THE TEMPERATURE AND SIZE HISTORIES

OF LIQUID H_2, O_2, and H_2O PARTICLES

RELEASED IN SPACE

March 6, 1970

CASE FILE
COPY

Bellcomm

THE TEMPERATURE AND SIZE HISTORIES

OF LIQUID H_2, O_2, and H_2O PARTICLES

RELEASED IN SPACE

March 6, 1970

A. C. Buffalano
R. D. Sharma

BELLCOMM, INC.   TR-105-5-1

ABSTRACT

Micron-size droplets of liquid H_2, O_2, and H_2O released in space during normal operations on Apollo lunar missions quickly freeze and reach equilibrium where the loss of energy from sublimation and emission of radiation just equals the absorption of radiation that is incident from the earth and the sun. For H_2 and O_2 the emission of radiation is negligible compared to sublimation but for H_2O it is very important and increases particle lifetimes significantly. Typically, at an altitude of 400 miles, where the earth is an important infrared source, sunlit particles decrease in radius with e-folding times of 15 (H_2), 120 (O_2), and 1200 (H_2O) secs. In cislunar space these times increase roughly by an order of magnitude. The accuracy of the results for H_2 and O_2 is limited by experimental uncertainties in the imaginary part of the index of refraction for these materials.

BELLCOMM, INC.

TABLE OF CONTENTS

INTRODUCTION

Water, liquid oxygen and liquid hydrogen are released in space during normal operations on Apollo lunar missions. Many such releases have been photographed from the ground and provide an opportunity to study the behavior of small particles of these substances in space [Lundquist 1969, Buffalano 1969, Edwards 1962]. A photograph taken during the Apollo 8 mission is shown in Figure 1. Studies of these particles are important for describing the spacecraft environment [Newkirk 1967, Kovar 1969, Grobman 1969, McPherson 1967] and for understanding the physics of interplanetary particles [Delsemme 1969, Franklin 1965, Kieffer 1968, Plummer 1969] and interstellar grains [Gehrels 1967, Wickramasinghe 1967, Krishna Swamy 1969].

Photo reduction of this kind of data requires a comprehensive model including both the particle motions in space and their size histories. This paper deals in detail with the second problem, the calculation of the size and temperature histories of water, oxygen and hydrogen droplets in the 0.1-100μ range. This range was chosen because we believe it includes the particles to be found in the Apollo releases.

The important physical processes are particle sublimation and emission and absorption of radiation. Our results show that the droplets freeze immediately, then rapidly reach temperatures where an energy balance is reached among these competing processes. Subsequent temperature changes occur as the continuous sublimation reduces the size of the particles and thereby reduces the absorption.

CONSERVATION EQUATIONS

Let E_S and E_R be the rate of loss of energy per unit surface area of a solid spherical particle of radius r and temperature T through sublimation and through emission of radiation, respectively. Let E_A be the rate of gain of energy per unit cross-sectional area through absorption of radiation. Let ρ and C be the density and specific heat and H_S be the heat of sublimation of the particle. These quantities are, in general, functions of the temperature and radius of the particle. The energy balance equation can be written as

$$\frac{4}{3}\pi r^3 \rho C \frac{\partial T}{\partial t} = -4\pi r^2 \left[E_S(T) + E_R(T) - \frac{1}{4} E_A(r) \right] \quad (1)$$

The time rate of change of radius is given by

$$\rho \frac{\partial r}{\partial t} = - \frac{E_S(T)}{H_S(T)} \quad (2)$$

Equations (1) and (2) are coupled first order differential equations whose solutions give T(t) and r(t).

SUBLIMATION

The rate at which sublimation removes energy from a particle depends directly upon the rate at which molecules leave the surface. This rate depends on the temperature of the particle and is the same whether the particle is in vacuum or in equilibrium with its own vapor. Since the molecular loss rate can be easily calculated when the particle is in equilibrium

with its vapor [Dushman 1949], one obtains for the energy
loss rate in vacuum

$$E_S = \alpha P \sqrt{\frac{m}{2\pi kT}} \; H_S \qquad\qquad (3)$$

where P is the equilibrium vapor pressure, m is the mass of
a molecule, k is the Boltzmann constant and α is the accommodation
coefficient, i.e., the fraction of molecules which impact the
surface and are absorbed from the vapor phase by the solid at
equilibrium.

The heat of sublimation at a given temperature is
related to the vapor pressure of the substance by the Clausius-
Clapeyron equation [Huang 1963].

$$H_S = \frac{kT^2}{m} \frac{\partial(\ln P)}{\partial T} \qquad\qquad (4)$$

This relation has been used in these calculations for H_2O and
O_2. However, the temperatures for H_2 will be found to be so
low that this relationship is not valid [Kelley 1935] and a
constant value of 122 cal/gm will be used. This is the
sum of the latent heat of fusion and the heat of vaporization
at $14°K$.

It has been found experimentally that the accommodation
coefficient is very nearly unity when a vapor is in equilibrium
with a solid of similar material [Dushman 1949]. Therefore
in subsequent calculations α has been taken to be one.

The vapor pressure for a large plane surface for all the substances can be written in the form

$$\log_{10} P \text{ (atm.)} = p + \frac{q}{T} + s \log_{10} T + uT + vT^2 \qquad (5)$$

The coefficients p to v are given in Table 1, for the temperature ranges of interest [Kelley 1935]. It is well known that the vapor pressure of small liquid droplets exceeds the vapor pressure of a plane surface of the liquid [Huang 1963]; however, the vapor pressure correction is very small for particles larger than 0.1μ and will subsequently be neglected.

