Freezing of Liquids on Sudden Exposure to Vacuum

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Evaporative cooling and freezing of liquids in a vacuum is analyzed. Preliminary consideration of the mechanism of the process resulted in a complex mathematical model. Therefore, it was necessary to make a number of simplifying assumptions to establish material and energy balances which were used, along with the kinetic theory of gases, as a basis for calculations. Results given for several cryogens and water indicate the effects of initial temperature, drop diameter, and ambient pressure on the time required for cooling to the triple point and subsequent freezing.

Nomenclature

a_i = coefficients in polynominal ($i = 1, 2, \ldots n$)
A = area of surface evaporating, cm^2
c_p = liquid heat capacity, cal/mole °K
D = drop diameter, microns, μ
ΔH_f = heat of fusion, cal/mole
ΔH_v = heat of vaporization, cal/mole
k = const = 5.833×10^{-2}
M = molecular weight
P = back pressure (pressure of vapor in contact with liquid drops), mm Hg abs
P_0 = vapor pressure of liquid, mm Hg abs
R = gas constant = 46.7 (mm Hg)^2-sec^2-cm^4/moles-°K-g
T = temperature, °K
ΔT = temperature change during evaporation step
W = mass of material, g
γ = surface tension, dynes/cm
ϵ = evaporization efficiency
θ = time, sec
μ = microns
ρ = liquid density, g/cm^3
— = vinculum indicates average over temperature range

Subscripts

g = vapor
l = liquid at start of vaporization stage
t = triple-point conditions

Introduction

Evaporative cooling and freezing of liquids are well known phenomena. However, the rates at which these processes take place may vary greatly, depending upon the pumping capacity and ultimate pressure attainable for the particular vacuum system. For launch and space vehicle operations, liquids may be subjected almost instantaneously to an environment that can be regarded as a vacuum system of infinite pumping capacity and approximately zero ultimate pressure.

To obtain a preliminary indication of the rate at which freezing of liquids takes place under vacuum conditions, liquid nitrogen was sprayed into a high-capacity vacuum system maintained at approximately 40 mm Hg. Freezing took place so rapidly that it was complete before the liquid reached the spray exit; consequently, no liquid was visible during any part of the test.

Extension of these studies to obtain quantitative information for a variety of liquids was not feasible because the pumping capacities of available vacuum systems imposed major limitations on the environmental conditions experimentally attainable. Moreover, considerable difficulties were anticipated in instantaneously subjecting a liquid to a vacuum environment and monitoring the resultant phenomena.

As an alternate approach, an analytical study of the problem was undertaken using equations derived from the kinetic theory of gases in conjunction with standard heat and material balances. This report summarizes results obtained by this method.

Mechanism of Process

Cooling and subsequent freezing of a droplet can be visualized as taking place in accordance with the following sequence of events:

1) A quantity of liquid is suddenly subjected to an ambient pressure below its triple-point vapor pressure.

2) Assuming that under conditions of free fall the only forces acting on the liquid mass are surface tension and the pressure differential across the surface, spontaneous fracture of the mass into smaller and smaller droplets would be expected. A cursory survey of the literature failed to reveal any information as to the stability of various drop sizes when exposed to high vacuum. A force balance[1,2] across a plane through the center of the drop, followed by adjustment of units, gives

$$D = 30\gamma/P_0 \tag{1}$$

Table 1 gives stable drop diameters calculated by Eq. (1) for the liquids considered in this paper. Effects of surface curvature on vapor pressure and surface tension have been neglected. The values given in Table 1 assume that the fracturing process takes place at constant temperature. Results of freezing rate calculations, described later in this report, suggest that cooling and fracturing probably take place simultaneously, with stable drop sizes being achieved only after considerable reduction in temperature. The effects of this cooling would be to reduce the value P_0 and increase γ in Eq. (1), thus resulting in stable drop diameters larger than those shown in Table 1. The extent of this effect cannot be estimated because the rates of fracturing cannot be determined readily.

3) Cooling of the surface establishes a temperature gradient within the droplet.

4) With the center of the droplet remaining the warmest spot, the entire droplet cools until the surface begins to freeze at the triple point. It is when this spherical shell has formed that the drop appears "frozen," when observed or recorded visually.

