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EFFECT OF SUBLIMATION ON THE BEHAVIOR OF CRYODEPOSITS

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16. Abstract

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SUMMARY

The rates of energy loss due to sublimation have been calculated for water, carbon dioxide, argon, krypton, xenon, and oxygen over the temperature range in which these materials are solids and have vapor pressures of less than 1 torr. These energy losses are compared with the possible thermal radiation losses of such deposits in the same temperature range.

The energy loss rate from these cryodeposits due to sublimation is quite sensitive to the surface temperature of the deposit. There is only a narrow temperature range over which the sublimation and radiation energy losses are of the same magnitude and in which both phenomena must be considered in a heat balance. At temperatures above this range sublimation is the dominant energy-loss mechanism; at lower temperatures the radiation energy loss is the more important.

The surface temperature, mass loss, and deposit lifetime of a subliming cryodeposit, both with and without an incident energy heat load, are evaluated. Numerical results are given for a typical ice cryodeposit, both with and without an incident energy heat load from a 300 K blackbody, for substrate temperatures ranging from 190 to 270 K, and for deposit thicknesses ranging from 10 micrometers to 1 centimeter.

INTRODUCTION

Early investigations of cryodeposit properties (refs. 1 to 5) were concerned mainly with the basic study of cryopumping and the storage of cryogenic fluids. Later, it was recognized that cryodeposits might present a problem to designers of space simulators. The cryodeposits formed on the walls of a space simulator, as a result of cryopumping, could change the thermal radiative properties of the simulator thereby making it possible for radiation to be reflected back to the model. Thus, the totally absorbing heat sink of space that must be simulated could be degraded.

A similar type of argument applies to the storage of cryogenic fluids. A cryodeposit that forms on a cryogenic storage tank, on a shadow shield protecting such a tank, or within the multilayer insulation around the tank could alter the thermal radiative properties of the system and upset the designed heat balance.

Actual space flights have proven that cryodeposits can form and remain stable on surfaces exposed to a space environment (refs. 6 to 8). Such deposits could alter the thermal radiative properties of surfaces and may be critically important to the thermal heat balance of a spacecraft.

These were the primary motivations for many of the more recent studies of the radiative properties of cryodeposits (refs. 9 to 15). Most of these investigations have been concerned with H_2O and CO_2 cryodeposits at liquid-nitrogen temperatures and lower. At these low temperatures sublimation rates are negligible and lifetimes are effectively infinite. Not only is the sublimation power loss from the surface of an H_2O or a CO_2 cryodeposit extremely small at 77 K, but it is several orders of magnitude smaller than the thermal blackbody radiation loss from a surface at that temperature. McConnell (ref. 15) considered the effect of sublimation on a cryodeposit that had formed on a 77 K substrate but did not define the effect that this term had on the overall heat balance.

Little attention has been paid to the behavior of cryodeposits at higher temperatures where the effect of sublimation on the heat balance could be significant. As a result of higher temperatures, cryodeposits will sublime more rapidly and exhibit characteristics greatly different from those found at low temperatures. The particular concern here is how the overall equilibrium heat balance is affected when the sublimation heat loss becomes significant. Specifically, it is desirable to know when sublimation heat transfer is an important part of the overall energy balance and how long the cryodeposit will persist.

In space flight these higher temperature cryodeposits could result from the jettisoning of spacecraft life support products, the efflux of thrustor propellant, or the warming of substrates upon which the more common low-temperature cryodeposits have formed. Also, if the presence of a cryodeposit would prove advantageous, means of growing the desired deposit could be developed.

It is the purpose of this report to present a definitive study of the effect of sublimation on the heat balance of various cryodeposits and to consider the interaction between a subliming cryodeposit and the electromagnetic radiation to which it is subjected. In particular, a method of determining the surface temperature of the cryodeposit will be presented that will permit the evaluation of the relative importance of the various heat-transfer mechanisms and the overall energy balance of an irradiated cryodeposit. Expressions for the rate of mass loss from the surface of the cryodeposit permit good estimates of the cryodeposit lifetime. As an example, numerical results are presented for one typical ice (H_2O) cryodeposit.

SYMBOLS

A	constant
B	constant
C_p	specific heat
d	cryodeposit thickness
$\overset{\circ}{d}$	time rate of change of deposit thickness
ΔF^o	free energy
I_d	energy flux reaching substrate
I_f	energy flux within the deposit
I_{inc}	energy flux incident on deposit surface
I_0	energy flux entering the deposit
k	thermal conductivity
L_{sub}	latent heat of sublimation
M	molecular weight
P	vapor pressure
q_{abs}	radiant energy absorbed per unit volume per time
Q_{dep}	energy absorbed by the deposit
Q_{net}	net energy loss at the deposit surface
Q_{rad}	radiation energy loss
Q_{sub}	sublimation energy loss
Q_{ss}	energy absorbed by the substrate
R	gas constant
$\mathscr{R}$	reflectance of the deposit complex
T	temperature
T_0	surface temperature
T_s	substrate temperature
t	time
W	sublimation rate
α	absorbtance of the deposit