The densities of H_2O, O_2 and H_2 are taken to be 1.0, 1.4 and 0.08 gms/cm^3, respectively. The specific heat of ice is taken as

$$C = (3.11 + 0.174 \, T) \, 10^{-2} \text{ cal/gm,} \qquad (5a)$$

and for oxygen as [Kelley 1935]

$$C = (-7.97 + 0.969 \, T) \, 10^{-2} \text{ cal/gm,} \quad 24 < T < 44$$
$$= 0.345 \text{ cal/gm,} \quad 44 < T < 54 \qquad (5b)$$

For hydrogen, experimental values (Orttung 1962) are approximated by

$$C = (0.125 + 0.010 \, T) \left[\frac{T}{10} \right]^3 \text{ cal/gm,} \quad T < 14^\circ \text{ K}$$
$$= 0.57 \text{ cal/gm,} \quad T > 14^\circ \text{ K} \qquad (5c)$$

ABSORPTION OF RADIATION

The sun and the earth are the major sources of the radiation that is incident upon the particle. Let $F(\lambda)$ be

the total radiation flux incident upon the particle, i.e.,
the amount of energy incident per unit time per unit cross-
sectional area per unit wavelength. Also let $Q(\lambda)$ be the
absorptivity defined as the fraction of the incident energy
absorbed at the wavelength λ. Then the rate at which energy
is absorbed by a unit cross sectional area of the particle can
be written as

$$E_A = \int_o^\infty Q(\lambda) \; F(\lambda) \; d\lambda \tag{6}$$

It is assumed that the earth and the sun radiate
energy as black-bodies, and consequently the flux which is
incident on the particle depends upon their temperatures.

$$F(\lambda) = \sum_{sources} B(\lambda, T_B) \; W \tag{7}$$

where B is the Planck's black-body radiation function

$$B(\lambda, T_B) = \frac{2\pi h \; c^2}{\lambda^5} \left\{ \frac{1}{e^{\frac{hc}{\lambda k T_B}} - 1} \right\} \tag{8}$$

and W is the view factor which depends upon the distance of
the particle from the source and upon the law of emission
from its surface. View factors for the earth's black-body
emission and for the earth's reflected visible sunlight
are given in Figure 2. In both cases the earth is
assumed to be a Lambert sphere [Pearse, 1963]. Because of its
great distance, the sun's view factor reduces to $(R_o/R_{AU})^2$
where R_o is the radius of the sun and R_{AU} is an astronomical unit.

The black-body temperature of the earth is taken as $280°K$ based upon experiments above the atmosphere [Valley 1965; Prabhakara 1968] when the seasonal and polar variations ($\sim 40°K$) are neglected. The corresponding Planck's function has a peak at 10.4μ, in the infrared. The black-body temperature of the sun is taken as $5900°K$ and the Planck's function is peaked at 0.5μ. If the particle is near the earth, reflected sunlight is also important. Thirty percent of the energy falling on the earth is taken to be reflected [Valley 1965].

The absorptivity Q is not only a function of the wavelength but also depends upon the size of the particle. Direct experimental data on $\dot{Q}$ for H_2O, O_2 and H_2 for all wavelengths of interest are not available so one turns to Mie theory for spherical particles [Van de Hulst 1957]. One can express the absorptivity as a function of the complex index of refraction $n(\lambda) = n_1(\lambda) - in_2(\lambda)$ and x, which is defined as $2\pi r/\lambda$. The absorptivities have been numerically calculated for a variety of values of n_1 and n_2 (Plass 1966). However, a modified analytic function due to Van de Hulst is used to calculate the absorptivity for $n_1 < 1.5$, $n_2 < 1$, and $x > 0.5$

$$Q = 2n_1 \left[\frac{1}{2} + \frac{e^{-w}}{w} + \frac{e^{-w}-1}{w^2} \right] \qquad (9)$$

where $w = 4n_2x$. For small values of x (<0.5), the Rayleigh

limit applies and the analytic expression [Krishna Swamy 1968]

$$Q = \frac{24\ n_1 n_2\ x}{(n_1^2 - n_2^2 + 2)^2 + (2n_1 n_2)^2} \tag{10}$$

is used to calculate the absorptivity directly.

For H_2O the complex index of refraction is experimentally available for the wavelength region of interest [Greenberg 1968, Irvine 1968]. A constant $n_1 = 1.33$ is chosen for all wavelengths and n_2 is shown in Table 2. Selection of mean values in the visible and infrared is reasonable since the black-body functions for the sun and the earth have peaks in these wavelength regions. For dirty ice, n_2 in the infrared is taken as 0.35 and in the visible as 10^{-4}. One of the biggest uncertainties in this treatment arises due to lack of experimental knowledge of $n(\lambda)$ for H_2 and O_2. Lattice vibrations from the solids could yield characteristic spectra in the infrared but such spectral data are not available. For liquid para-H_2, measurements of the dielectric constant, as a function of the density of the liquid, yield $1.01 < n_1 < 1.15$ for $0.01 < \rho < 0.10$ gms/cm^3. At the density of the solid, n_1 is likely to be 1.10 [Wickramasinghe, 1968]. The values of n_2 used are shown in Table 2. According to recent studies [Krishna Swamy 1968] the value of n_2 for H_2 may rise as high as 0.05 if there are trapped impurities and radiation damage, otherwise pure H_2 is a perfect dielectric with zero absorptive index in the visible and it is not likely

to vary appreciably with λ [Wickramasinghe 1968]. In the absence of other data the same values are chosen for O_2 as for H_2. Even though the precise values of n_2 for O_2 and H_2 are not known, they are likely to be smaller than those for H_2O which is a more complex crystalline substance and has large absorption in the infrared [Whalley 1969].

EMISSION OF RADIATION

The radiation emitted by a black-body is characterized by its temperature alone but for real materials it is customary to define a spectral emissivity $\varepsilon(\lambda)$ as the fraction of black-body flux radiated at wavelength λ. Thus

$$E_R = \int_0^\infty \varepsilon(\lambda)\, B(\lambda,T)\, d\lambda$$

$$= \bar{\varepsilon}\sigma T^4 \tag{11}$$

where σ is the Stefan Boltzmann constant and $\bar{\varepsilon}$ is an average emissivity. Dependence of emissivity on the radius of the particle is neglected in this treatment [Van de Hulst 1957]. It will be shown that emission plays no significant role for H_2 and O_2 even when $\bar{\varepsilon}$ is taken as one. For H_2O, experiments show that $\bar{\varepsilon}$ is likely to be greater than 0.94 [Griggs 1968], so it will be taken to be one.

PHASE CHANGE

During Apollo missions, material is released as a liquid near its freezing point. However, the evaporation rate of the liquid is so high that in a very short time enough material is evaporated to bring the drop to its freezing

point. Continuing sublimation causes no change in the temperature of the particle as the phase changes. If the initial radius of the drop is r_0 and the latent heat of fusion is H_f then the radius, r, at the completion of phase change is

$$r = r_0 \left[\frac{1}{1 + \dfrac{H_f}{H_s}} \right]^{1/3} \tag{12}$$

and the time t required for the phase change is

$$t \cong \frac{\rho H_s r_0}{E_s} \left\{ 1 - \left[\frac{1}{1 + \dfrac{H_f}{H_s}} \right]^{1/3} \right\} \tag{13}$$

If the latent heat of fusion is taken at 80 cal/gm for ice, 4 cal/gm for oxygen, and 14 cal/gm for hydrogen, then the change in radius is always less than 5%, and the time required for the phase change is less than 10^{-2} sec for the largest (100μ) particle. A simple calculation shows that the time required for heat transfer through the drop is of the same order of magnitude so the actual time required for the phase change may be slightly larger. It is also well known that solids exist in many phases having quite different optical properties. Which of these phases will be acquired by the freezing particles in vacuum is not clear, hence the most common phases [Kelley 1935] are assumed here.

