΔF is the free energy of forming crystal embryos containing i atoms. For nuclei that are spherically shaped $a = 16\pi/3$ and

$$(A/9\pi)^{1/3} = (\sigma/kT)^{1/3} (2v/9\pi)^{1/3}, \quad (4)$$

where v = volume/atom of the crystal.

The free energy of forming crystal embryos and nuclei on the surface of nucleation catalysts can be described² in terms of i , σ , ΔF_v , and θ , the equilibrium contact angle between the crystal nucleus and catalyst when surrounded by supercooled liquid. By combining earlier concepts^{2,4} an approximate expression for the frequency of nucleation/area of catalyst, I_s , may be written as follows,

$$I_s = K_s \exp[-a\sigma^2 f(\theta)/(\Delta F_v)^2 kT], \quad (5)$$

where

$$K_s = n^*(A/9\pi)^{1/3} n_s (kT/h) \exp[-\Delta F_A/kT]. \quad (6)$$

¹ R. Becker and W. Döring, Ann. Physik [5] 24, 719 (1935).

² Nucleation that occurs without the catalytic aid of foreign bodies is designated "homogeneous." "Heterogeneous" nucleation is catalyzed by such bodies. D. Turnbull, J. Chem. Phys. 18, 198 (1950).

³ M. Volmer and H. Flood, Z. physik. Chem. 170A, 273 (1934).

⁴ D. Turnbull and J. C. Fisher, J. Chem. Phys. 17, 71 (1949).

⁵ In earlier publications, n was erroneously defined as the number of atoms/sample though the calculations were based upon a correct definition of n . The author is indebted to R. S. Bradley for calling his attention to the error made in the definition. A. D. Turnbull, J. Appl. Phys. 21, 1022 (1950). D. Turnbull, J. Chem. Phys. 18, 768 (1950).

n_s = number of liquid atoms in contact with catalyst/area. For nuclei having the form of spherical sectors,

$$f(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2/4 \\ (A/9\pi)^{1/2} = (\sigma/kT)^{1/2}(2v/9\pi)^{1/2}[(2 - \cos\theta + \cos^3\theta)/4]^{1/6}.$$

The factors that, according to Eqs. (1) and (5), determine I and I_s are at least approximately known excepting σ^6 and θ . Therefore, the validity of the nucleation theory can be tested by measuring the variation of I or I_s with temperature and comparing the values of $(K_v)_{\text{exp}}$ or $(K_s)_{\text{exp}}$ computed from these experimental results with the theoretical values predicted by Eqs. (1) or (5).

Crystal nucleation frequencies of large continuous masses of supercooled liquid are generally unsuitable for testing the predictions of nucleation theory because these masses almost inevitably contain nucleation catalysts of unknown composition and variable potency.^{2,7,8} Let the number of these accidental catalytic centers in a given mass of liquid be m_0 . It has been postulated^{2,8,9} that if the mass is broken into a number of isolated droplets $m \gg m_0$ crystal nuclei must form in the major portion of the droplets homogeneously or with the aid of a known crystalline film sometimes used to isolate the droplets. The evidence supporting this postulate has been fully summarized elsewhere.^{5,10} If a mass of liquid is dispersed to a number of droplets $m \approx m_0$, it may be found that the rate of nucleation in the majority of the droplets, though greater than the rate of homogeneous nucleation, is very much less than the rate of nucleation of the original mass. This result is explained if, following Levine,¹¹ the additional hypothesis is made that the concentration of accidental catalytic centers with a given catalytic potency, $p = 1/f(\theta)$, increases as p decreases. Levine has given a formal treatment of the problem that is analogous to the statistical theory of brittle fracture by stress raisers of variable potency developed by Weibull¹² and Fisher and Hollomon.¹³ Levine's theory successfully describes the experimental results of Dorsch and Hacker¹⁴ on the freezing of water droplets.

It appears that the most promising method of testing the predictions of the theory of crystal nucleation in

supercooled liquids is the measurement of the nucleation frequency in a collection of small droplets sufficiently dispersed to make $m \gg m_0$.^{2,9} Then crystal nucleation in droplets isolated by films that are not nucleation catalysts should be homogeneous and describable by Eq. (1). In droplets coated with crystalline films that catalyze nucleation, the nucleation frequency should be proportional to the surface area of the films and describable by Eq. (5).

It has been demonstrated^{2,15} that the rate determining step in the solidification of very small metal droplets is nucleation. Thus the nucleation frequency in small droplet dispersions can be computed from direct measurement of the solidification rate on the basis that the period of crystal growth is negligible in comparison with the nucleation period.

Consider the kinetics of isothermal solidification of a dispersion of droplets having a wide distribution of diameters. We make the following definitions: D = diameter of the droplet, v_D = volume of droplets of diameter D , a_D = surface area of droplets of diameter D , and V_D = total volume of all droplets of diameter D that remain liquid at time, t . A function $y(t)$ is defined by the equation

$$y(t) = \sum_{D=0}^{D=D} V_D / \sum_{D=0}^{D=\infty} V_D = (1/V) \int_0^D V_D dD. \quad (7)$$

At $t=0$

$$y(t) = y^0 = (1/V^0) \int_0^D V_D^0 dD. \quad (8)$$

Also from (7) and (8) $dy(t)/dD = V_D/V$ and $dy^0/dD = V_D^0/V^0$. Let the nucleation frequency per droplet = k_D ; it follows from the assumptions that the volume rate of solidification of droplets of diameter D conforms to the radioactive decay law and is given by,²

$$-dV_D/dt = k_D V_D. \quad (9)$$

The total volume rate of solidification is,

$$-dV/dt = \sum_{D=0}^{D=\infty} k_D V_D = \int_0^\infty k_D V_D dD. \quad (10)$$

Integration of (9) and (10) gives

$$V_D = V_D^0 \exp[-k_D t], \quad (11)$$

$$V = \sum_{D=0}^{D=\infty} V_D^0 \exp[-k_D t] \\ = \int_0^\infty V_D^0 [\exp(-k_D t)] dD. \quad (12)$$

For homogeneous nucleation

$$k_D = I v_D, \quad (13)$$

¹⁵ D. Turnbull and R. E. Cech, J. Appl. Phys. 21, 804 (1950).

⁶ There is a good possibility (particularly in view of the quantitative success of the Becker-Döring theory applied to the nucleation of droplets) that σ may be approximately equal to the appropriate liquid-crystal interfacial tension σ' measured in macroscopic systems. As yet σ' has not been measured with sufficient accuracy to test this possibility.

⁷ M. Avrami (Now Melvin) J. Chem. Phys. 7, 1103 (1939).

⁸ D. Turnbull, J. Appl. Phys. 20, 817 (1949).

⁹ D. Turnbull, Trans. Am. Inst. Mining Met. Engrs. 188, 1144 (1950).

¹⁰ D. Turnbull, *Thermodynamics in Physical Metallurgy* (Am. Soc. Metals, Cleveland, Ohio, 1950), pp. 282-306.

¹¹ J. Levine, Nat. Advisory Comm. Aeronaut. Repts., Tech. Mem. Notes 2234 (1950).

¹² W. Weibull, Roy. Swed. Inst. Eng. Research No. 151, (1939).

¹³ J. C. Fisher and J. H. Hollomon, Metals Technol. 14, No. 5 (1947).

¹⁴ R. G. Dorsch and P. T. Hacker, Nat. Advisory Comm. Aeronaut. Repts. Tech. Mem. Notes 2142 (1950).

TABLE I. Summary of methods used to prepare dispersions of mercury droplets.

Coating on droplets	Designation ^a	Method of dispersion	Fluid	Composition of dispersing mixture Oxidizing agent	Acid	Droplet diameter range (microns)	Dilatometer fluid
Mercury sulfide (black)	Hg(S)	Manual shaking	CS ₂ (30 cc)	Sulfur 0.05 g	...	50-200	Ethyl alcohol (EtOH)
Sodium oleate (adsorbed)	Na Oleate	Manual shaking	EtOH saturated with Na Oleate	...	...	100-400	EtOH
Mercury iodide (yellow)	Hg ₂ I ₂ ^b	Manual shaking	EtOH (30 cc)	0.3 g iodine	...	15-70	EtOH
Mercury acetate	Hg(Ac)	Waring blender	Silicone oil (150 cc)	0.2 g acetyl peroxide	...	4-12	Methyl cyclopentane
Mercury stearate	Hg(St)	Waring blender	Mineral white oil (150 cc)	Air	0.5 g stearic acid	2-7	Methyl cyclopentane
Mercury laurate	Hg(Lau)	Waring blender	Silicone oil (150 cc)	0.5 g lauroyl peroxide	0.1 g lauric acid	2-8	Methyl cyclopentane
Mercury benzoate	Hg(Bz)	Waring blender	Silicone oil (150 cc)	0.7 g benzoyl peroxide	0.3 g stearic acid	2-8	Methyl cyclopentane

^a These designations are not intended to indicate the precise chemical formula of the film but only the method of its formation. The author did not find the data necessary for calculating whether the Hg₂⁺⁺ or Hg⁺⁺ salts are thermodynamically more stable under the experimental conditions. Also, it is possible that some of the carboxylates are oxy salts.