ϵ'	effective emissivity ratio of the deposit
ρ	density
σ	Stefan Boltzmann constant
τ	relaxation time
τ_l	deposit lifetime

ANALYSIS

General Case

Consider a planar cryodeposit that has formed on a thin metallic substrate in a vacuum. The deposit is subliming and there is a mass loss from the surface. The analysis presented herein starts with the existance of a cryodeposit and does not consider any further deposition. Actually, simultaneous deposition and sublimation (or evaporation) will exist to some extent in any cryodeposit. When deposition vapor pressure and substrate temperatures are such that the deposition rate exceeds the sublimation rate, a cryodeposit will continue to grow until an equilibrium deposit thickness is reached. At this time the deposition rate is equal to the sublimation rate. For the equilibrium situation to change requires that one of the governing parameters change. This could come about by a decrease, or even an effective elimination, of the deposition vapor pressure or an increase in the substrate and hence the cryodeposit temperature.

The net heat transfer at the surface of the cryodeposit is the algebraic sum of the sublimation energy loss, the thermal radiation energy loss, and the energy absorbed from any incident thermal radiation. The relative magnitude of these various heat-transfer mechanisms determines when they are important in the heat balance and when they can be neglected.

The power loss, due to sublimation, from the surface of a solid in a high vacuum is a strong function of and is uniquely determined by the surface temperature. The details of the method used to determine this sublimation loss are given in the appendix.

If the cryodeposit is opaque, or even if it is translucent but can be considered a "gray" emitter, the radiation loss Q_{rad} can be obtained simply and is written as $\epsilon'\sigma T^4$ where the effective emittance of the deposit has been denoted by ϵ'.

The assumption of a gray deposit may not be very realistic for deposits that are highly transparent over large portions of the spectrum of the emitted radiation. However, more exact solutions taking the spectral properties of the deposit into account require detailed knowledge of these optical properties. And even with such detailed information, the actual computations could be very time consuming. McMahon (ref. 16), Gardon (refs. 17 to 19), and Merriam (ref. 12) treat this problem of the emissivity of translucent materials when the translucency and magnitude of this thermal radiation term for any particular cryodeposit are sufficient to warrant this refinement of the analysis.

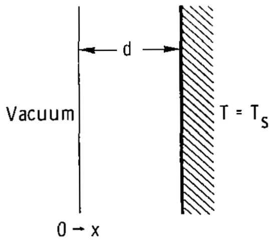
All the heat-transfer mechanisms are interrelated since each will affect the surface temperature and both the sublimation and radiation power losses are strong functions of the surface temperature.

The analytical determination of the surface temperature of a subliming cryodeposit will now be considered with the additional assumption that the substrate is a constant temperature energy source. Furthermore, because of the temperature range under consideration and the small temperature variation through the deposit, it is assumed that there is no net radiant transfer between different regions of the cryodeposit.

The temperature profile of a subliming cryodeposit is determined by the equation for the energy balance of a volume element within the cryodeposit:

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{d^2 T}{dx^2} + q_{abs} \tag{1}$$

where ρ is the density (g/cm^3), C_p is the specific heat (J/(g)(K)), T is temperature (K), t is time (sec), k is the thermal conductivity (W/(cm)(K)), q_{abs} is the radiant power absorbed (W/cm^3), and the coordinate system is as follows:



and the boundary conditions are

$$T(d) = T_s \tag{2}$$

$$k \left. \frac{\partial T}{\partial t} \right|_{x=0} = Q_{sub}(T_o) + Q_{rad}(T_o) \tag{3}$$

where Q_{sub} is the sublimation power loss and Q_{rad} is the radiation power loss from the surface of the cryodeposit.

Equation (1) is a time-dependent equation that is quite difficult to solve because it contains a moving boundary, namely, the subliming deposit's surface. Using a time-independent approach is justified if the fractional change in thickness of the solid over a typical thermal relaxation time is very small. Mathematically, this is expressed as

$$\left(\frac{\overset{o}{d}}{d}\right)\tau << 1 \qquad (4)$$

where $\overset{o}{d}$ is the time rate of change of the deposit thickness and τ is the thermal relaxation time of the deposit. If this condition is satisfied, then it is possible to calculate temperature distributions and sublimation rates at any given instant and subsequently determine the deposit thickness as a function of time.

Thermal relaxation times for problems of this type are typically given by reference 20

$$\tau \leq \frac{4d^2}{\pi^2} \rho \frac{C_p}{k} \qquad (5)$$

In the present report, deposit thicknesses ≤ 1 centimeter are considered and $\overset{o}{d}$ are obtained from the time independent solution. Inequality (4) was found to be satisfied for all cases considered, and in fact $\overset{o}{d}\tau/d$ never exceeded 10^{-2} even for the irradiated deposits. Thus, the analysis is continued using the steady-state form of equation (1):

$$k \frac{d^2T}{dx^2} = -q_{abs} \qquad (6)$$

with the boundary conditions (2) and (3).