RESULTS AND CONCLUSIONS

After the phase change is completed, continued sublimation and emission reduce the temperature of the particle

until an equilibrium is reached with absorption. Figures 3,4,
5 are typical energy diagrams for particles near the earth.
The temperature scale in each diagram is chosen to include the
range in which 1-100µ solid particles come to equilibrium. Since
absorption is temperature independent, a drop will quickly reach
thermal equilibrium where the absorption line crosses the com-
bined sublimation and emission curves. For example, a 100µ
oxygen particle will reach equilibrium at 40°K (Figure 4). If
the absorption cross section were only proportional to the area
then particles of all sizes would reach the same equilibrium
temperature. Since Mie cross sections are used, drops of
different sizes will reach different equilibrium temperatures.
As the drop continues to sublime and change size it will slowly
ride down the energy curve toward lower temperatures continuously
assuming the equilibrium temperature appropriate for its size.
This behavior is clearly seen in Figure 6 for O_2 particles of
different initial size. A very rapid decrease from the phase
change temperature to the equilibrium temperature is followed by
a much longer period of near constant temperature. Then as the
drop size changes the temperature again begins to fall. Water
and H_2 also show this behavior and reach equilibrium in 10 sec
and 10^{-3} sec, respectively.

The energy diagrams also show that for O_2 and H_2 in
the size and temperature ranges considered, sublimation is the
dominant energy remover so the choice of a particle emissivity
is unimportant. Furthermore, this means that the lifetimes of
O_2 and H_2 can be computed to the same accuracy as the absorption
is known. This is not the case for water where small errors in

the absorption can produce very large errors in the lifetime.

Figure 7 shows the size history of particles initially 100μ in radius. For H_2 and O_2 the absorption is nearly proportional to the radius so the particle radii decrease exponentially. For water, however, particle size changes very slowly once emission becomes the dominant process for energy loss. Table 2 shows the e-folding times* for particles both near and far from the earth in the sunlight. It also shows the range in e-folding times introduced by uncertainties in n_2 in the IR.

A more accurate analysis can be attempted when experimental data on the index of refraction become available. Future studies and measurements may also provide estimates of effects due to asphericity of the particles.

A. C. Buffalano

R. D. Sharma

$1011-\dfrac{ACB}{RDS}-sh$

---

*Time for an e-fold decrease in the radius of the particle.

ACKNOWLEDGEMENTS

REFERENCES

Buffalano, A. C., Effects of particle size and lifetimes on debris brightness. Program for Symposium on Optical Contamination in Space, Rocky Mountain Section, Optical Society of America, Aspen, Colorado, Aug. 13-15, pp. 4,7, 1969.

Delsemme, A. H. and D. C. Miller, A new model of the cometary nucleus and coma. Abstracts of Papers, The 130th Meeting of The American Astronomical Society, The State University of New York at Albany, p. 74, Aug. 11-14, 1969.

Dushman, S., Vacuum Techniques, J. Wiley & Sons, New York, pp. 16, 780, 1949.

Edwards, H. D., Optical observations of a high altitude release of water over Wallops Island, Va., on March 2, 1962, Tech. Report No. 1, Project A-597, Georgia Institute of Technology, Atlanta, Ga. 1962.

Franklin, F. A. and A. F. Cook, Optical properties of Saturn's rings. II. Two color phase curve of the two bright rings. Astron, J., 70, p. 704, 1965.

Gehrels, T., Wavelength dependence of polarization IX. Interstellar particles. Astron. J., 72, p. 1967.

Greenberg, J. M., Interstellar grains, in Nebulae & Interstellar Matter, ed., B. M. Middlehurst and L. H. Aller, Univ. of Chicago Press, Ch. 6, p. 221, 1968.

Griggs, M., Emissivities of natural surfaces in the 8- to 14-micron spectral region, J. Geophys. Res., 73, 7545, 1968.

Grobman, W. D. and A. C. Buffalano, New conclusions concerning the observation of faint sources from a sunlit spacecraft, Planet. Space Sci., 17, 1089, 1969.

Huang, K., Statistical Mechanics, J. Wiley & Sons, New York, p. 38, 1963.

Irvine, W. M. and J. B. Pollack, Infrared optical properties of water and ice spheres, Icarus, 8, 324, 1968.

Kelley, K. K., Contributions to the data on theoretical metallurgy. III. The free energies of vaporization and vapor pressures of inorganic substances, U. S. Department of the Interior, Bureau of Mines, Bulletin 383, pp. 49, 51, 80, 1935.

Kieffer, H. H., Near infrared spectral reflectance of simulated Martian frosts. Ph.D. Dissertation, California Institute of Technology, Pasadena, 1968.

Kovar, N. S., R. P. Kovar, and G. P. Bonner, Light scattering by manned spacecraft atmospheres, Planet. Space Sci. 17, p. 143, 1969.

Krishna Swamy, K. S. and N. C. Wickramasinghe, On the temperature of interstellar grains, Monthly Notices of Royal Astronomical Society, 139, 283, 1968.

Krishna Swamy, K. S. and N. C. Wickramasinghe, Strength of the fundamental bands of ice and solid hydrogen in composite grains, The Observatory, 89, 57, 1969.

Lundquist, C. A., Photometry from Apollo tracking, XII Plenary Meeting of COSPAR, Prague, May 1969.

McPherson, D. G., Apollo telescope mount-extended applications
    study program, Ball Brothers Research Corporation, NASA
    Contractor Report CR-61173, 1967.

Newkirk, G., The optical environment of manned spacecraft,
    Planet. Space Sci., 15, 1267, 1967.

Orttung, W. H., Theory of the anomalous heat capacity in
    solid hydrogen and deuterium at low o-hydrogen and
    p-deuterium concentration, J. Chem. Phys., 36, 652, 1962.

Pearse, C. A., Photometry and polarimetry of the moon and
    their relationship to physical properties of the lunar
    surface, Bellcomm, Inc. Technical Report TR-63-211-6,
    Appendix A., 1963.

Plass, G. N., Mie scattering and absorption cross sections for
    absorbing particles, Applied Optics, 5, 279, 1966.