^b According to thermodynamic calculations, Hg₂I₂ is the more stable phase (relative to HgI₂) in equilibrium with mercury under the experimental conditions.

and Eq. (12) may be rewritten

$$V = \sum_{D=0}^{D=\infty} V_D^0 \exp(-Iv_D t) = \int_0^{\infty} V_D^0 [\exp(-Iv_D t)] dD. \quad (14)$$

In case nucleation is catalyzed by the film on the droplet surface,

$$k_D = I_s a_D \quad (15)$$

and Eq. (12) becomes

$$V = \sum_{D=0}^{D=\infty} V_D^0 \exp(-I_s a_D t) = \int_0^{\infty} V_D^0 [\exp(-I_s a_D t)] dD. \quad (16)$$

Experimentally, we obtain $y^0 = f(D)$ and $V = f(t)$ at various constant temperatures. By using the relation $y^0 = f(D)$, Eqs. (14) and (16) may be compared with the experimental relation $V = f(t)$ by a numerical or analytical procedure. From this comparison it may be decided whether the data are fit best by assuming the nucleation frequency proportional to the volume of the droplet [Eq. (14)] or to its surface area [Eq. (16)].

It follows that $\partial^2 X / \partial t \partial T|_{x=x_1}$, where $X = (V_0 - V) / V_0$, is proportional to dI/dT or dI_s/dT for a given dispersion. Therefore $d \ln I / dT$ or $d \ln I_s / dT$ can be evaluated from $V = f(t)$ for a given dispersion at various constant temperatures even though $y^0 = f(D)$ is not known.^{5b}

Vonnegut¹⁶ has measured the isothermal rate of solidification of tin droplets (1-10 micron diameter)

¹⁶ B. Vonnegut, J. Colloid Sci. 3, 563 (1948).

isolated from each other by an oxide film as a function of temperature. Analysis of his data^{5b} indicated that the magnitude of $\partial^2 X / \partial t \partial T|_{x=x_1}$ is in approximate agreement with the prediction of Eq. (14). However, $y^0 = f(D)$ was not determined. Later measurements of Pound and LaMer¹⁷ of $V = f(t)$, in conjunction with measurements of $y^0 = f(D)$, on oxide-coated tin droplets showed that $(\partial X / \partial t)_T$ decreased much too rapidly with time to be compatible with a single value of I or I_s .

We have measured $V = f(t)$ at various temperatures for dispersions of mercury droplets coated with various surface films. Preliminary reports of some of the results have been published elsewhere.^{5b, 18, 19} The purpose of this paper is to describe and analyze these and additional results more completely.

EXPERIMENTAL

A. Materials and Preparation of Dispersions

Purified triple-distilled mercury was used in all the preparations to be described. In forming one group of dispersions 2 cc of mercury and the forming solution were shaken up in a test tube. To form the second group, 5 cc of mercury and the forming solution were agitated in a Waring Blender for net times of three to eight minutes. The agitation was interrupted at intervals in order to prevent excessive heating of the blender contents.

The method of forming the dispersions, the composition of the forming solutions, and the range of droplet diameters contributing significantly to the volume of the dispersed mercury are indicated in Table I. All of

¹⁷ G. M. Pound and V. K. LaMer, J. Am. Chem. Soc. (to be published).

¹⁸ D. Turnbull, Science 112, 448 (1950).

¹⁹ D. Turnbull, Phys. Rev. 83, 880 (1951).

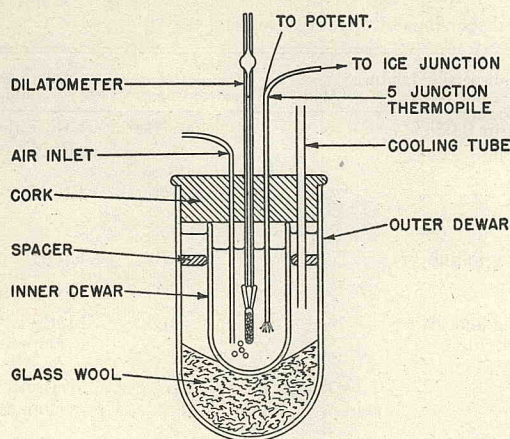


FIG. 1. Schematic drawing of bath for maintaining constant temperature.

the organic compounds used in the preparations were Eastman cp chemicals, excepting that purified lauroyl peroxide²⁰ was furnished by W. E. Cass and acetyl peroxide was obtained in the form of 25 percent dimethyl phthallate solution from Buffalo Electrochemical Company. The iodine and sulfur used were reagent grade materials.

It is believed that the film on the droplet surface consisted of a mercury compound in all cases excepting for the dispersion formed in the alcoholic sodium oleate solution. When the air pressure in the blender containing the stearic acid solution was reduced to about 0.001 atmosphere, the mercury did not break up into droplets. Therefore, it is believed that the Hg(St) film formed as a result of reaction of the stearic acid with an oxide film formed by the interaction of air and mercury. The chemical film formed in peroxide solution is believed to result from the acid catalyzed direct addition of mercury to peroxide.

In all cases the amount of the film forming agent used was less than that required to form by complete reaction an Hg_2^{++} salt constituting a volume fraction of 0.02 of the dispersed mercury.

Measurements of the droplet size distribution [$y^0 = f(D)$] in the dispersions where time, temperature, and medium of dispersion were varied to the extent used in the experiments established that $y^0 = f(D)$ was not measurably affected by these variations, with the possible exception of Hg(S) dispersions (on which such observations were not made) and the Na Oleate dispersions. However, Hg_2I_2 dispersions did coarsen with time when one-half the indicated amount of iodine was used in forming them.

B. Temperature Measurement and Control

The extent of solidification of mercury was measured dilatometrically. In these measurements two schemes were used on occasion to maintain the temperature con-

stant. The first of these schemes was used in the experiments on Hg(St) and Hg_2I_2 coated aggregates. The constant temperature chamber consisted of a well-insulated can containing freon 11 entirely surrounded, excepting for outlets, by a bath of the same fluid. Further details on the construction of this bath have been published.⁹ To maintain the temperature of the outer bath constant to within $\pm 0.2^\circ\text{C}$ the potential developed by a five junction thermopile, having one set of junctions in the outer bath and the other set in a Dewar flask containing a constant temperature mixture, was used to activate a General Electric Recording potentiometer. The recorder was part of a relay circuit so that as the bath reached the control temperature, the recorder needle closed a relay circuit thus causing the bath heater circuit to open. Liquid nitrogen was circulated in cooling coils in the outer bath. This method of temperature control requires a compound in the Dewar flask at a phase transition temperature within 5 to 10° of the bath temperature to be maintained. With the indicated degree of control of the outer bath, the inner bath temperature remained constant to within $\pm 0.01^\circ\text{C}$. The inner bath was agitated by bubbling air through it and its temperature was checked every three to five minutes.

In the other isothermal experiments, a much simpler and equally effective method was used to control temperature. In this method the outer bath was a 4-liter Dewar filled to a level well above the fluid level in the inner bath with a partly melted compound at a temperature 20 to 30° lower than the temperature to be maintained in the inner bath. The container for the inner bath was a 1-liter unsilvered Dewar flask maintained in position by glass wool support and Teflon spacers so that its top was 2 in. to 3 in. below the top of the outer Dewar. The space between the top of the outer and inner Dewars was filled with a cork insulator. Figure 1 shows the arrangement schematically. Heat leaked slowly from the inner to the outer bath. To compensate for this loss, air originally at the ambient temperature was passed through the inner bath. This rate of air flow was regulated by a flowmeter and valve arrangement sufficiently sensitive so that a given pressure differential could be maintained to within a millimeter of water. After the system reached thermal equilibrium with a given rate of air flow, the temperature in the inner bath was held constant to within 0.01°C by small manual adjustments of the rate at intervals ranging from three to fifteen minutes. To determine when these adjustments would be necessary, the temperature of the inner bath was measured every two to five minutes. In the isothermal measurements on Hg(Lau) coated droplets (-117 to -120°) freon 12 was used in the inner bath and an equilibrium mixture of liquid and solid freon 12 in the outer bath.

The temperature was calculated from the potential developed by a five junction copper-constantan thermopile. This potential was measured on a Type K poten-

²⁰ The source and purity is described elsewhere. W. E. Cass, J. Am. Chem. Soc. 72, 4915 (1950).

tiometer. One set of thermocouple junctions was placed in the bath a small distance from the middle of the dilatometer bulb. The other set was immersed in a Dewar containing an equilibrium mixture of distilled water and ice made from distilled water. After each set of measurements, the thermocouple calibration was checked against the melting temperature of pure mercury. In all cases, this calibration agreed with the standard calibration charts for copper-constantan thermocouples to within 0.05°C .