5) After solidification has occurred at the surface, the surface temperature continues to fall toward some equilibrium temperature determined by the existing pressure in the vacuum chamber and the vapor pressure of the subcooled solid.

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Table 1 Maximum stable drop diameter in total vacuum

Liquid	Temperature, °K	Diameter, μ
H_2O	313	38.0
H_2O	373	2.3
O_2	90.2	34.8
CH_4	111.7	5.5
N_2	77.4	2.7
H_2	20.4	1.1

6) As the surface temperature decreases and the drop continues to cool internally, the solid/liquid interface moves toward the center of the drop until the sphere becomes completely solid; at this time an internal temperature gradient still exists.

7) Eventually the surface temperature comes to equilibrium; however, unsteady state transfer of internal heat continues until the entire droplet has reached the equilibrium temperature, and evaporation ceases to occur if no energy is transferred into the system. With the high vacua considered, virtually eliminating the possibility of conductive or convective heat transfer to the droplet, and the small surface areas and extremely short times involved minimizing radiant transfer, it is believed that the assumption of an adiabatic process is justified.

In a rigorous mathematical analysis of the forementioned process, equations of continuity for heat transfer within the liquid and the solid must be considered, along with heats of vaporization, sublimation, and fusion. A moving boundary problem appears as well.

While the complexity of the transient process has precluded a rigorous treatment at this time, a comparison of rates of conductive heat transfer and evaporative cooling was made and indicated that, for droplets small enough to be stable, preliminary estimates, based on the assumption that the temperature within the droplet is uniform and that freezing occurs at the triple point, would be of interest. To the extent that these assumptions are not realized, the formation of an external shell of solid will require shorter times, whereas the complete solidification of the droplets will require longer times than those calculated.

Mathematical Development

The weight of material leaving the surface of any liquid per unit time is related to the vapor pressure and temperature of the liquid by the expression[3]:

$$dW/d\theta = A\epsilon P_0(M/2\pi RT)^{1/2} \tag{2}$$

This equation is based on the assumption that the process takes place in a perfect vacuum.

An "evaporation efficiency" (ϵ) term is included to account for discrepancies between theoretical and experimental rates. For the purposes of this study, ϵ was assumed to have a value of unity. This value may be realistic for the three cryogenic liquids considered, but it is undoubtedly high for water for which values of roughly 0.05 usually are reported.[4–11]

In the more common case of evaporation against a finite pressure, a fraction of the molecules leaving the surface collide with other molecules and return. The fraction returning is related to the pressure and temperature by an expression similar to Eq. (2).[12] Consequently, the net rate of weight loss from any liquid surface in contact with its own vapor can be approximated by

$$dW/d\theta = A\epsilon(P_0 - P)(M/2\pi RT)^{1/2} \tag{3}$$

The preliminary experimental studies showed that the times required for cooling and freezing of relatively small drops of liquid nitrogen were short, apparently much less than 1 sec. Rather than providing a valid comparison between experimental and calculated data, these results emphasize the need for calculation because of the difficulties in carrying out experimental measurements for these systems. Refinements in experimentation are underway, however.

Because heat transfer to and from the liquid should be negligible for short exposures in a vacuum environment, a heat and mass balance may be written in which the heat required for vaporization is equated to that required for cooling to any selected temperature, or partitioned between that required for cooling to the triple point and freezing at that temperature.

Considering a temperature step sufficiently small so that average values for c_p and ΔH_v may be applied, the heat balance for cooling becomes

$$(W_l - \tfrac{1}{2}W_g)\bar{c}_p\Delta T = W_g\overline{\Delta H_v} \tag{4}$$

The $\frac{1}{2}W_g$ arises because there is concurrent cooling and vaporization, so that part of the material is precooled as a liquid prior to evaporation. Equation (4) implies that the gas leaves at the temperature of the liquid, which is believed to be a reasonable approximation. For freezing at triple point,

$$(W_{lt} - W_g)\Delta H_{ft} = W_g\Delta H_{vt} \tag{5}$$

Direct combination of Eqs. (3–5) becomes extremely cumbersome when c_p and ΔH_v are nonlinear functions of temperature. As an alternate solution, an incremental calculation may be used with Eqs. (4) and (5) to obtain the basic information necessary for numerical integration of Eq. (3). The temperature range is divided into ten equal increments for each case, W_g is determined using average c_p and ΔH_v over the increment, and W is calculated for the end of each step. Typical values for spherical droplets are given in Table 2.