Plummer, W. T., Infrared reflectivity of frost and the Venus
    clouds, J. Geophys. Res., 74, 3331, 1969.

Prabhakara, G., Feasibility of determining atmospheric
    ozone from outgoing infrared energy, Goddard Space
    Flight Center Reprint X-622-68-203, Greenbelt, Md., 1968.

Valley, S. L., Editor, Handbook of Geophysics and Space
Environments, Air Force Cambridge Research Lab., McGraw
    Hill Book Co., Inc., New York, Chapter 3, 10, and 16,
    1965.

Van deHulst, H. C., Light Scattering by Small Particles,
    J. Wiley & Sons, New York, 1957.

Whalley, E., The far IR spectrum of ice, Bull. Am. Phys.
    Soc., 14, 565, 1969.

Wickramasinghe, N. C. and K. S. Krishna Swamy, Solid hydrogen
   coated graphite particles in the interstellar medium,
   I., Preprint of the Steward Observatory, University of
   Arizona, November 1968, Tucson, Arizona.

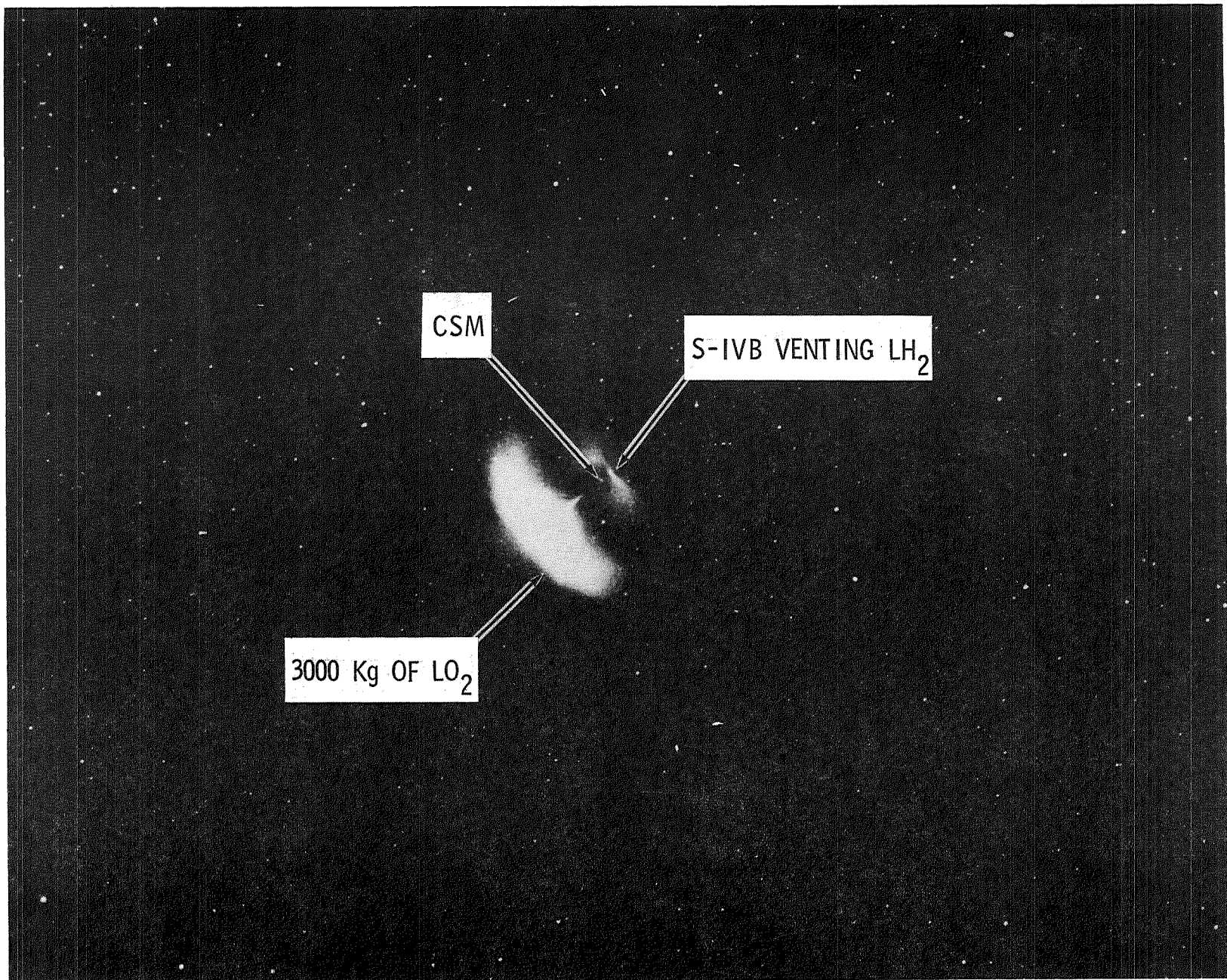Wickramasinghe, N.C., Interstellar Grains, Chapman and
   Hall, 1967.