C. Dilatometry

A general description of the dilatometer has been published.⁹ The dilatometer bulbs were about 6- to 7-cm long and ~ 0.5 -cm internal diameter. Five to seven g of mercury (*ca* $\frac{1}{2}$ cc) droplets from a given dispersion were introduced into the dilatometer bulb and the dispersing medium changed to the fluid indicated in Table I by several decantations and additions. The capillary bores of the various dilatometers were from 0.055- to 0.065-cm diameter. The drop in fluid level in the dilatometer capillaries caused by the complete isothermal solidification of mercury ranged from 4.5 to 6.5 cm. The fluid level in the capillary was measured, relative to a fixed point on the outer surface of the capillary, to within 0.02 cm by means of a cathetometer.

Preliminary experiments were made on each of the dispersions to determine the temperature range in which solidification occurs at a reasonable rate. The experimental procedure used in these "continuous" cooling experiments has been described.⁹ Figure 2 shows the dilatometer readings obtained from a cooling-heating cycle on Hg(St)-coated droplets. A linear section of the cooling curve *AB* was established corresponding to the thermal contraction curve for the dilatometer fluid and the liquid mercury. It was confirmed that the curve *B*→*A* was identical to *A*→*B* and it was therefore concluded that no appreciable solidification had taken place at $T > T_B$. The curve *CD* is the thermal expansion curve of dilatometer fluid and solid mercury.

xy, the vertical displacement of the lines *AB* and *CD* at T_{xy} is the dilatometer contraction, Δh_0 , proportional to the change in volume of the dispersion if all the mercury contained in it solidified isothermally at T_{xy} . The variation of Δh_0 with temperature in the range of rapid solidification is negligible. Δh_0 was measured to within one percent uncertainty.

Temperatures of beginning solidification T_i and of final solidification T_f measured in the cooling-heating experiments are defined as the temperatures between which the points on the cooling curves do not fall, within experimental error, on the extrapolation of either of the lines *AB* or *CD*. Actually, T_f and T_i are weak functions of the rate of cooling and in this investigation are specified for a cooling rate of $1^{\circ}/\text{minute}$.

No values of T_f and T_i were accepted as characteristic of a given dispersion unless two additional conditions were established as follows: (1) The volume contraction

presumed to be associated with solidification was registered as an expansion during the heating cycle at the accepted melting temperature of mercury. (2) The sample evolved a substantial quantity of heat (heat of solidification) when cooled through the temperature range T_i to T_f .

The temperature range in which the heat of solidification was evolved was determined by measuring as a function of temperature the deflection, δ , of a sensitive galvanometer activated by a differential thermocouple having one junction in a well embedded in the sample and the other junction embedded in a well in the temperature bath. When the bath was cooled at a constant rate of $1^{\circ}/\text{min}$, δ exhibited a pronounced maximum at a temperature between T_i and T_f . Values of T_i and T_f measured by this method were in excellent agreement with values measured dilatometrically in all cases, excepting for some experiments where a dispersing fluid was used that gelled at $T < T_i$.

In the isothermal dilatometric experiments the sample bulb was always thoroughly dispersed by shaking immediately before the experiment in order to insure that the rate of volume contraction would not be limited by the flow of fluid into the mercury. The dilatometer bulb and part of the capillary, which had been precooled to a temperature about 10° above that of the inner bath, were immersed in the inner bath after a constant temperature T_C had been established in it, and dilatometer readings $h(t)$ were taken as a function of time. After measuring $h(t)$ over a three- or four-hour period, the sample was either (a) quickly quenched into an auxiliary bath maintained at a temperature about 10° below T_f , held in this bath for about 15 minutes then returned to the original bath at T_C , or (b) the bath at T_C was slowly cooled to about 10° below T_f , held for 15 minutes at the lower temperature, and then warmed back up to T_C . In either event after about 15 minutes more of thermal equilibration at T_C a final dilatometer reading h_f was taken. The dilatometer reading h_i corresponding to the fraction of sample

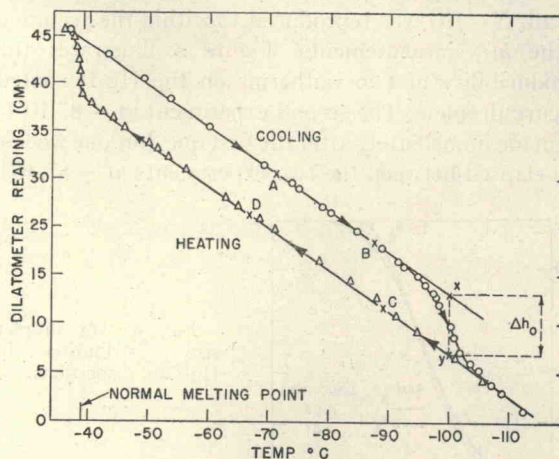


Fig. 2. Cooling-heating cycle for dispersion of Hg(St)-coated Hg droplets.

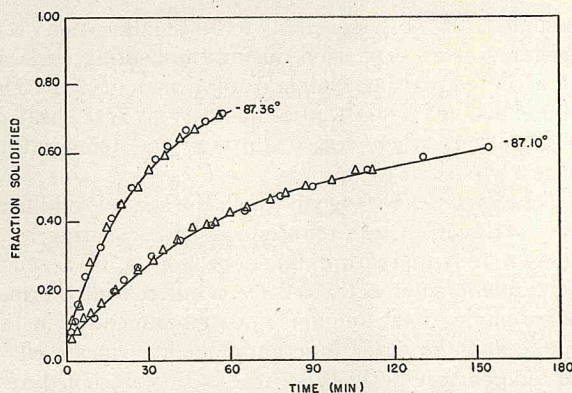


FIG. 3. Comparison of duplicate isotherms on a dispersion of Hg_2I_2 -coated Hg droplets.

solidified $X=0$ at T_c is calculated from the equation $h_i = h_f + \Delta h_0$. $X = f(t)$ is given by $X = [h_i - h(t)] / \Delta h_0$. The time origin was taken as the ordinary time when $h(t) = h_i$.

Additional experiments were carried out on the $\text{Hg}(\text{Lau})$ -coated droplets to find out how closely the temperature of the sample approached the temperature of the bath. For this purpose, a dilatometer was used containing an embedded thermocouple well. The potential difference developed in a thermocouple with one junction in the well and the other in the bath was measured as a function of time at constant bath temperatures. In the same experiments $X = f(t)$ was measured. It was found that for transformation rates $R \leq 0.05$ g of mercury/min the temperature difference registered by the differential couple was $< 0.02^\circ\text{C}$. After quenching the precooled dilatometer into the bath at T_c , the temperature inside the dilatometer generally approached T_c within a period of about five minutes. In most of the isothermal data to be reported R was well below 0.05 g/min.

The reproducibility of the isotherms was checked by repeating measurements on several for each dispersion. For all, $X = f(t)$ was reproduced to within the accuracy of the $h(t)$ measurements. Figure 3 illustrates the reproducibility of two isotherms on the Hg_2I_2 coated mercury droplets. The second experiment at -87.10°C was made immediately after the first one, but one week's time elapsed between the two experiments at -87.36° .

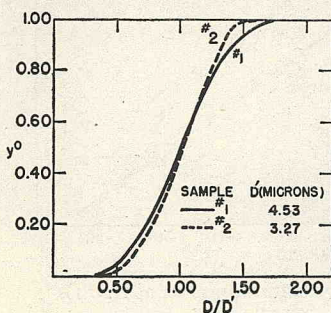


Fig. 4. Hg droplet size distribution in $\text{Hg}(\text{Lau})$ dispersions.

D. Droplet Diameter Measurement

To measure droplet diameter, a Spencer microscope with an apochromat lens and Aplanat eyepiece was used. The lens had a 4-mm objective and was fitted with a correction collar. Illumination was provided by transmitted light from a zircon arc source. A prism was used to project the field on the wall and the diameter of the image measured, after bringing it into focus, to within $\frac{1}{2}$ mm. For droplets having diameters in the range 2–12 microns, the magnification factor was 1160. Samples were taken directly from the dilatometer after the isothermal measurements and dispersed in mineral white oil. Due precautions were taken to obtain representative samples and to insure that the droplets would not be flattened by the microscope cover glass.