The power absorbed by an elemental volume q_{abs} may be determined as follows. If I_{inc} is the incident power per unit area at the deposit surface, a fraction $(1 - \mathscr{R})I_{inc}$ is removed from the incident radiation field where $\mathscr{R}$ is the reflectance of the deposit substrate composite. This absorbed power is divided into a portion that is transmitted through the deposit and is absorbed directly by the substrate Q_{ss} and a portion that is absorbed throughout the deposit thickness Q_{dep}. Thus,

$$(1 - \mathscr{R})I_{inc} = Q_{ss} + Q_{dep} \qquad (7)$$

and

$$\int_0^d q_{abs}\,dx = Q_{dep} \tag{8}$$

The calculation of $\mathscr{R}$, Q_{ss}, Q_{dep}, and q_{abs} is a problem in the optics of thin absorbing films and is not a thermophysical problem. For specular surfaces and nonscattering deposits, q_{abs} and Q_{dep} may be obtained using the equations of classical thin film optics (ref. 14); for nonspecular, scattering, and absorbing media, the method of Merriam (ref. 12) may be used.

For convenience set

$$q_{abs} = Q_{dep} f(x) \tag{9}$$

so that

$$\int_0^d f(x)dx = 1 \tag{10}$$

and f(x) expresses the fractional distribution of radiation absorbed within the deposit. We now solve equation (6), which is rewritten as

$$k \frac{d^2T}{dx^2} = Q_{dep} f(x) \tag{11}$$

Integrating equation (11) twice and using the boundary conditions (eq. (2)) and (eq. (3)) yield

$$T_o = T_s - Q_{sub}(T_o)\frac{d}{k} - Q_{rad}(T_o)\frac{d}{k} + \frac{Q_{dep}}{k}\int_0^d dx \int_0^x f(x')dx' \tag{12}$$

This is the equation that determines the surface temperature of the cryodeposit. Equation (12) expresses the fact that the surface temperature of the deposit is lowered by the sublimation and radiation energy loss and raised by the energy absorbed from the incident radiation. Whether T_o is greater than or less than T_s depends on the relative magnitude of these three terms. Since the expression for Q_{sub} (given in the appendix) contains T_o in both an exponential and a square root term, equation (12) is transcendental. The last term of equation (12) considers the distribution of the absorbed energy. This term is independent of T_o and T_s insofar as the optical constants of the deposit and the substrate are independent of temperature. Thus, the energy absorbed in the deposit is coupled to the thermophysical problem only through the fact that the deposit thickness d changes due to sublimation. Any f(x) that expresses the fractional distribution of the absorbed energy, whether from a single pass through the deposit, from multiple reflections within the deposit, or even from a spectral analysis of the incident radiation, can be used in the solution of equation (12) if it can be specified.

Since the absorbed power term is independent of temperature, equation (12) is algebraic in nature and can be solved numerically. The absolute and the relative magnitude of the terms of equation (12) will determine which of the heat-transfer mechanisms has a negligible effect and which should be included to determine surface temperature.

The analysis thus far applies if substrate temperatures are independent of time. This is a valid assumption for deposits that have formed on cryogen tanks. However, for other surfaces such as shadow shields, a deposit might play a major role in determining substrate temperature. The energy loss due to sublimation will tend to lower the surface temperature.

However, the assumption of constant substrate temperature may not be too restrictive for the following reason: the thermal response time of the deposit-substrate complex will be of the order of, at least, seconds, while the characteristic thermal relaxation time of the deposit (eq. (4)) will usually be in the millisecond range. Thus, one may use the time-independent solution to calculate an instantaneous surface temperature and power loss for any given substrate temperature and then use these quantities in a numerical solution of the equations that determine the temperature of the substrate. That is to say, the deposit layer will equilibrate fast enough to follow the more slowly changing substrate temperature.

Optically Thick Case

A fairly simple example has been chosen to illustrate the application of these methods.

First, we assume that the incident radiation is absorbed by a translucent cryodeposit according to the usual exponential law of absorption with no multiple reflections within the deposit. Thus, the intensity of the energy flux at any location within the deposit is given by

$$I_f(x) = I_o e^{-\alpha x} \qquad (13)$$

where I_o is the intensity of the entering incident energy flux at the surface and the total power absorbed in a single pass through the deposit is

$$Q_{dep} = I_o - I_d = I_o(1 - e^{-\alpha d}) \tag{14}$$

Since the power absorbed in an incremental thickness is

$$\frac{\Delta(I_f)}{\Delta x} = I_o \alpha e^{-\alpha x} \tag{15}$$

the fractional energy distribution within the deposit which is $f(x)$ is given by

$$\frac{\dfrac{d(I_f)}{dx}}{I_o - I_d} \equiv f(x) = \frac{\alpha}{1 - e^{-\alpha d}} e^{-\alpha x} \tag{16}$$