FIGURE 1 – SMITHSONIAN ASTROPHYSICAL OBSERVATORY
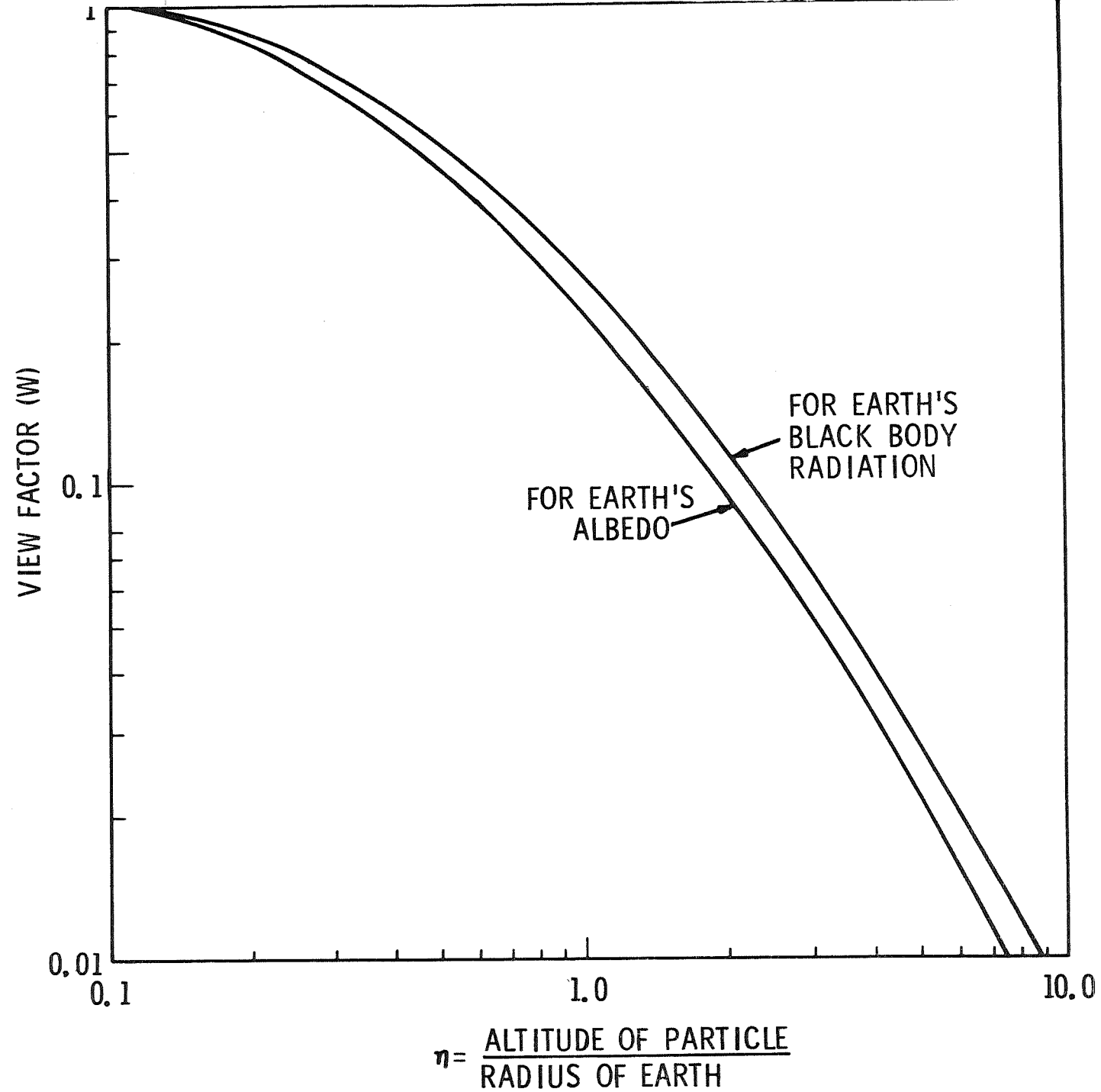PHOTOGRAPH OF APOLLO 8 CRYOGEN RELEASE.
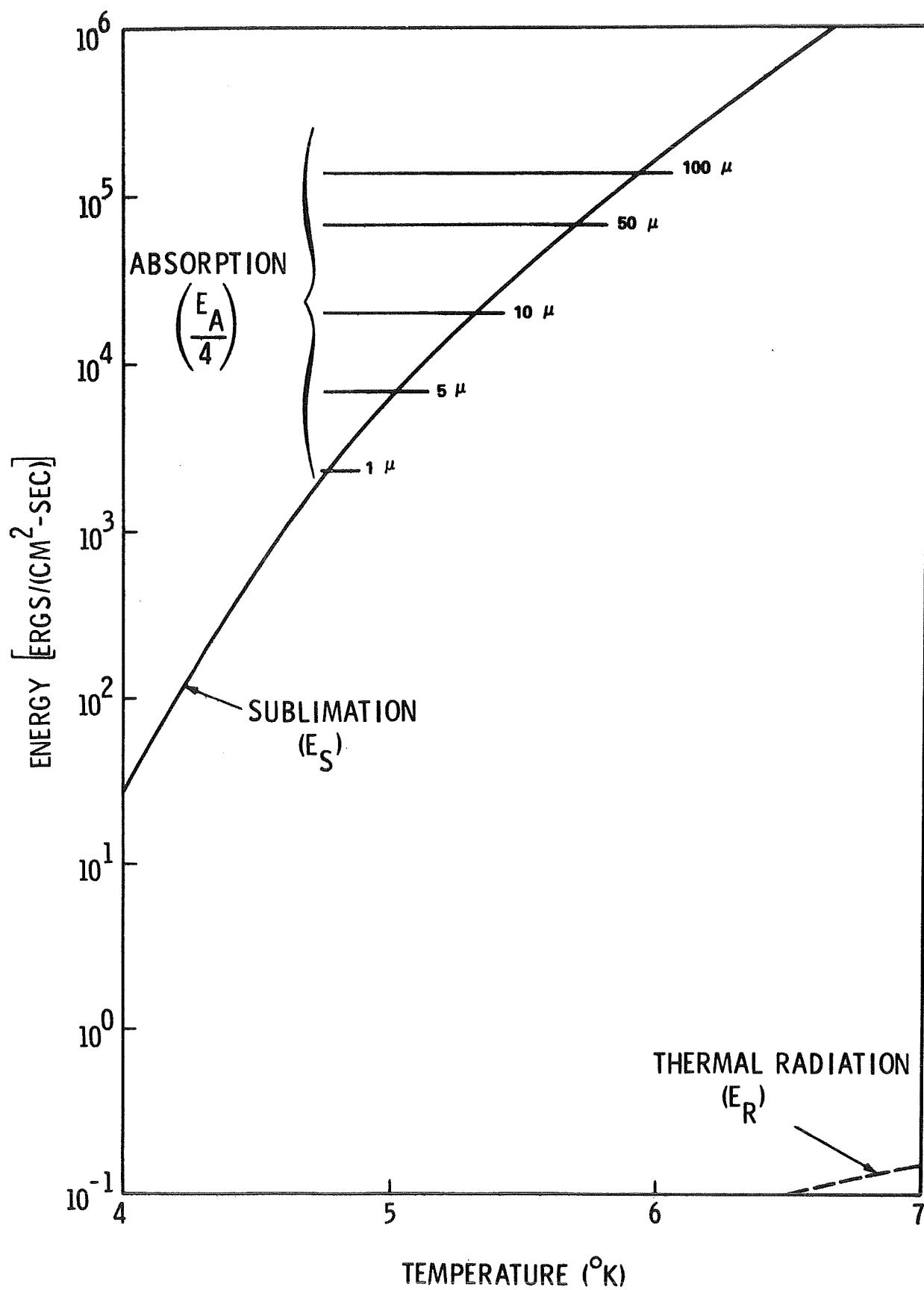
FIGURE 2 - VIEW FACTORS

