FINAL REPORT

OF RESEARCH ON:

THERMODYNAMIC PROPERTY DETERMINATION IN LOW GRAVITY

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By

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Table of Contents

I. Abstract

II. Calorimetry on Earth

III. Space Calorimetry

IV. Heating and/or Cooling Curve Methods

V. Experimental Considerations
- A. Choice of Materials for Study
- B. Choice of Atmosphere
- C. Temperature Distribution
- D. Thermal Conductivity
- E. Density
- F. Heat Capacity
- G. Results
- H. Rate of Energy Loss
- I. Rate of Power Reduction
- J. Temperature Determination
- K. Mass Determination
- L. Time of Experiment
- M. Control of Heating Program
- N. Time Line
- O. Generality of Approach
- P. Future Plans/Task Sequence

VI. Conclusions

I. ABSTRACT

Techniques for determining heat capacities and other properties of molten metals have been investigated and critically evaluated. One of the best is the levitation calorimetry technique although difficulties arise on certain classes of metals which suggest that the approach should be modified somewhat. In the micro-gravity environment of space, levitation is routine and it should be possible to determine heat capacities of metals which have low electrical conductivities, are very dense, or which have excessive vapor pressures.

Precisely determining heat capacities calorimetrically in space poses several problems. The weight of a drop calorimeter block along with the necessity of obtaining a large number of data points tend to make traditional approaches appear unfeasible. However, for many substances exhibiting sufficiently high thermal conductivities and with known emissivities, it appears possible to investigate their properties by observing the rate of cooling of a levitated sphere which is initially at a uniform temperature above the melting point. A special advantage of the levitation method is that considerable supercooling is expected, making the study of the heat capacities of molten metals both above and below their melting points possible.

II. CALORIMETRY ON EARTH

The traditional experiment by which one determines the heat capacities of molten metals consists of heating a sample of known mass to the desired temperature, followed by quickly placing it in a calorimeter of known heat capacity. From the temperature rise of the calorimeter, the enthalpy of the sample can be determined. If the procedure is done at two or more temperatures, then the heat capacity can be deduced from the slope of the enthalpy-temperature graph.

Actual investigations of course are not that simply performed, and when one is dealing with liquid metals, special problems arise. For example, traditional drop calorimetry involves a container in which the sample is heated and ideally, no reaction between the two occurs. For molten metals, most of which are notoriously corrosive, there is a tendency for alloying to occur with even the least reactive of containers. For this reason the technique of levitation calorimetry was developed. In it, the sample is levitated in a high frequency electromagnetic field in an inert gas or vacuum environment. Because of the containerless feature, no contaminating reactions occur. The sample can be dropped into a calorimeter positioned below the work coil by simply cutting power. (see Figure 1). Although this technique has allowed for the first time the accurate investigation of heat capacities and enthalpies of solid and liquid phases and heats of fusion of numerous metals,[1] the approach has several limitations.

One of these limitations is that the sample to be levitated must be conductive enough to levitate. Semiconductors, such as silicon, levitate poorly unless doped, a process which adds a