After completion of these preliminary calculations, a polynominal is fitted to the cooling process data by the method of least squares to obtain an equation of the form

$$(P_0 - P)/T^{1/2} = a_0 + a_1W + a_2W^2 + \ldots + a_nW^n \tag{6}$$

Table 2 Cooling process data from preliminary calculations (LN_2, P = 0)

T, °K	P_0, mm Hg	D, μ	Moles × 10^{14}	$\Delta H_v \times 10^{-3}$	ρ, g/cm³	c_p, cal/mole-°K	$W \times 10^{13}$, g	$W^{2/3} \times 10^9$, $g^{2/3}$	$(P_0 - P)/T^{1/2}$
77.4	760	1.000	1.511	1.337	0.808	13.67	4.232	5.64	86.4
76.0	643	0.994	1.491	1.347	0.814	13.66	4.174	5.59	73.8
74.0	500	0.984	1.461	1.363	0.823	13.64	4.091	5.51	58.1
72.0	383	0.974	1.432	1.379	0.831	13.60	4.011	5.44	45.1
70.0	288	0.964	1.405	1.395	0.740	13.56	3.933	5.37	34.4
68.0	213	0.955	1.377	1.410	0.848	13.49	3.858	5.30	25.8
66.0	154	0.946	1.352	1.425	0.857	13.42	3.786	5.23	19.0
64.0	109	0.937	1.327	1.439	0.865	13.33	3.716	5.17	13.7
63.1	96	0.933	1.317	1.444	0.869	13.29	3.686	5.14	12.1

Best polynominal is $(P_0 - P)/T^{1/2} = 629.73 - 417.52\,(W \times 10^{13}) + 141.79\,(W \times 10^{13})^2 - 38.38\,(W \times 10^{13})^3 + 4.97\,(W \times 10^{13})^4$
Regression coefficient = 0.99999^{+}

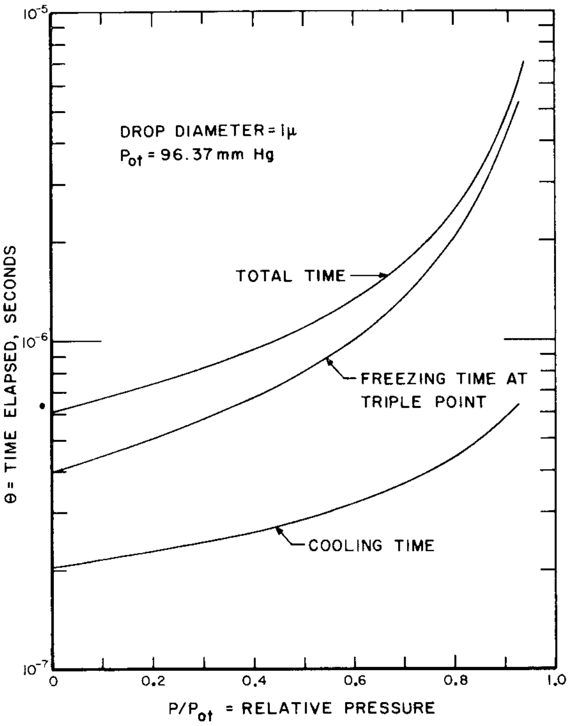

Fig. 1 Cooling and freezing times for liquid nitrogen at its boiling point.

In the present investigation, polynominals of degree 2–6 were obtained and that giving the best fit of the data was selected.

Combining Eqs. (3) and (6), and expressing surface area of a sphere as a function of weight, yields an equation of the form

$$\int\left[\left(\frac{\rho}{W}\right)^{2/3}\left(\frac{dW}{a_0 + a_1W + \ldots + a_nW^n}\right)\right] = 4\pi\left(\frac{M}{2\pi R}\right)^{1/2}\left(\frac{3}{4\pi}\right)^{2/3}\int d\theta = kM^{1/2}\int d\theta \quad (7)$$

Numerical integration§ of Eq. (7), using an average density, gives the time required for cooling the liquid to the triple-point temperature.