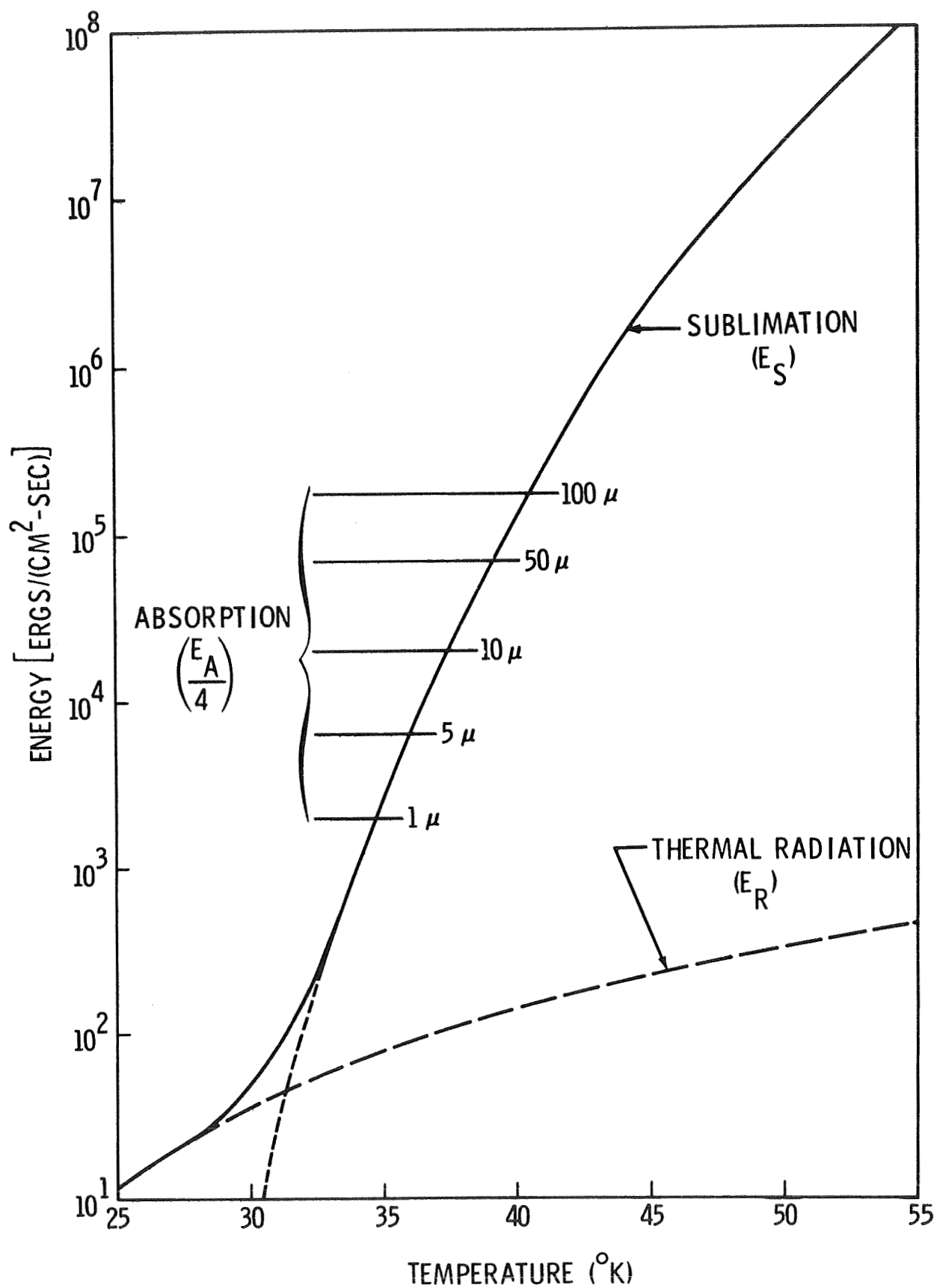FIGURE 3 - ENERGY DIAGRAM FOR H_2 (ALT. 400 MILES)