Then,

$$\int_0^d dx \int_0^x f(x')dx' = \frac{d}{1 - e^{-\alpha d}}\left[1 + \frac{1}{\alpha d}(e^{-\alpha d} - 1)\right] \tag{17}$$

Thus, the absorbed power term in equation (12) for radiation absorbed according to the usual exponential law of absorption with no reflection at the substrate will be

$$I_o \frac{d}{k}\left[1 + \frac{1}{\alpha d}(e^{-\alpha d} - 1)\right] \tag{18}$$

And for the optically thick case where the value of αd is large enough so that essentially no radiation reaches the substrate, this expression reduces to

$$I_o \frac{d}{k}\left(1 - \frac{1}{\alpha d}\right) \tag{19}$$

In the limit, the magnitude of the absorbed power term will be $I_o\, d/k$ which is the opaque case.

Since an opaque layer yields the maximum effect on the surface temperature, this limiting case will be used in the remainder of this example. In the case of the ice (H_2O) frosts considered in reference 14, any thickness greater than 20 micrometers is optically thick. For such deposits $I_d = 0$ since no radiation reaches the substrate and $(1 - \mathscr{R})I_{inc} = Q_{dep}$. Since $(1 - \mathscr{R}) \approx 1$ (ref. 14), $Q_{dep} = I_{inc}$, and (eq. (12)) becomes

$$T_o = T_s - Q_{sub}(T_o)\frac{d}{k} - \epsilon'\sigma T_o^4 \frac{d}{k} + I_{inc}\frac{d}{k} \tag{20}$$

Equation (20) must be solved for T_o to obtain the net power lost by the irradiated deposit

$$Q_{net}(T_o) = Q_{sub}(T_o) + \epsilon'\sigma T_o^4 - I_{inc} \tag{21}$$

which may be positive or negative depending on the magnitude of the incident radiation and T_s.

Finally, the lifetime of a subliming deposit of thickness d is given by

$$\tau_l = \int_0^d \overset{o}{d}^{-1}\, d(d) \tag{22}$$

where the rate of decrease of the thickness $\overset{o}{d}$ may be obtained from equations (A1) and (A2) as

$$\overset{o}{d} = \frac{W}{\rho} = \frac{Q_{sub}(T_o)}{\rho L_{sub}} \tag{23}$$

RESULTS

The sublimation power loss for water, carbon dioxide, argon, krypton, xenon, and oxygen over the temperature range that these materials are solids has been calculated and the results are shown in figure 1. These calculations were based on equations (A1) and (A2). The thermal radiation loss from the deposit is also shown in figure 1 for deposit effective emittances of 1.0 and 0.1. Such a range should encompass the emittance of almost any cryodeposit and therefore yield an overall, qualitative comparison between sublimation and radiation heat transfer. Figure 1 also indicates the level of the

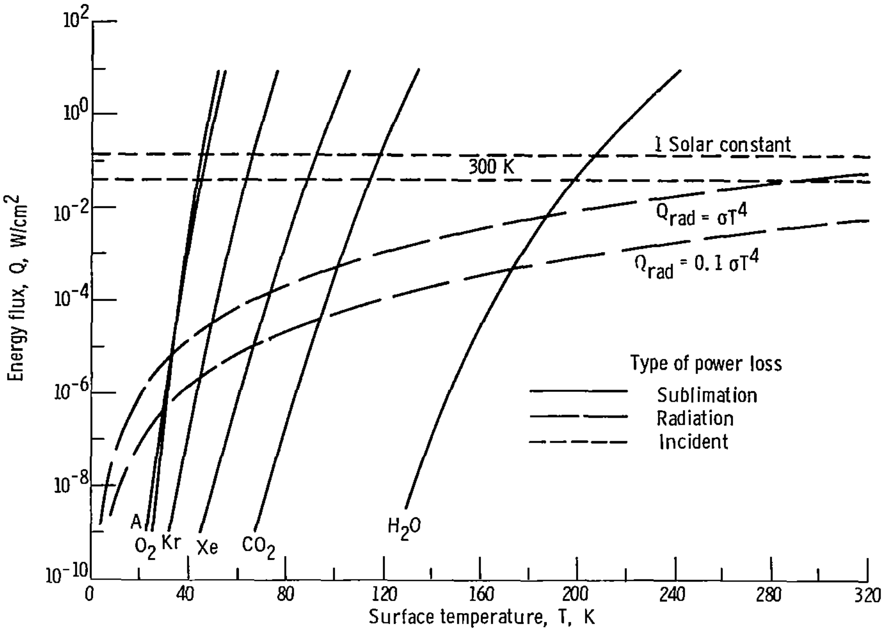


Figure 1. - Sublimation loss and radiation loss as functions of surface temperature for water, (H_2O), carbon dioxide (CO_2), xenon (Xe), krypton (Kr), argon (A), and oxygen (O_2).

power gained from a 300 K blackbody source and from 1 solar constant if all the incident radiation is absorbed at the surface.