The freezing process takes place under conditions of constant temperature and vapor pressure. Substituting the triple-point values for these variables into Eq. (3), and expressing surface area as a function of weight, yields an equation of the form

$$\int\frac{dW}{W^{2/3}} = 4\pi\left(\frac{M}{2\pi RT_t}\right)^{1/2}\left(\frac{3}{4\pi\rho_t}\right)^{2/3}(P_{0t} - P)\int d\theta$$
$$= k\left(\frac{M}{T_t}\right)^{1/2}\left(\frac{1}{\rho_t}\right)^{2/3}(P_{0t} - P)\int d\theta \quad (8)$$

Integration of Eq. (8) gives the time required for freezing at the triple point.

Discussion

Calculations for liquid nitrogen, oxygen, hydrogen, methane, and water under selected operating conditions are given in Figs. 1–4. Inspection of the various curves confirms the observation that the times required for freezing are very short when the pressure against which evaporation is carried out is low relative to the triple-point pressure. For opposing pressures greater than approximately 50% of the triple-point vapor pressure, the freezing times increase markedly, approaching the triple-point vapor pressure asymptotically, where freezing ceases to occur. In general, the time required for freezing is longer than that for cooling and, therefore, is rate determining. As expected, freezing times decrease with decreasing droplet size and decreasing starting temperature, but increase with decreasing triple-point vapor pressure.

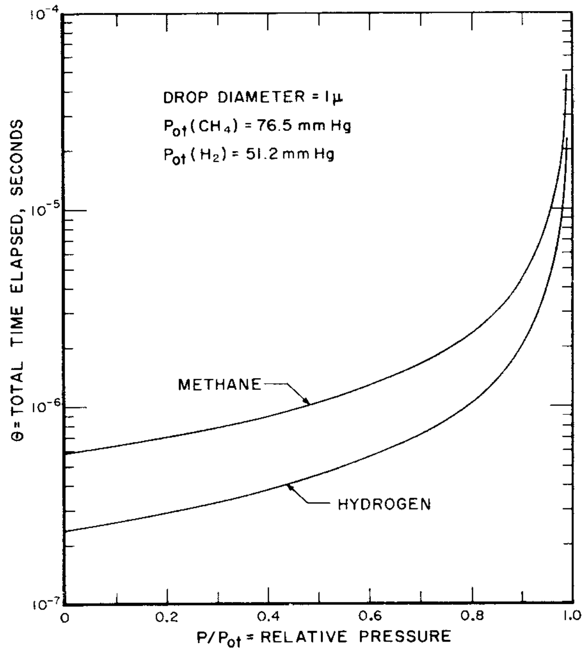

Fig. 2 Total freezing times for liquid methane and hydrogen at their respective boiling points.

Figure 1 shows that the freezing time is greater than the cooling time for nitrogen. Although the magnitudes of these values are dependent upon the relative values of ΔH_v, ΔH_f, and c_p, and on the temperature range between the boiling point and triple point for a given compound, the freezing

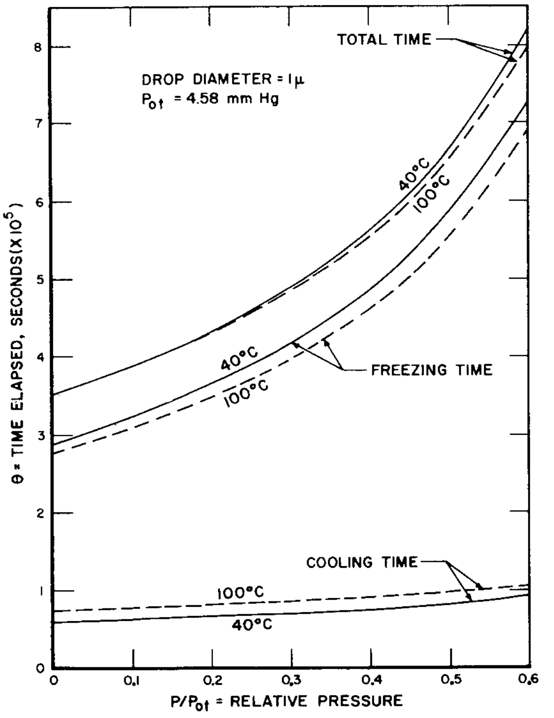

Fig. 3 Effects of initial temperature on freezing time of liquid water.