FIGURE 4 – ENERGY DIAGRAM FOR O_2 (ALT. 400 MILES)
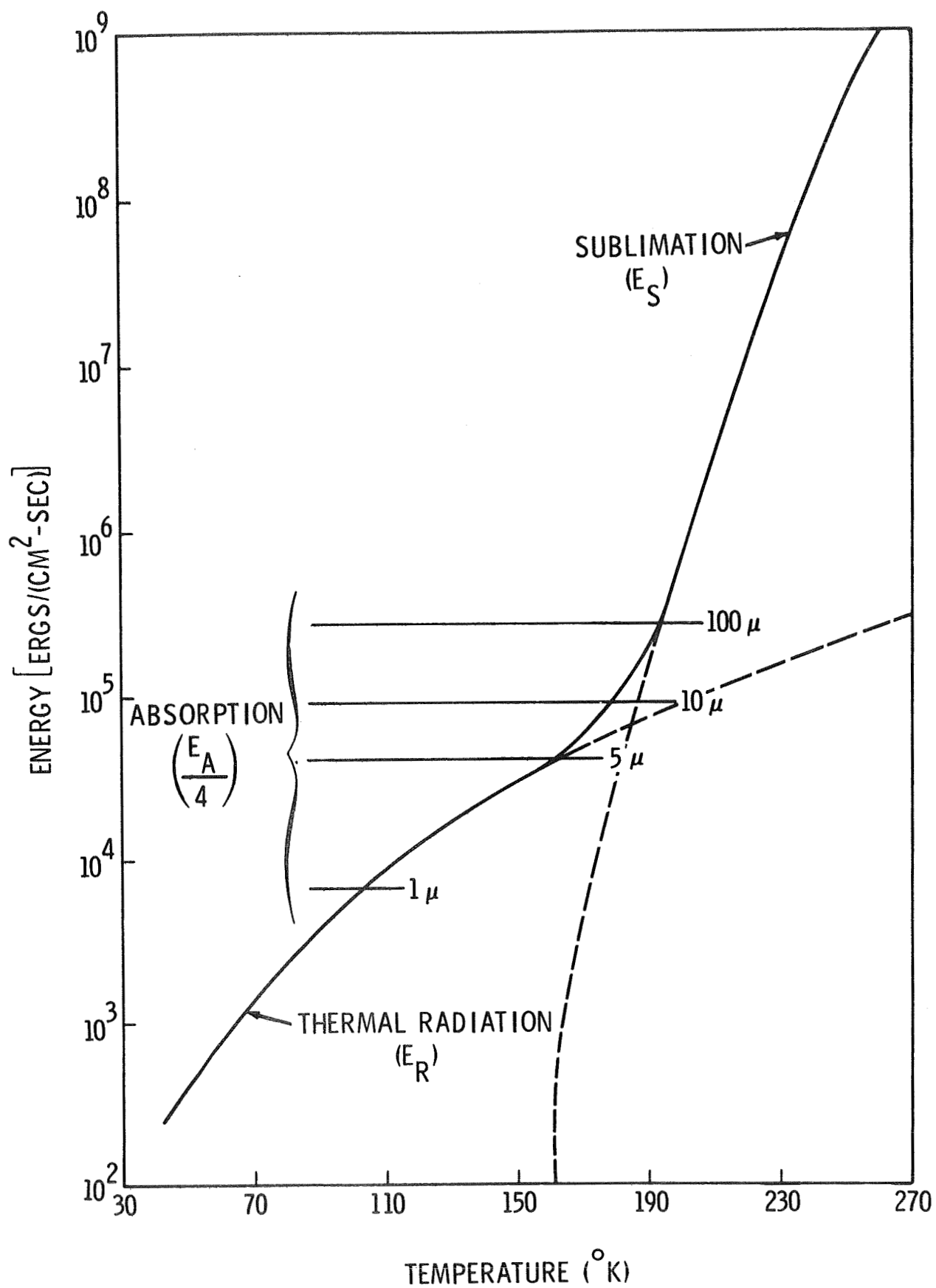
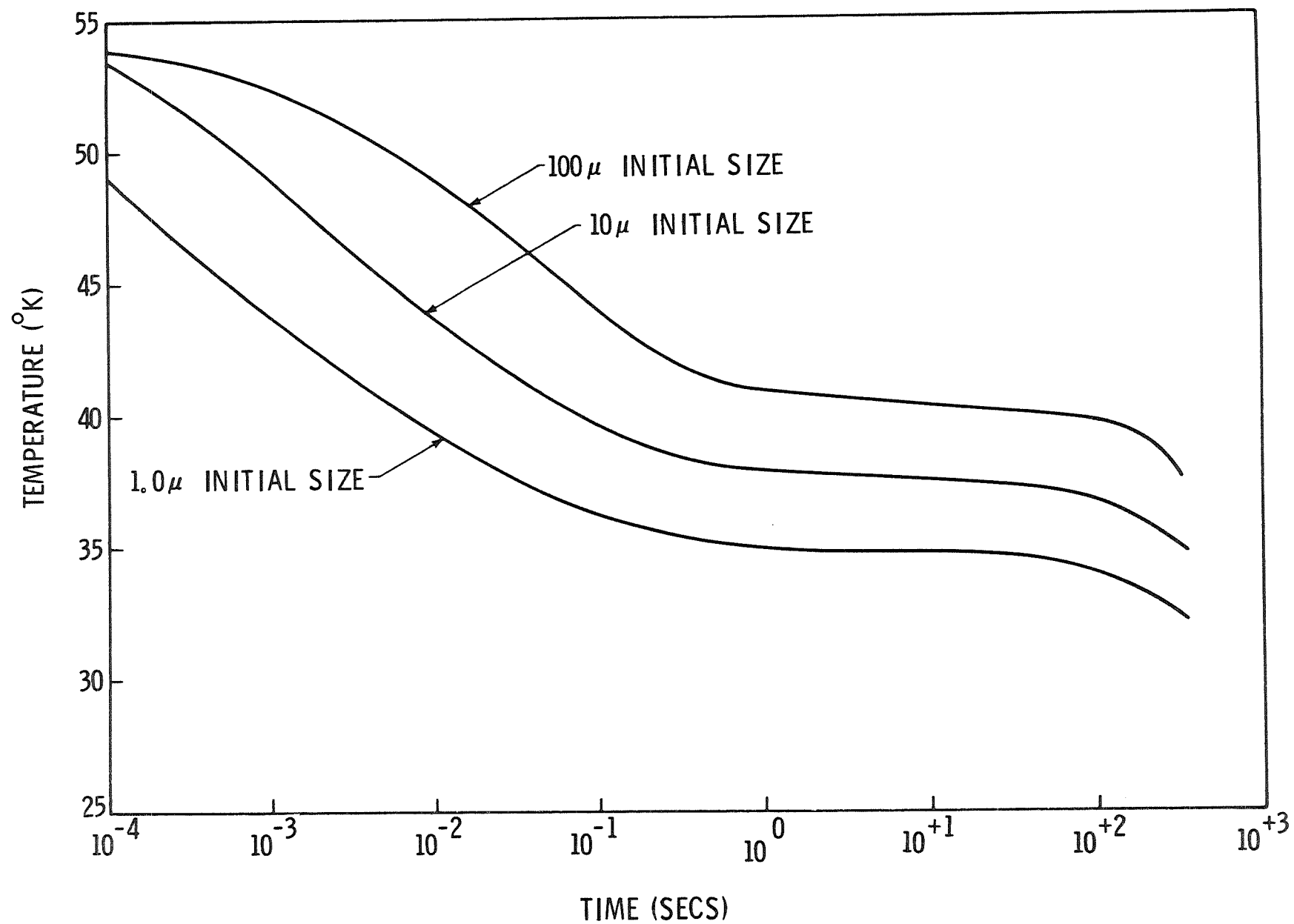FIGURE 5 - ENERGY DIAGRAM FOR H_2O (ALT. 400 MILES)

FIGURE 6 - TEMPERATURE HISTORY OF O_2 PARTICLES (ALT. 400 MILES)