Figure 1 shows that the heat balance analysis of a cryodeposit complex can be divided into high, middle (or transition), and low temperature regions. In the high-temperature region the deposit's thermal blackbody radiation energy loss is insignificant compared with the sublimation energy loss. In the low temperature region the sublimation energy loss is negligible compared with the thermal blackbody radiation energy loss. Only in a fairly narrow temperature range are the sublimation and the thermal blackbody radiation heat losses of comparable magnitudes so that both must be considered in the heat balance analysis. When incident radiation is absorbed by the deposit, it is possible for both the sublimation and the thermal blackbody power loss to become unimportant in a heat balance, particularly at low temperatures.

Equation (20) has been numerically evaluated for T_o by the Newton-Raphson technique for ice layers from 0.001 to 1 centimeter thick on substrates for which $T_s = 190$, 200, 210, . . . 270 K for one particular set of frost parameters ($\rho = 0.917$ g/cm^3; $C_p = 0.7$ J/(g)(K); k / 0.04 W/(cm)(K); and $\epsilon' = 1.0$), both with and without an incident energy heat load from a 300 K blackbody. The effect of ice layers of thickness <10 micrometers may be obtained by simple extrapolation of the curves to be discussed. However, it should be recognized that the assumption that the layer is optically thick (no radiation reaches the substrate) may not be valid for smaller thicknesses. The radiationless case may be extrapolated without error.

The temperature drop across the subliming frost layer is presented in figure 2 as a function of frost thickness for all substrate temperatures. For this particular ice deposit there is essentially no temperature gradient through the frost layer for a substrate temperature of less than 200 K. However, above this temperature the surface temperature of a 1-centimeter-thick frost is appreciably lower than the substrate temperature, in fact, as much as 45° lower for the 270 K substrate case.

The radiation equivalent to that coming from a 300 K blackbody tends to lower the temperature drop across the frost, but only in the case of the 190 K substrate is the effect of this irradiation enough to counteract the losses due to sublimation and radiation. The maximum effect that an incident radiation can have on the surface temperature of a cryodeposit will occur at low temperatures where only the last term of equation (20) must be considered. Thus the maximum temperature rise through a 1-centimeter deposit will only be 1 K for the 300 K blackbody case and 3.5 K for 1 solar constant absorbed at the deposit surface. If the deposit is not a blackbody radiator, the temperature drop will be diminished even further, but the effect is small. For the frosts considered here, eliminating the thermal radiation term entirely changes the surface temperature by only 0.18 K for the most sensitive case (T_s = 190 K, d = 1 cm).

With the surface temperature of the frost known, it is now possible to solve equations (22) and (23) for the frost lifetimes that have been plotted as a function of the frost thickness (fig. 3). Note that the curves for the lowest temperature substrates are quite straight and have slopes close to 45°. This is because there is little temperature gradient across these deposits so that the surface temperature is nearly independent of frost thickness and nearly equal to the substrate temperature. Consequently, the sublimation rates are nearly constant. As the temperature of the substrate increases, the upward curvature of the lifetime curve increases. This curvature for the frosts with an appreciable temperature gradient is due to the fact that thicker frost implies lower surface temperature, lower sublimation rate, and hence longer lifetime. If the temperature gradient through the frost had not been considered for the 270 K substrate temperature deposit, the 800-second life predicted would be only 17 seconds.

The lifetime curves for the irradiated frosts are seen to be only slightly below the curves for the unirradiated frost, indeed, for frost temperatures >230 K the irradiated case is not indicated because they coincide, within plotting accuracy, with the unirradiated lifetime curves. This behavior results because the radiant energy heat load of a 300 K blackbody is very small compared with the sublimation energy loss, which completely dominates the energy transfer in this temperature range.

Finally, note that the thickness as a function of time may be obtained from figure 3 by starting time at some value of τ_l and moving down to the left on the appropriate