Droplet size determinations were made on two or more withdrawals from each dilatometer sample. The droplet size distributions for these withdrawals checked satisfactorily. The diameter of a total of about 2000 droplets in each dilatometer sample was measured. The volume of sample having droplet diameters between

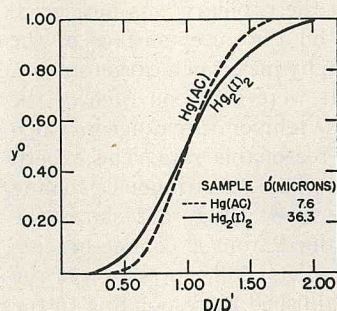


Fig. 5. Hg droplet size distributions in Hg_2I_2 and $\text{Hg}(\text{Ac})$ dispersions.

D and $D + \frac{1}{2}D$ (where $\frac{1}{2}D = 500/1160$ microns for the magnification factor of 1160) was plotted against D . From smoothed curves $[(V^0 dy^0/dD) = f(D)]$ through these points curves were constructed of the function $y^0 = f(D)$ (see Figs. 4 and 5). D' is defined by

$$0.5 = (1/V^0) \int_0^{D'} V_D^0 dD = (1/V^0) \int_{D'}^{\infty} V_D^0 dD. \quad (17)$$

RESULTS

A. Continuous Cooling Experiments

Figure 6 is a diagram that compares the results of the continuous cooling (rate $\sim 1^\circ/\text{minute}$) experiments for the various dispersions. The ordinate is the supercooling, ΔT ($\Delta T = T_m - T$ where T_m is the melting temperature), and the abscissa is the logarithm of the droplet volume. $T_m - T_i$ and $T_m - T_f$ calculated from the continuous cooling experiments are the ΔT coordinates of the corners of each rectangle. The $\log v$ coordinates of the corners define the range of volume of droplets that contribute significantly to the total volume of the mercury. A change of a factor of 10 in the cooling

rate shifts the ΔT coordinate of the rectangles 1° or less. These experiments prove conclusively that a very small droplet size in itself is not a sufficient condition for marked supercooling of liquids, for in most instances the size distribution in the various dispersions overlap considerably or even completely yet their nucleation frequencies differ by many orders of magnitude.

It must be concluded that the most important factor determining the position of a dispersion in the solidification diagram (Fig. 6) is the potency of the most effective nucleation catalyst on the surface or in the volume of the constituent droplets. Compared to this factor, the effects of droplet volume and cooling rate are second order. Nucleus formation must be initiated by catalysts in all of the dispersions with the possible exception of Hg(Lau) and Hg(Bz).

The chemical composition and structure of the effective catalytic substance may not correspond to that of the compound covering the major part of the droplet surface. Minute amounts of impurity in the forming compound could have formed a catalyst more potent than that formed by the compound itself, (though different samples of the forming substance gave the same result). However, the fact that the supercooling of the dispersions varies so widely even though their droplet size distributions overlap proves that, with the exception of Hg(Lau), Hg(Bz), and Na Oleate dispersions, the effective catalysts could not have been bodies suspended in the mercury prior to the formation of the dispersion. Further, the fact that the solidification range of a given dispersion is very narrow indicates that the effective catalytic substances in the dispersion must be chemically identical or closely related.

It has been established⁹ that the solidification of Na Oleate dispersions is coincident with a breakdown in the protective action of the absorbed film. Therefore, the position on the solidification diagram may not indicate the actual ΔT — $\log v$ relationship for Na Oleate dispersions. The main interest attaching to the Na Oleate results is that droplets so large (0.4-mm diameter) can be supercooled so much (35°).

After long holding periods at room temperature, the solidification behavior of Hg(Lau) and Hg(St) dispersions changed discontinuously from that defined by the Hg(St) and Hg(Lau) rectangles in Fig. 6 to that defined by the HgX rectangle with no accompanying change in droplet size distribution. Before this transition is complete, two discrete ranges of solidification [HgX and Hg(St) or Hg(Lau)] are found in the same dispersion. No measurable part of dispersions coated with Hg(Bz) reverted to the Hg(X) class over a two-week period. Holding Hg(Lau) dispersions at -40°C or lower completely suppressed the transition for at least several weeks.

Addition of small amounts of glacial acetic acid to HgX dispersions in methyl cyclopentane caused a marked increase (by a factor of 10 to 20) in the mean droplet diameter and a discontinuous transition in

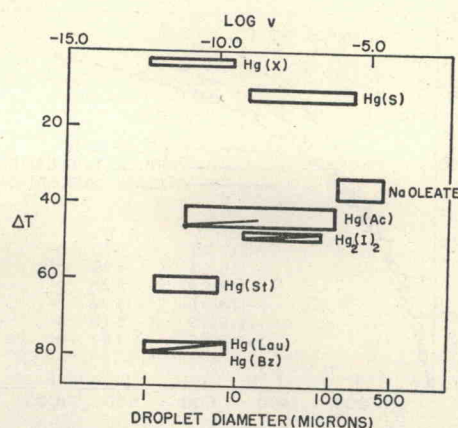


FIG. 6. Solidification diagram for mercury—curves in certain rectangles are isokinetic relations.

solidification behavior to that characteristic of Hg(Ac) dispersions.

These facts seem consistent with the following hypotheses: (a) Hg(Lau) and Hg(St) films hydrolyze to form patches of mercury oxide on the surfaces of the droplets. (b) Mercury oxide is an effective catalyst for the nucleation of mercury crystals. (c) Acetic acid converts the oxide to mercury acetate. In further support of these ideas, it was observed that the transition to Hg(X) was made markedly slower by increasing the viscosity of the dispersing medium and in some instances by greatly increasing the shortest available diffusion path between the droplets and atmospheric components.

B. Homogeneous Nucleation

Isothermal Solidification of Hg(Lau) Coated Droplets

From our interpretation of the continuous cooling experiments, it follows that the temperature range of rapid homogeneous nucleation should either correspond to or fall below $T_i > T > T_f$ for Hg(Lau) or [Hg(Bz)] coated droplets. Therefore, it is important to find whether or not the isothermal solidification behavior of these dispersions follows the predictions of the homogeneous nucleation theory.

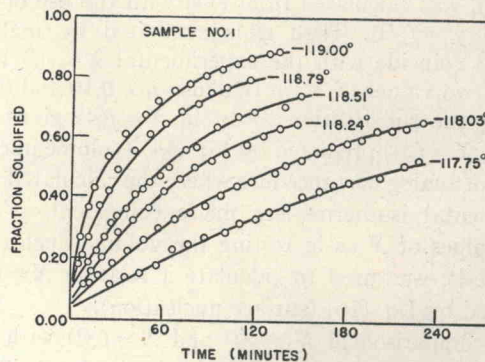


FIG. 7. Solidification isotherms of Hg(Lau)-coated droplets—Sample No. 1.

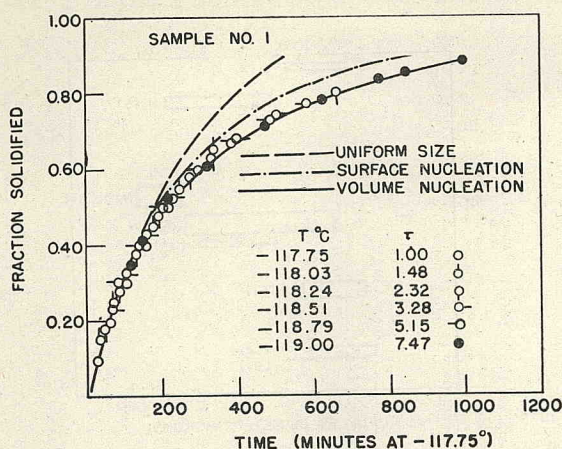


FIG. 8. Comparison of isotherms calculated on the basis of volume or surface nucleation hypotheses with master isotherm for solidification of Hg(Lau)-coated Hg droplets—Sample No. 1. The “uniform size” curve was calculated on the assumption of a uniform droplet diameter.

For the isothermal experiments, two Hg(Lau) dispersions having different droplet size distributions were prepared. $y^0 = f(D)$ for these dispersions is given in Fig. 4. To prepare the dispersion (Sample No. 2) having the smaller D' value, the blender was run for a longer period of time than for Sample No. 1.

$X = f(t)$ curves for Sample No. 1, calculated from dilatometric data at six temperatures in the range -117.75 to -119.00° , are plotted in Fig. 7. In order to test the volume and surface nucleation hypotheses, it is convenient to shrink all the data to a “master isotherm” by letting the magnitude of the time unit vary with temperature. Figure 8 shows the master isotherm and the best multiplying factors τ to apply to the ordinary time units to obtain the best superposition of the isotherms.