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§ A more sophisticated alternative would be closed-form integration, possible by curve fitting a polynomial in W to $(\rho/W)^{2/3}[T^{1/2}/(P_0 - P)]$ and substituting into Eq. (7).

time generally is dominant. Note that the cooling time appears disproportionately large on the semilog scale.

Hydrogen freezes more quickly than methane when the starting conditions for both materials are their boiling points at 1 atm (Fig. 2). The predominant factors appear to be molecular weight counterbalanced by density. A drop of methane of any given diameter contains about 5–6 times as much mass as a like-size drop of hydrogen.

Figure 3 shows that a drop of water at 100° C freezes faster than one at 40° C, although the difference is slight. This is due to the high freeze time/cool time ratio (~5), and the fact that by the time the 100°C drop reaches 40°C it has lost 16% of its original mass. Thus, there is less freezing to take place in the rate-controlling step for the drop which was initially hotter.

The larger a drop, the longer the time required for freezing, all other conditions being equal (Fig. 4). Cross-plotting would show a practically linear relationship between drop diameter and total freezing time. Keeping in mind the assumption of a spherical drop geometry, it may be seen that the area available for evaporation is proportional to D^2, whereas the volume that must be cooled and subsequently frozen is proportional to D^3. Thus, the rate of freezing should be proportional to D^2/D^3 or to $1/D$, and the time required should vary in direct proportion to D. This reasoning can be verified by the linear results obtained when the data from Fig. 4 are cross-plotted as time elapsed vs drop diameter, for various P/P_{0t} ratios.

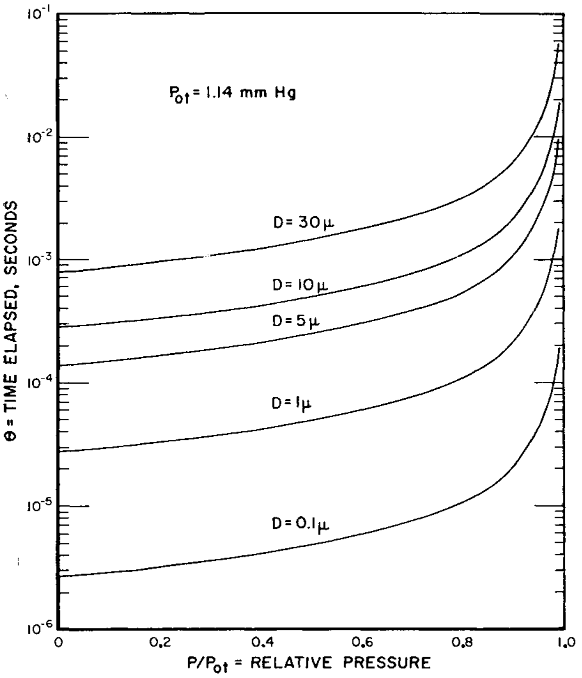

Fig. 4 Effect of drop diameter on total freezing time of liquid oxygen at its boiling point.

Further Considerations

Aside from the heat-transfer problem, which can be resolved in principle if not in practice, two of the concepts just discussed, which merit more careful scrutiny, are those of evaporation efficiency and stable drop size.

Evaporation efficiencies have been studied extensively by many workers, and a multitude of values are available. However, a wholly satisfactory method of predicting these values has yet to be presented.

Although disintegration of jet discharges has been explored by many workers, a cursory literature survey failed to reveal any work directly applicable to the present case in which 1) there is no energy input to the droplet, 2) ambient pressure is extremely low so that rapid evaporative cooling is occurring, and 3) free fall eliminates gravitational effects.

Since the relative rates of cooling and spontaneous disintegration of drops cannot be calculated readily, it appears that experimental observations of these phenomena would be of value. Limited work has shown that liquid nitrogen, indeed, does not freeze as tiny droplets but rather as a frothy mass. It was not determined, however, whether freezing took place without the proposed disintegration occurring or whether the tiny droplets agglomerated during or after freezing.

The method of calculation presented in this report is not rigorous, since numerous assumptions and approximations regarding the nature of the process and the form of the equations relating the several variables were necessary. Nevertheless, the agreement between the calculated values and the results of preliminary experiments with liquid nitrogen suggests that the method yields sufficiently close approximations for many applications.

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