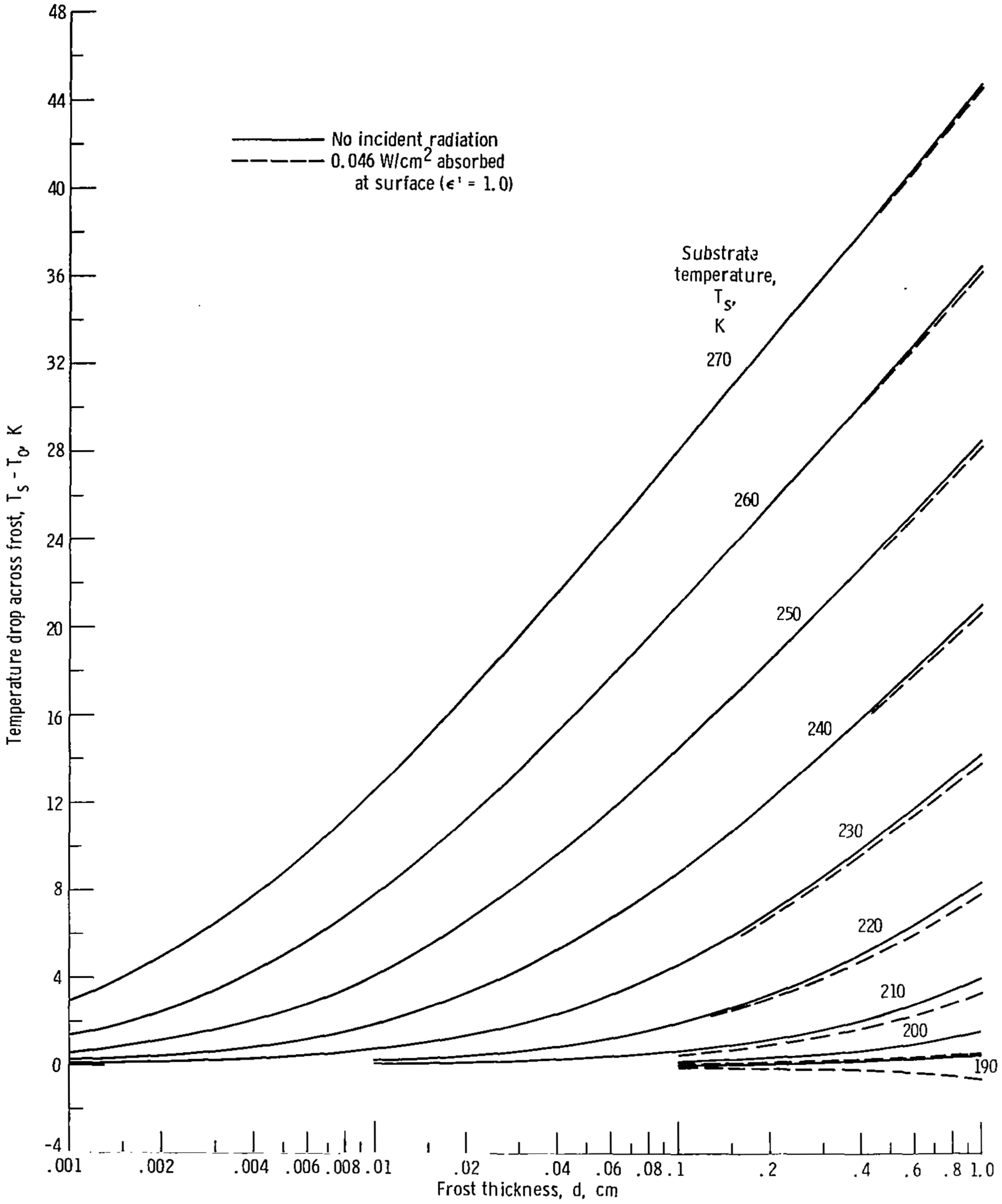


Figure 2. - Temperature drop across frost as function of frost thickness.