In constructing this isotherm, the data obtained at the shortest times at the lowest temperatures were disregarded because the transformation rate under these conditions substantially exceeded 0.05-g Hg/min. In order to test Eq. (14) derived from the homogeneous (or volume) nucleation, hypothesis $X = f(t')$, where $t' = \alpha t$ and t is expressed in time units at -117.75° ($\tau = 1.0$), was calculated from (14) with the use of the relation $y^0 = f(D)$. Then α is evaluated by making $X = f(t')$ coincide with the experimental $X = f(t)$ relation at two values of X , in this instance 0.10 and 0.30. Making the substitution $t' = \alpha t$ in $X = f(t')$ gives the relation $X = f_v(t)$ predicted by Eq. (14) (volume nucleation). An analogous procedure where the calculated and experimental isotherms are made coincident at the same values of X as in testing the volume nucleation hypothesis, was used to calculate a relation $X = f_a(t)$ predicted by Eq. (16) (surface nucleation).

The comparison of $X = f_v(t)$ and $X = f_a(t)$ with the master isotherm $X = f(t)$ determined experimentally is shown in Fig. 8. The data are described by $X = f_v(t)$ to

well within the experimental uncertainty but $X = f_a(t)$ falls somewhat outside the range of uncertainty in the experimental points for $X > 0.5$.

The same order of agreement of $X = f_v(t)$ and $X = f_a(t)$ with the data was obtained when the unsmoothed droplet diameter distribution was used in place of the smoothed $y^0 = f(D)$. From this result, it is concluded that the errors that may have been made in determining the droplet size distribution are not of sufficient magnitude to affect the validity of the conclusion that the data are best fitted on the basis of the volume nucleation hypothesis.

From the described analysis, values of k_D and [from Eq. (13)] I are calculated for -117.75° . I for the other temperatures is found by multiplying I at -117.75° by the appropriate τ -factor listed in Fig. 8.

The sources and probable magnitude of the principal errors that affect the intercomparison of I values measured on the same sample are as follows:

1. $\pm 0.02^\circ$ uncertainty in the control and measurement of temperature may cause ± 3 percent error in I .
2. ± 0.03 cm uncertainty in final cathetometer reading may lead to ± 1 percent error in I .

Thus the probable deviation of I values measured on the same dispersion at the same temperature is of the order of 4 percent.

The greatest part of the probable deviation of I values measured on different samples, prepared in the same way, is contributed by the uncertainty in the measured droplet size distribution, for any error in the measurement of D is magnified three times when I is calculated. It is estimated that (considering errors in sampling, microscope magnification, measurement, and curve smoothing) D' was measured with an accuracy of ± 5 percent, therefore, the corresponding probable error in I is ± 15 percent. An additional term, affecting the intercomparison of different samples is the ± 2 percent probable error in I caused by ± 0.05 cm, uncertainty in Δh_0 . By taking all these terms into account, the maximum probable error in the absolute magnitude

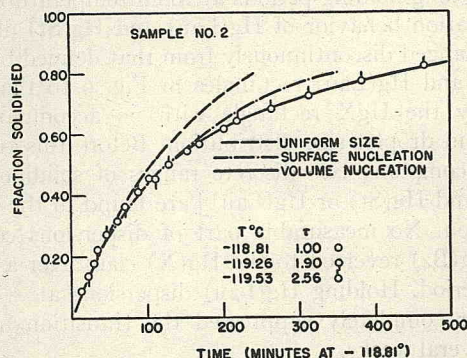


FIG. 9. Comparison of isotherms calculated on the basis of volume or surface nucleation hypotheses with master isotherm for solidification of Hg(Lau)-coated Hg droplets—Sample No. 2. The “uniform size” curve was calculated on the assumption of a uniform droplet diameter.

of I and the maximum probable deviation when samples prepared in the same way are intercompared is ± 21 percent.

Three isotherms were measured on Sample No. 2. The master isotherm and τ -values calculated from these data are given in Fig. 9. Analysis of the results by the same method used on Sample No. 1 established that they are best described (and satisfactorily so) on the basis of the volume rather than the surface nucleation hypothesis. I values were calculated as before.

Equation (1) gives $I = f(T)$ based on the homogeneous nucleation theory. From thermodynamic principles,

$$d(\Delta F_v)/dT = -\Delta S_v, \quad (18a)$$

where ΔS_v is the entropy of solidification/volume. According to the existing thermodynamic data,²¹ ΔS_v is virtually independent of temperature;²² therefore, to a good approximation,

$$\Delta F_v = -(\Delta S_v)\Delta T \quad (18b)$$

and Eq. (1) may be rewritten

$$I = K_v \exp[-a\sigma^3/(\Delta S_v)^2(\Delta T)^2kT]. \quad (19)$$

If σ is assumed to be independent of temperature, it follows that $\ln I$ is a linear function of $1/T(\Delta T)^2$ having the slope,

$$d \ln I / d[1/T(\Delta T)^2] = -a\sigma^3/(\Delta S_v)^2k; \quad (20)$$

$\log I$ is plotted against $1/T(\Delta T)^2$ for both samples in Fig. 10, and an excellent straight line relation obtains for each sample as required by Eq. (1). The average deviation from the mean value of I between Samples 1 and 2 in the overlapping temperature range of the two sets of measurements is 14.5 percent and within the calculated maximum deviation of 21 percent.

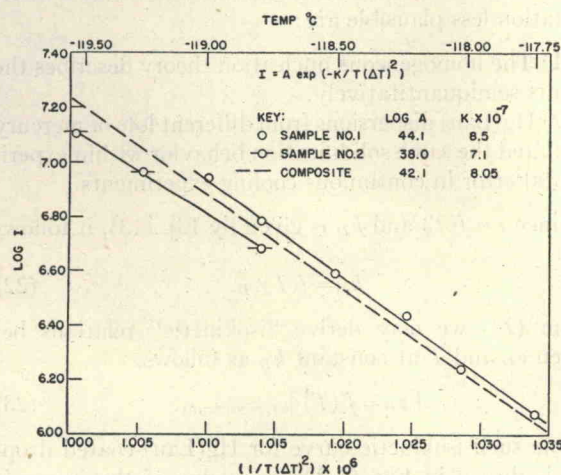


FIG. 10. Variation of nucleation frequency/volume, I , with supercooling, ΔT , in the solidification of Hg(Lau)-coated Hg droplets.

²¹ K. K. Kelley, Bureau of Mines Bulletins No. 371 (1934) and No. 393 (1936).

²² The author is indebted to R. A. Oriani for establishing this fact.

TABLE II. Summary of results on kinetics of homogeneous and heterogeneous nucleation in mercury.

Surface coating	Type of nucleation	σ erg/cm ²	θ	log K_v		log K_s	
				Exptl.	Calc.	Exptl.	Calc.
Hg(Lau)	Volume (Homogeneous)	31.2	...	42.1	35.1	...	...
Hg(Ac)	Surface (Heterogeneous)	31.2	72°	...	...	26.8	27.3
Hg ₂ I ₂	Volume (Heterogeneous)	^a	...	69.6	35.5	...	...
Hg(St)	Heterogeneous	31.2	87°	31.	35.	27.4	27.3

^a The nucleation frequency in iodide coated droplets can be satisfactorily described by an apparent value of $\sigma = 29.2$ erg/cm².

A further check on the validity of the volume nucleation hypothesis is obtained from these data by comparing the measured value of k_D' for Sample No. 2 with the values calculated from the results on Sample No. 1 on the basis of the surface $(k_D')_a$ and volume $(k_D')_v$ hypothesis. At the temperature -118.81° in Sample No. 2, the experimental value of $k_D' = 0.0052 \text{ min}^{-1}$ in fair agreement with $(k_D')_v = 0.0065 \text{ min}^{-1}$ and in marked disagreement with $(k_D')_a = 0.0095 \text{ min}^{-1}$. Though it is recognized that the deviation between $X = f(t)$ and $X = f_a(t)$ for any one set of data is hardly large enough to be convincing, it is believed that the result just cited and the fact that $X = f(t)$ is in best agreement with $X = f_v(t)$ for two dispersions fully substantiates the conclusion that k_D' in these experiments is proportional to droplet volume.

From the $\ln I$ vs $1/T(\Delta T)^2$ lines for the two samples a composite straight line was constructed as shown in Fig. 10. Assuming that mercury crystal nuclei are spherically shaped ($a = 16\pi/3$), σ was calculated from the slope of the composite line [Eq. (20)] to be 31.2 ergs/cm². (Also see summary of results—Table II.) The radius of the nucleus²³ $r^* = -2\sigma/(\Delta F_v)$ was calculated to be 11.8° at -118° ; whence it follows that it contains 830 atoms and $n^* = 220$.

To calculate K_v from the theory of homogeneous nucleation [Eq. (2)] it was assumed that $\Delta F_A = (\Delta F_A)_{vis}$, where $(\Delta F_A)_{vis}$ the free energy of activation for viscous flow is calculated from the viscosity of mercury using the equation for viscosity calculated from absolute rate theory.²⁴ In the temperature range of the measurements $\exp(-\Delta F_A/kT) \approx 10^{-2}$. With this assumption $\log K_v$ calculated from Eq. (2) is 35.1 and is to be compared with the experimental value of 42.1 ± 2 determined from the intercept of the composite line in Fig. 10 on the $\log I$ axis.