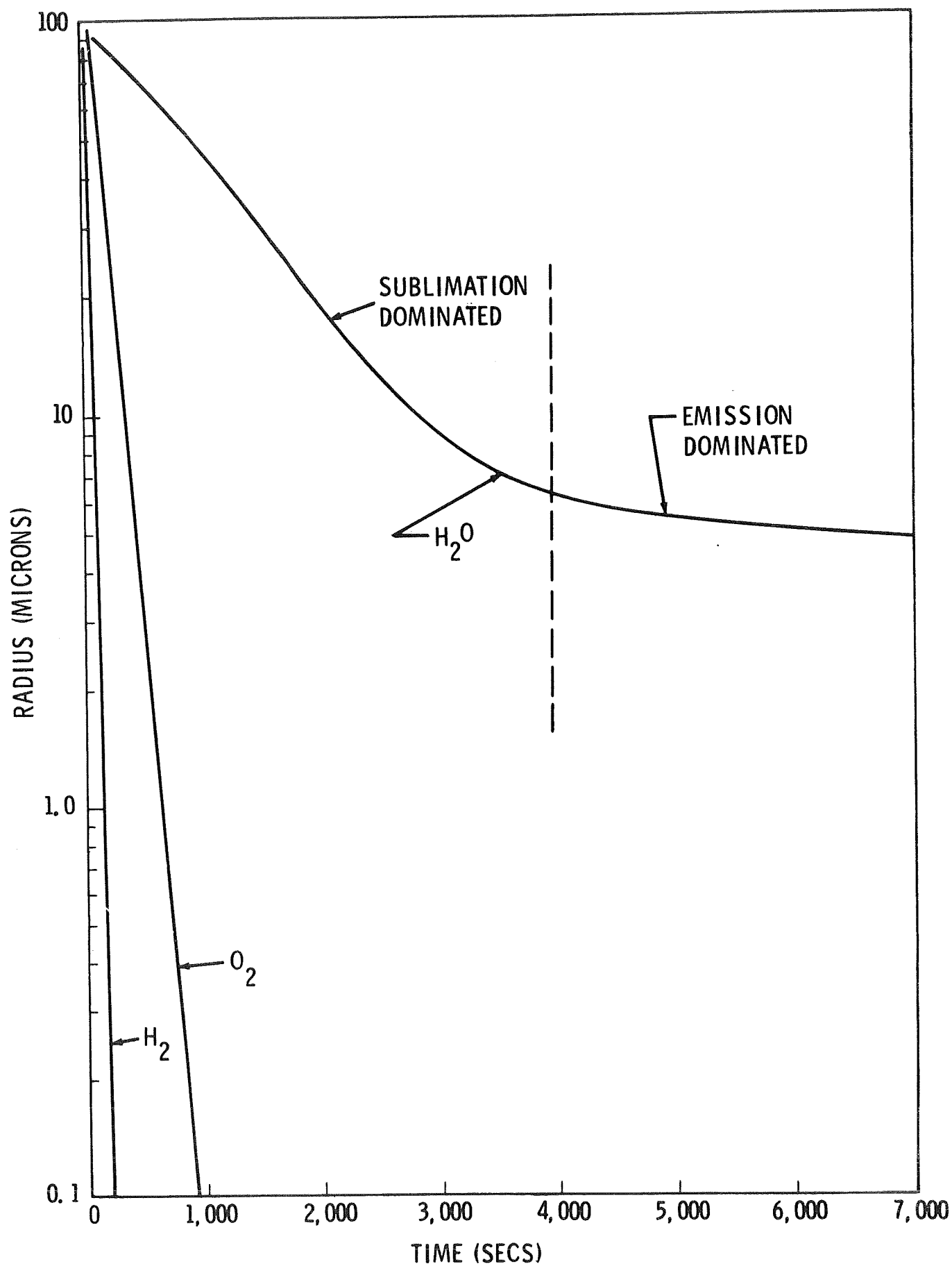FIGURE 7 – SIZE HISTORY OF PARTICLES (ALT. 400 MILES)

TABLE 1. COEFFICIENTS FOR VAPOR PRESSURE

SUBSTANCE	TEMPERATURE RANGE ($^\circ$K)	p	q	s	u	v
H_2 *	T < 14	-1.1108	-40.123	2.5	0	0
O_2	T < 24	-1.086	-454.64	5.084	-0.0356	0
	24 < T < 44	-0.819	-452.02	4.782	-0.0339	0
	44 < T < 54	9.516	-478.25	-2.055	0	0
H_2O	T < 273	-1.673	-2461.2	3.856	-0.0034	-4.87×10^{-8}

* SMALL CORRECTIONS FOR HYDROGEN BELOW 7°K

TABLE 2. INDEX OF REFRACTION AND e-FOLDING TIMES

$$n(\lambda) = n_1(\lambda) - in_2(\lambda)$$

SUBSTANCE	n_1 $0<\lambda<\infty$	n_2 $\lambda \leqslant 2\mu$	n_2 $\lambda > 2\mu$	e-FOLDING TIMES (SECS)		UNCERTAINTY RANGE NEAR EARTH (ALT. 400 MILES)	
				CIS-LUNAR SPACE	NEAR EARTH ALT. 400 MILES	n_2 $(\lambda > 2\mu)$	e-FOLDING TIMES
H_2O	1.33	.0001	0.05	9500	1200[#]	0.05 - 0.35	1200-200
H_2	1.10	0.0001	0.01	36	15	0.0001-0.1	27-5
O_2	1.10	0.0001	0.01	320	120	0.0001-0.1	250-30

\# FOR SUBLIMATION DOMINATED REGION (SEE FIG. 7)

BELLCOMM, INC.

NASA Headquarters

W. O. Armstrong/MTX
P. E. Culbertson/MT
M. Dubin/SG
E. W. Hall/MTG
T. A. Keegan/MA
R. L. Lohman/MF
D. R. Lord/MF
J. L. Mitchell/SG
L. Roberts/OART-M (2)
N. G. Roman/SG
A. D. Schnyer/MTV
H. J. Smith/SS
M. G. Waugh/MTP
J. W. Wild/MTE

Ames Research Center

D. E. Gault/SSP
C. A. Ponnamperuma/LXE

Goddard Space Flight Center

B. D. Donn/616
J. A. O'Keefe/640

Kennedy Space Center

G. F. Killmer, Jr. PA-ASE
G. M. Preston/DE

Manned Spacecraft Center

J. O. Annexstad/TH4
R. P. Kovar/TG4

Marshall Space Flight Center

J. B. Dozier/S&E-SSL-X

Cornell University

J. P. Pollack
C. Sagan

Department of Interior

S. F. Singer

Harvard University

R. M. Goody

High Altitude Observatory Boulder, Colorado

G. Newkirk

Kitt Peak National Observatory

J. W. Chamberlain

Smithsonian Astrophysical Observatory

A. F. Cook
F. A. Franklin
C. A. Lundquist

University of Calif. At Berkeley

J. Gaustad
G. C. Pimentel

University of Colorado

P. Bender

Bellcomm, Inc.

G. M. Anderson
D. J. Belz
A. P. Boysen, Jr.
D. A. Corey
C. L. Davis
D. A. DeGraaf
F. El-Baz
D. R. Hagner
N. W. Hinners
W. W. Hough
B. T. Howard
D. B. James
J. Kranton
H. S. London
K. E. Martersteck
J. Z. Menard
G. T. Orrok
W. B. Thompson
J. W. Timko
J. E. Waldo
M. P. Wilson
D. B. Wood
All Members Division 101
Department 1024 File
Central File
Library

Abstract only

I. M. Ross
R. L. Wagner