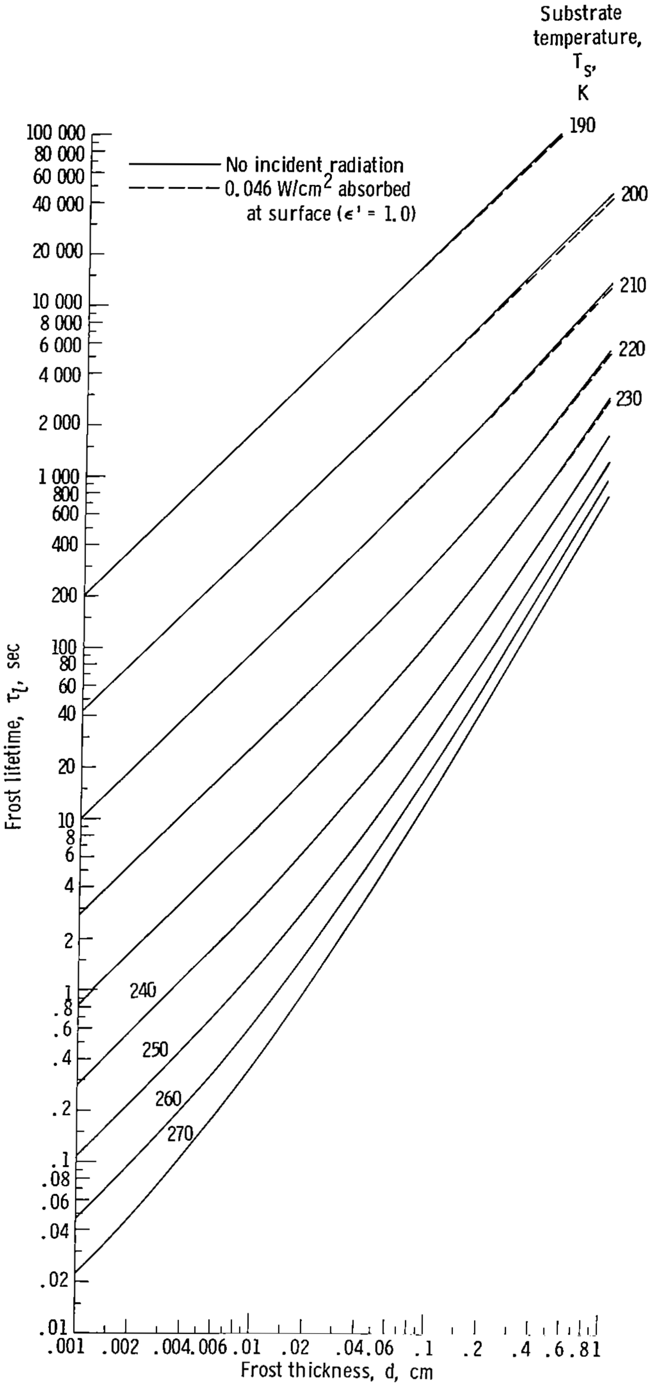


Figure 3. - Frost lifetime as function of frost thickness.

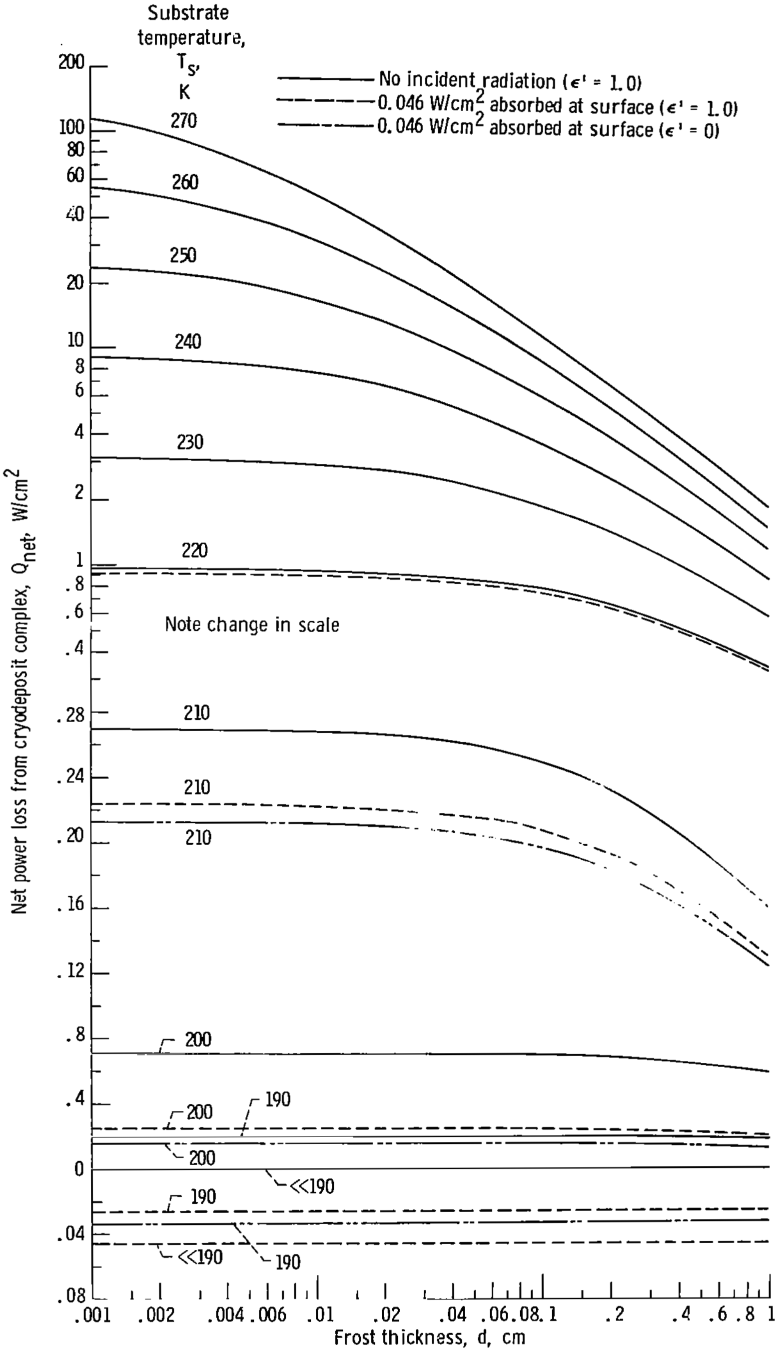


Figure 4. - Net power loss of frost as function of frost thickness.

curve. For instance, let us say that at $t = 0$, $d = 0.1$ centimeter and $T_s = 230$ K. Then $\tau_l = 110$ seconds corresponds to $t = 0$, and we find that after 80 seconds (110 - 30) the frost thickness has decreased to 0.033 centimeter.