To explain this disagreement of a factor of at least 10^5 between the K_v and $(K_v)_{exp}$, some of the assumptions made in deriving and applying the theory have to

²³ M. Volmer, *Kinetik der Phasenbildung* (Steinkopff, Leipzig, Germany (1939).

²⁴ Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 477-516.

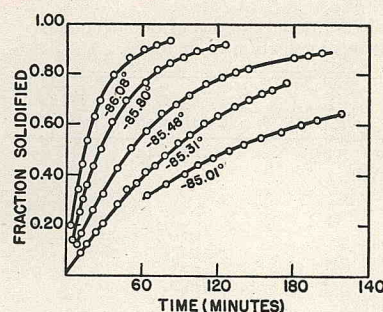


FIG. 11. Solidification isotherms of dispersion of Hg(Ac)-coated Hg droplets.

be examined more critically. In the derivation of the theory the frequency factor for the addition of an atom to the nucleus from the liquid was assumed to be (kT/h) from the absolute rate theory. There is no assurance that this assignment is valid for an atomic process as complex as the nucleation reaction. In addition, it is assumed that crystal embryos mix ideally with the supercooled liquid. It is believed that together these factors might lead to an uncertainty as large as $10^{\pm 2}$ in the calculated K_v . However, the assumptions that ΔS_v and σ are temperature independent are probably of more importance. The term $\exp[-a\sigma^3/(\Delta F_v)^2 kT]$ is very temperature sensitive (such that I changes by a factor of 5/ $^{\circ}\text{C}$) so that even a very small dependence of σ or ΔS_v upon temperature has a potent effect upon the measured slope $[d \ln I / d(1/T(\Delta T)^2)]$ and hence on $\log(K_v)_{\text{exp}}$. For example, suppose that σ depends upon temperature according to the equation: $\sigma = \sigma_0 + bT$ and that ΔF_v is given by $\Delta F_v = -\Delta S_v^0(\Delta T)(1 + c\Delta T)^{\frac{1}{2}}$. It follows,

$$d \ln I / d[1/T(\Delta T)^2] \approx [-a\sigma^3/(\Delta S_v)^2 k] \times \{1 + [T(T_m - T)/(3T - T_m)][3b/\sigma + c]\}. \quad (21)$$

In Eq. (21) the factor $-a\sigma^3/(\Delta S_v)^2 k$ is the slope that would be measured if σ and ΔS_v were temperature independent.

If $c=0$ a value of $b \approx 0.0008/^{\circ}$ is sufficient to change the slope 18 percent and the apparent value of K_v by a factor of 10^6 . In order to cause a change of the same order of magnitude when $b=0$, c must be $0.0016/^{\circ}$.

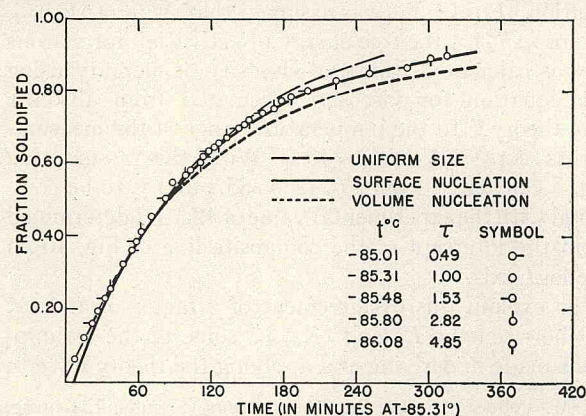


FIG. 12. Comparison of isotherms calculated from volume and surface nucleation hypotheses with master isotherm for Hg(Ac)-coated Hg droplets.

It seems reasonable to suppose that the combined effect of b , $c \neq 0$, and the relatively large ΔT values obtaining in the experiments accounts for the major part of the disagreement between K_v and $(K_v)_{\text{exp}}$.²⁵ On the basis of this analysis, it may be concluded that the experimental results are compatible with the predictions of the homogeneous nucleation theory.

The only other possible interpretation of the data that seem to merit serious consideration is that nucleation is catalyzed by inclusions colloiddally suspended in the mercury. In order to account for the results, the minimal concentration of the inclusions would have to be 10^{13} to $10^{14}/\text{cm}^3$ (corresponding to a volume fraction 10^{-5} to 10^{-8}) all having equal catalytic effectiveness/ cm^2 . Since the same results are obtained in continuous cooling experiments with Hg(Bz), and two-Hg(Lau) dispersions gave the same I within experimental error, it is concluded that these inclusions could not have had their origin in the preparation of the dispersion but, if present, must have been suspended in the original mercury sample.

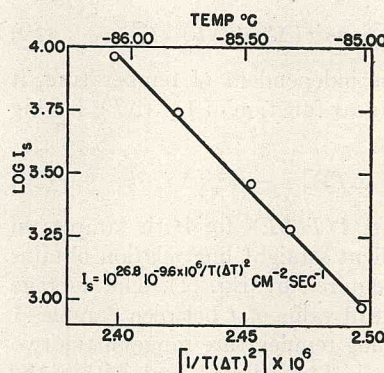


FIG. 13. Variation of I with ΔT for solidification of Hg(Ac)-coated Hg droplets.

The arguments that make the colloidal catalyst interpretation less plausible are:

- (1) The homogeneous nucleation theory describes the results semiquantitatively.
- (2) Hg(Lau) dispersions from different lots of mercury exhibited the same solidification behavior within experimental error in continuous cooling experiments.

Since $I = f(T)$ and k_D is given by Eq. (13), it follows that

$$k_D = f(T)v_D. \quad (22)$$

From (22) we may derive "isokinetic" relations between v_D and T at constant k_D as follows,

$$[v_D = f'(T)]_{k_D = \text{constant}}. \quad (23)$$

One such isokinetic curve for Hg(Lau)-coated droplets is drawn in Fig. 6. The k_D value of this curve is

²⁵ We do not assert that the signs of b and c are actually as indicated. Intuitively it might be believed that b should be negative rather than positive. However, our knowledge of liquid-crystal nuclei interfaces is not sufficiently advanced to justify such a belief. Our purpose is to show that the neglect of the factors b and c might, so far as our present knowledge goes, account for the disagreement between K_v and $(K_v)_{\text{exp}}$.

fixed by the co-ordinates of a corner of the Hg(Lau) rectangle.

C. Heterogeneous Nucleation

1. k_D Proportional to Droplet Area: Isothermal Experiments on Hg(Ac)-Coated Droplets

The primary purpose of this investigation was to measure the kinetics of homogeneous nucleation of mercury crystals. Consequently, the isothermal solidification behavior of dispersions in which nucleation is believed to be heterogeneous was studied in less detail than that of the Hg(Lau) dispersions.

Figure 11 shows the $X=f(t)$ isotherms obtained at five different temperatures on a dispersion of Hg(Ac) coated droplets. The isotherm at -85.01° does not extrapolate to $X=0$ at $t=0$ because the dispersion was inadvertently precooled to a temperature just below -85.01° for a short time prior to the running of the isotherm.

The data were analyzed by the same methods used to analyze the data on the Hg(Lau) dispersion. Figure 12

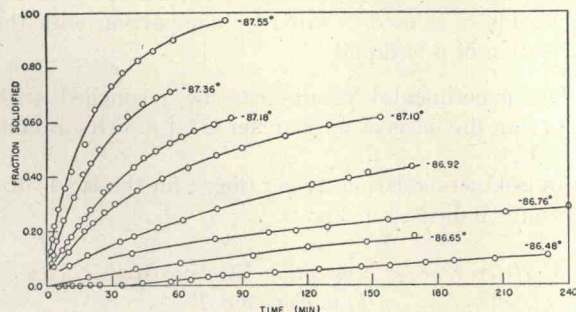


FIG. 14. Solidification isotherms of dispersion of Hg₂I₂-coated Hg droplets.

shows the master isotherm and Fig. 5 the smoothed curve for $y^0=f(D)$. In evaluating α the calculated and experimental curves were made coincident at $X=0.3$ and 0.5 . Comparison of the calculated curves with the master isotherm is made in Fig. 12. Clearly the data are most satisfactorily described on the basis of the surface nucleation hypothesis [Eqs. (15) and (16)]. For $0 \leq X \leq 0.2$ the experimental rate is greater than calculated on the basis of either the surface or volume nucleation hypotheses, but this departure is not considered significant in view of the small values of X and t .

I_s was calculated at various temperatures from the τ values shown in Fig. 12. $\log I_s$ is a linear function of $1/T(\Delta T)^2$ as shown in Fig. 13. From the measured slope and the value of σ obtained from the experiments on homogeneous nucleation, the contact angle θ was calculated to be [see Eq. (5)] 72° . $\log(K_s)_{\text{exp}}$ was found to be 26.8 which compares well with the value 27.4 calculated from Eq. (6) on the assumption that all elements of area in the droplet surface are equally effective for nucleation catalysis.

This excellent agreement between theory and experi-

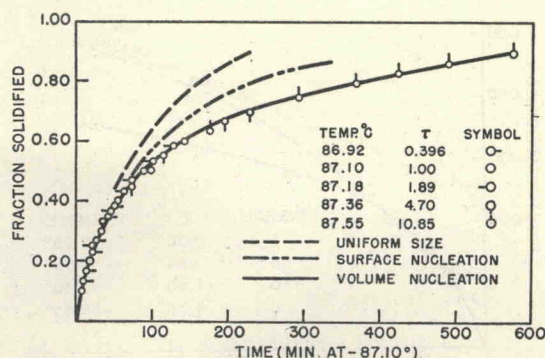


FIG. 15. Comparison of isotherms calculated from volume and surface nucleation hypotheses with master isotherm for Hg₂I₂-coated Hg droplets.

ment fully supports the concept developed earlier that the kinetics of heterogeneous nucleation can be described with the use of a single parameter, θ , in addition to those required to describe homogeneous nucleation. Deviations between theory and experiment due to any temperature dependence of ΔS_v and σ will be smaller in these experiments²⁶ than in the case of homogeneous nucleation because ΔT is much smaller.

An isokinetic relation between $\log v$ and ΔT for this dispersion is indicated on the solidification diagram in Fig. 6.

2. k_D Proportional to Droplet Volume: Isothermal Experiments on Hg₂I₂-Coated Mercury Droplets

$X=f(t)$ curves measured at eight temperatures on a Hg₂I₂-coated dispersion are plotted in Fig. 14. Because of the extraordinary magnitude of the temperature coefficient of the rate, every isotherm was rechecked, with the exception of the one at -87.55° . In all cases, the agreement is excellent.

$y^0=f(D)$ for this dispersion is given in Fig. 5. The master isotherm and the test of its agreement with the volume and surface nucleation hypotheses is shown in Fig. 15. A much better fit (also an entirely satisfactory one) is obtained on the basis of the volume than on the

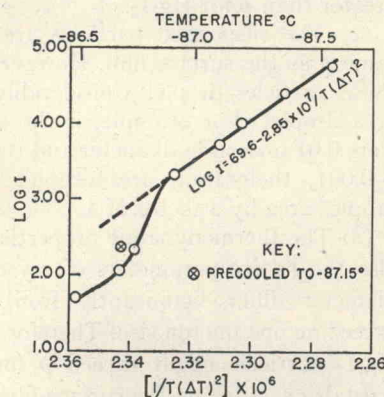


FIG. 16. Variation of I with ΔT for the solidification of Hg₂I₂-coated Hg droplets.

²⁶ Of the order of 10^2 if it is accepted that the deviation in the homogeneous nucleation results is caused by the temperature dependence of σ and ΔS_v .

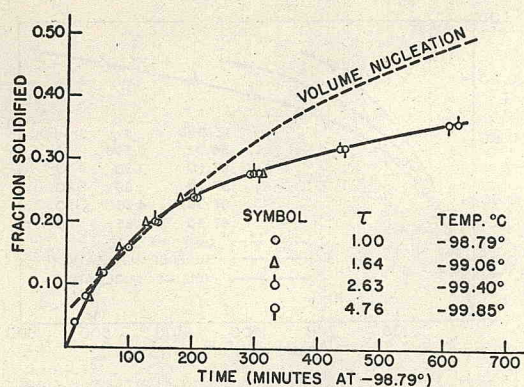


FIG. 17. Comparison of isotherm calculated from volume nucleation hypothesis with master isotherm for dispersion of Hg(St)-coated Hg droplets.

surface nucleation hypothesis. $\log I$ is plotted against $1/T(\Delta T)^2$ in Fig. 16. A good straight line relation is obtained at the five lowest temperatures; $(K_v)_{\text{exp}}$ and the apparent σ value derived from the constants of this line are listed in Table II. At temperatures higher than -86.9° I is much lower (by a factor of 4) than predicted by the low temperature linear relation. When the dispersion was precooled below -86.9° then warmed to a temperature above -86.9° , the transformation rate at the higher temperature was significantly larger than if the sample had not been precooled.

These results can be explained on the hypothesis that the nucleation is catalyzed by colloidal particles suspended throughout the volume of the mercury droplet. For reasons already given it seems likely that these catalysts must have had their origin in the preparation of the dispersion rather than in some earlier stage of the mercury processing.

The greater total catalytic effect of the suspended particles in comparison with the Hg_2I_2 film on the droplet surface might be accounted for in one of the following ways:

(1) The suspended particles are not chemically identifiable as Hg_2I_2 and their catalytic potency, p , is greater than p for Hg_2I_2 .

(2) The suspended particles are Hg_2I_2 having the same p as the surface film. However, the total area of these particles/droplet considerably exceeds the film area/droplet. For example, if the suspended particles were 0.01 micron in diameter and their volume fraction ~ 0.001 , their total area/droplet would exceed the droplet area by a factor of 4.

(3) The thermodynamic properties and undoubtedly also the lattice parameters of crystals 0.01 micron in diameter differ significantly from those of crystals exceeding one micron size. Therefore, p for 0.01 micron Hg_2I_2 particles might exceed p for the larger Hg_2I_2 crystals constituting the surface film.

As a consequence of the exceptionally marked dependence of I on T (a factor of about $200/^\circ$) $(K_v)_{\text{exp}}$

$\sim 10^{70}$ is many orders of magnitude larger than maximum $K_v \sim 10^{85}$ calculable from nucleation theory. On the basis of the known facts, it is not possible to reconcile this disagreement with nucleation theory without an additional hypothesis. It can be verified from the theory that the temperature coefficient of nucleation in heterogeneous processes is larger, the nearer the process is in temperature to the equilibrium temperature. Therefore, the results on the Hg_2I_2 dispersion suggest that the rate controlling process is the formation of the nucleus of a phase in equilibrium with liquid mercury (or with Hg_2I_2) at a temperature well below the normal melting point of mercury. Two possible rate-controlling mechanisms to account for the results are suggested:

1. Formation of a nucleus of a new Hg_2I_2 phase having a greater catalytic potency for formation of mercury crystals than the parent Hg_2I_2 phase.

2. Nucleation of a crystalline mercury phase, β , having a melting temperature well below -38.87°C . It is supposed that the nucleation of β is more strongly promoted by Hg_2I_2 than is the nucleation of the most stable crystalline phase α . Also it is assumed that the nucleation of α in β is rapid by comparison with the nucleation of β in liquid.

The experimental results can be reconciled with theory on the basis of mechanism (2) if β melts around -70°C .

An isokinetic relation $\Delta T = f(\log v)$, for the Hg_2I_2 dispersion is indicated in Fig. 6.

3. Heterogeneous Nucleation Showing Multiplicity of I_s at Constant T

(a) *Results on Hg(St) Dispersion.*— $\gamma^0 = f(D)$ for this dispersion was practically identical in shape with $\gamma^0 = f(D)$ for Sample No. 1 shown in Fig. 4 but with $D' = 3.8$ microns. $X = f(t)$ was measured at four temperatures and the master isotherm constructed from these data is plotted in Fig. 17. After an earlier analysis^{5b} of these results, it was concluded that the conditions for homogeneous nucleation were approached in these experiments. However, it proved impossible to describe the data on the basis of the volume nucleation hypothesis with a single value of I and the discovery was made that Hg(Lau) and Hg(Bz) dispersions supercool to temperatures 18 – 20° lower than Hg(St) dispersions. Therefore, it is believed that the earlier conclusion was mistaken and that mercury crystals are nucleated heterogeneously in the Hg(St) dispersion. The comparison of the master isotherm with the curve calculated on the basis of volume nucleation is given in Fig. 17. The experimental rate of solidification decreases with increasing X much more sharply than does the calculated rate. These facts can be interpreted on the hypothesis that two or more fractions of the dispersed droplets have different I_s values at constant temperature.

k_D' may be roughly estimated at a specified value of X by assuming the validity of the relation

$$k_D' = dX/dt(1-X). \quad (24)$$

Apparent values of I and I_s were evaluated from k_D' at $X=0.3$ using Eqs. (13) and (15). The constants θ and $(K_s)_{\text{exp}}$ of Eq. (5) calculated from these data and the τ -values in Fig. 17 are listed in Table II. In calculating the $\log K_s = 27.3$ given in the table, it was assumed that every mercury atom in the droplet surface was in the catalyst surface. Actually, it seems probable that the fraction of surface mercury atoms also in the catalyst surface was substantially less than unity.