The net power loss (eq. (20)) from the frost is plotted in figure 4 for the same range of d and T_s that was used in figure 2. The sublimation power loss decreases for increasing d since the surface temperature decreases. For $T_s \geq 230$ K the radiant heat load makes a negligible contribution to the energy balance. The irradiated frost continues to lose power until $T_s < 200$ K. For $T_s = 190$ K the irradiated frost gains a net 0.026 watt per square centimeter, which is essentially independent of thickness. For $T_s << 190$ K, the sublimation and radiation power losses are negligible, and the frost complex keeps the full 0.046 watt per square centimeter that it absorbs from the incident radiation field.

If the radiation power loss is eliminated from the problem, by setting emittance ϵ' equal to zero, the change in the net power is even less than the effect of the incident energy heat load, for the frost and temperatures considered here, and is not significant for the higher temperature frosts.

CONCLUSIONS

The sublimation energy loss of a cryodeposit is quite sensitive to the surface temperature of the deposit. There is a narrow band of temperatures over which the sublimation and radiation power losses are of the same magnitude, and both must be considered in an energy balance. Above these temperatures sublimation becomes the dominant energy loss mechanism, and the thermal blackbody radiation loss may be ignored. In fact, under many conditions even an incident thermal (300 K) heat load becomes insignificant compared with the sublimation energy loss. Consequently, the ''absorptance'' of the deposit complex is of little concern because the absorptance of incident radiation makes little difference in the power balance. At temperatures below this band, the sublimation energy loss is negligible and only radiation energy loss need be considered in a heat balance.

Although the radiation power loss could be important in the low temperature region, results indicate that this loss has no appreciable effect on the surface temperature of a cryodeposit. Hence including the radiation energy loss in the surface temperature determination, is an unncessary refinement.

Cryodeposits, and in particular ice deposits, that form on cold surfaces in a space environment, will persist for long times. Thermal, or even solar radiation should prove ineffective in removing a cryodeposit rapidly. In fact, for the higher substrate temperatures, the incident energy load equivalent to radiation from a 300 K blackbody has essentially no effect on the calculated lifetime of the frost. Hence, it appears that in space the only means of eliminating an undesired cryodeposit in a reasonable time, is to raise the substrate temperature.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 11, 1971,
124-09.

APPENDIX - ENERGY AND MASS LOSS FROM A SUBLIMING CRYODEPOSIT

Consider a planar cryodeposit with surface temperature T_o in a vacuum. The deposit is subliming and there is an energy and mass loss from the surface. The sublimation mass loss rate is found from the Langmuir equation (ref. 21):

$$W(T_o) = \frac{P(T_o)}{17.14}\sqrt{\frac{M}{T_o}}\left(\frac{\text{gm}}{\text{cm}^2 - \text{sec}}\right) \tag{A1}$$

where $P(T_o)$ is the vapor pressure (in torr) of the subliming solid of molecular weight M and absolute temperature T (K). This equation is generally restricted to values of $P(T_o)$ of 1 torr or less.

The sublimation power loss is then

$$Q_{sub}(T_o) = W(T_o)L_{sub}\left[\frac{\text{W}}{(\text{cm}^2)(\text{sec})}\right] \tag{A2}$$

where L_{sub} is the latent heat of sublimation (in J/g).

Evaluation of these losses requires knowledge of the vapor pressure at the cryodeposit temperature.

The most reliable method for correlating experimental observations on vapor pressure data is based on the calculation of the free energy. Expressions for the free energy are given by Kelley (ref. 22) for most elements and many inorganic compounds. Denoting the free energy by ΔF^o, the vapor pressure in torr may be derived by means of the relation

$$\ln P = -\frac{\Delta F^o}{RT} + \ln 760 \tag{A3}$$

Vapor pressure data are also available in references 23 and 24.

Kelley (ref. 22) also presents values for the latent heat of sublimation in calories per mole which are needed in equation (A2).

When expressions for the vapor pressure and latent heat of sublimation are unavailable for any particular cryodeposit, a good approximation for these values may be obtained in the following manner.

For vapor pressures below about 1 torr, it has been observed that for most materials, the vapor pressure can be represented as a function of T by the relation

$$\ln P = A - \frac{B}{T} \tag{A4}$$

where A and B are constants.

This is certainly valid for a narrow range of temperature variation. Assuming that the vapor pressure of ice obeys such an expression between the values given by Kelley (ref. 22) for the temperature range of 170 to 220 K, the data are fitted by the expression

$$\ln P = 23.907 - \frac{6118.63}{T} \tag{A5}$$

The heat of sublimation can then be obtained from Clapryon's equation

$$L_{sub} = -R\frac{d \ln P}{d\left(\frac{1}{T}\right)} \tag{A6}$$

where the slope $d \ln P/d(1/T)$ can be calculated from equation (A5).

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