Since Hg(Lau) films apparently do not catalyze the nucleation, it is not considered likely that any one of the effective catalysts in the Hg(St) dispersion is a mercury stearate. It seems more likely that the catalysts are mercury oxystearates and/or substances formed by the reaction of minor components in the stearic and forming solution with mercury.

(b) *Hg(X) Dispersion.*—Rates of solidification of Hg(X) dispersions increased slowly as a result of room temperature aging. Four isotherms measured over a two-day period, during which time aging is hardly perceptible, are plotted in Fig. 18. These isotherms can only be described by several values of I_s that differ widely (by factors of at least 1000) at constant temperature. Apparently, the curves approach in time an X asymptote, $X \approx 0.2$ at -41.72° to $X \approx 0.9$ at -42.77° . This general behavior is similar to that observed by Vonnegut¹⁶ and by Pound and LaMer¹⁷ in the solidification of tin.

(c) *Interpretation.*—The $X=f(t)$ relations for both the Hg(X) and Hg(St) dispersions can be described by the general analytical relation,

$$X = X_1^0[1 - \exp(-k_1 t)] + X_2^0[1 - \exp(-k_2 t)] \cdots X_i^0[1 - \exp(-k_i t)], \quad (25)$$

where $X_1^0, X_2^0, \dots, X_i^0$ are fractions of the total dispersion, each characterized by a single nucleation frequency ($k_1, k_2, \dots, k_i$ per droplet). It is assumed for simplicity, and for the present purpose without a significant loss in rigor, that the droplet size in a given dispersion is uniform. So we have then to interpret directly a multiplicity in k that corresponds to a multiplicity in I_s .

Two terms of Eq. (25) with $X_1^0 = 0.3$ and $k_1 \sim 100 k_2$ are sufficient to describe the Hg(St) isotherms. At least five terms are required for the description of the HgX isotherms.

Two basic interpretations of the multiplicity of k seem worthy of serious consideration. First, it may be supposed that each k value characterizes the catalytic potency of a different chemical substance. In our experiments these were introduced during the dispersion forming process or formed in a subsequent chemical reaction (as was definitely the case for the HgX dispersion). An essential requirement of this interpretation is that the average number, m , of crystallites or surface

patches per droplet of the most potent catalytic substance should not greatly exceed unity.

A second basic interpretation is that catalysis is effected by one chemical substance having different catalytic potencies in different parts of its surface or when formed on droplets of different size. For example, it may be supposed that nucleation takes place preferentially at nonthermally equilibrated defects in the surface of the catalytic crystallite. A specific example of such a defect is the step present in a crystal surface caused by the termination of a screw dislocation in it.²⁷ The specific structure and catalytic potency of these defects may vary considerably and considering the small mass of their containing crystallites, the average number m /droplet of the defects most effective in nucleation catalysis can be of the order unity. It follows that the formal treatment of the problem of the kinetics of nucleation catalyzed by such defects is entirely analogous to the treatment of k multiplicity as a result of catalysis by a variety of chemical substances.

A second possible explanation for a differing catalytic potency in the same chemical substance follows from the fact that the thickness of the droplet surface coating is only of the order of 0.05 micron. Therefore, its thermodynamic properties, lattice parameter, and catalytic potency will be comparatively sensitive functions of its thickness and surface charge density. It is conceivable that the film thickness and its surface charge density may be related to the droplet size in such a way that $X=f(t)$ is described by equations of type (25).

The kinetic treatment of the k multiplicity caused by suspended crystallites, surface patches, and structural defects must take into account the statistical distribution of units of a particular catalyst among the droplets. Kimball and Halford²⁸ have treated this problem formally considering only one kind of catalyst. Their method was to write an equation of type (25) where each term corresponds to a droplet class containing a specified number of catalytic units. Then the X_i^0 's and k_i 's are

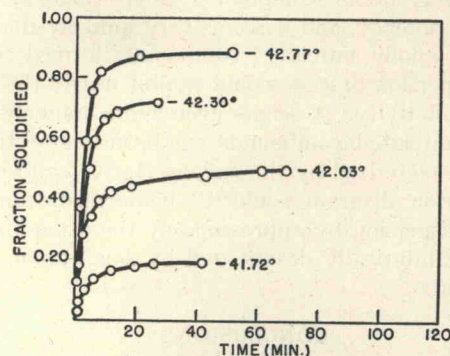


FIG. 18. Solidification isotherms of dispersion of Hg(X)-coated Hg droplets.

²⁷ Burton, Cabrera, and Frank, *Nature* **163**, 398 (1949).

²⁸ Kimball and Halford (private communication to Pound and LaMer, reference 17).

related to m and k , the nucleation frequency of a droplet containing one unit, through the Poisson distribution law. The resulting $X=f(t)$ relation is,

$$X = 1 - \exp\{-m[1 - \exp(-kT)]\} \quad (26)$$

and X approaches an asymptote $[1 - \exp(-m)]$ at $t \rightarrow \infty$, for small values of m (26) reduces to $X = m[1 - \exp(-kt)]$ which corresponds to a single term in Eq. (25) with $m = X_i^0$.

None of the existing data showing multiplicity of k values can be described by the Kimball-Halford theory on the assumption of a single catalyst; to fit the data to this theory requires several more terms of Eq. (26), approximately the same number as would be required with Eq. (25), corresponding to the additional active catalysts. For example, the Hg(St) data require two Kimball-Halford terms.

Pound and LaMer¹⁷ have fitted two of their isotherms on tin with the Kimball-Halford formula. Their analysis shows that at least two specific catalysts were active and inspection of their other isotherms indicates that several other catalysts were probably active. The simple Kimball-Halford theory predicts that m is proportional to droplet volume if catalysis is effected by suspended crystallites or to droplet area if effected by chemical or structural heterogeneities in the droplet surface. Pound and LaMer's results are better described on the assumption that m is proportional to droplet area.

Applying the procedure used on the Hg(St) data Pound and LaMer's data gives $(K_s)_{\text{exp}} \sim 10^{31}$, compared with $K_s = 10^{27.5}$ calculated on the assumption that every atom in the droplet surface is in an active catalytic surface.

It seems probable that the different catalysts responsible for the k multiplicity in the Hg(St) and Hg(X) dispersions are very closely related chemically, and in the case of Hg(X) they may be chemically the same and differ only structurally. The basis of this conclusion is that the solidification diagram (Fig. 4) shows that different crystalline compounds differ widely in their catalytic potency, and it seems very unlikely that two or more wholly unrelated compounds formed in the same dispersion process would exhibit nearly the same catalytic activity. It seems even more unlikely that several unrelated compounds exhibiting catalytic activity characterized by the narrow Hg(X) band in the solidification diagram could all be formed from the Hg(St) dispersion by approximately the same kinetics and all catalytically deactivated by small amounts of acetic acid.

CONCLUSIONS

In this investigation it has been demonstrated unequivocally for the first time, to the best of the author's knowledge, that the rate of crystal nucleation in several dispersions of supercooled mercury droplets follows first-order reaction kinetics described at constant tempera-

ture for a given dispersion by a single value of nucleation frequency/volume or area.

Convincing evidence has been obtained that 2-8 micron diameter mercury droplets coated by a mercury laurate film solidify from nuclei formed homogeneously. It is demonstrated that the data are in satisfactory agreement with the Turnbull-Fisher theory of homogeneous nucleation in condensed systems. This agreement lends credence to the use made of the theory^{5a} to calculate liquid-crystal nucleus interfacial energies of metals where the homogeneous nucleation frequency is known at only a single temperature. (In calculating σ from I and a theoretical value of K_v , it should be remembered that an uncertainty of only one percent is introduced into σ for every factor of ten uncertainty in K_v .)

In an earlier publication,^{5a} it was pointed out that "gram-atomic interfacial energies" σ_g of the strictly metallic elements calculated from presumed homogeneous nucleation frequencies are related to the corresponding gram atomic heats of fusion, ΔH_f , by the equation,

$$\sigma_g/\Delta H_f = 0.46 \pm 0.04. \quad (27)$$

When treated according to the earlier procedure, for purposes of comparison, the new data on mercury give $\sigma_g/\Delta H_f = 0.61$. This deviation from the average for the other metallic elements, though significant, is not sufficient to invalidate the generalization that $\sigma_g/\Delta H_f \approx \text{constant}$ for the metallic elements.

The first instance has been established, in the Hg(Ac) dispersion data, in which the nucleation frequency is proportional to the surface area of the supercooled droplet. These results are in good agreement with the theory of heterogeneous nucleation kinetics derived from concepts advanced in earlier papers.^{2,4,5a} In this case the nucleation catalytic potency of the surface film can be conveniently characterized by a contact angle θ .

For two mercury dispersions and for all tin dispersions thus far studied a multiplicity of I_s values measured at constant temperature is found. It is believed that the catalysts responsible for this multiplicity in mercury are either structural defects of different severity in a common crystalline substance or very closely related chemical substances.

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