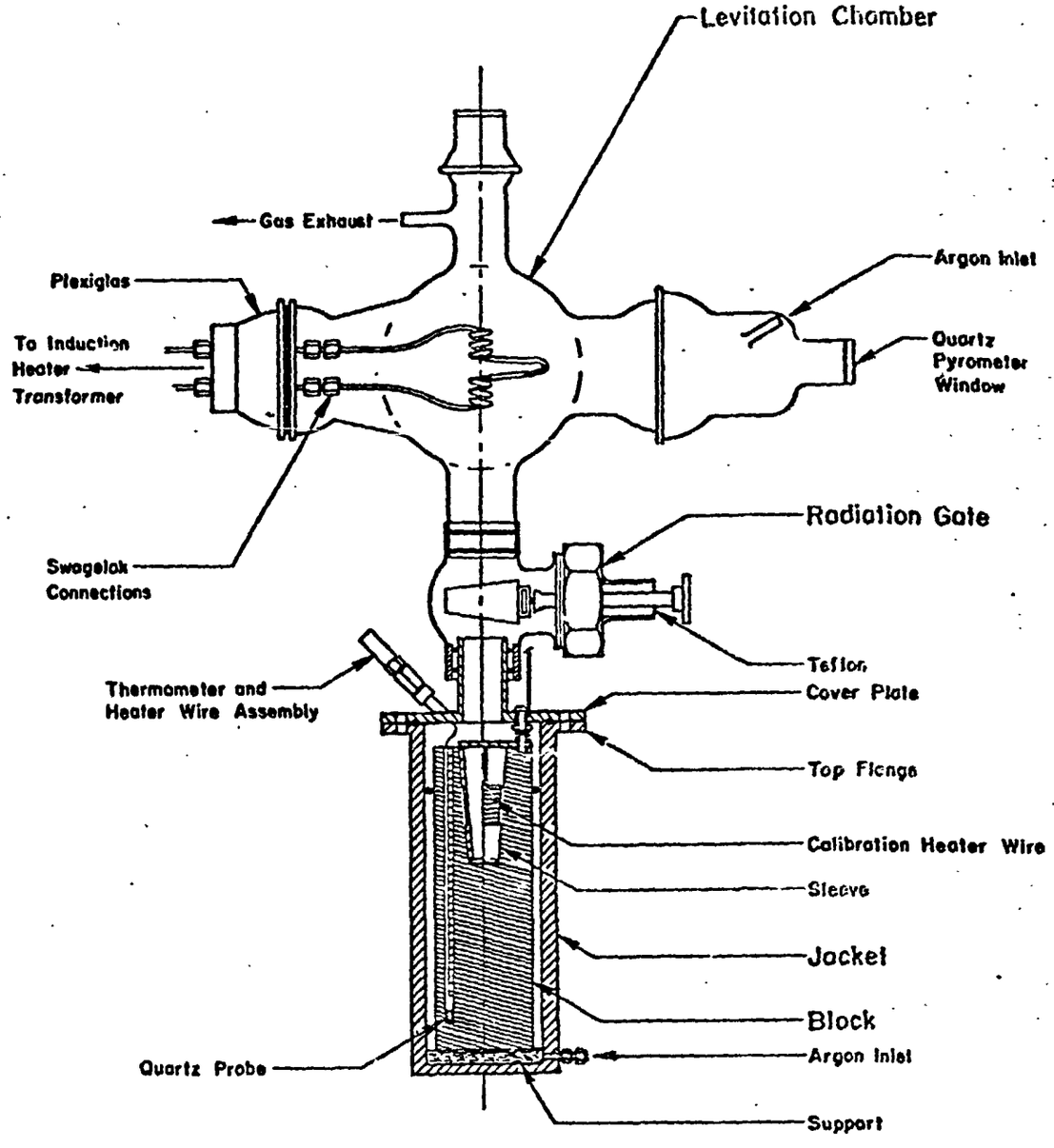

Figure I. Levitation Calorimeter

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degree of ambiguity to any results obtained.

Another problem is density. Some dense metals require an elaborate coil design and then only a small range of temperatures can be reached while levitated.

Still another problem is that of vapor pressure. Because temperatures are determined via optical pyrometry, a clear pathway to the sample is needed. When the vapor pressure of a sample is much above 10^{-4} atm, the volume of gaseous material evaporating is such that the sample may be obscurred.[2] Sometimes the amount evaporating is so great that the coil is shorted out, dropping the sample prematurely.

Finally, because so much power is necessary on the ground to levitate, the samples are usually heated far above the desired temperature by the necessary current. The high temperatures and associated high vapor pressures can cause the shorting out mentioned above. Variations in temperature are most conveniently obtained by the use of a conductive unreactive gas like He or Ar.

Several of these problems can be eliminated in space:

1. Because levitation is uncoupled from heating, conductivity and density no longer pose problems.
2. Lower power can be used, since only heating is required.
3. One has finer control of temperature.
4. Excessive superheating should be eliminated.

It is in anticipation of these advantages and with the extreme needs for better high temperature data in mind that this report describing a new calorimetric approach to determining properties of liquid metals at high temperatures has been prepared.

III. SPACE CALORIMETRY

One of the first obstacles encountered in a hypothetical space experiment is that of placing the sample in the calorimeter. Either (1) the sample must be pushed into the calorimeter, or (2) a calorimeter must be designed that could engulf the sample, or (3) the sample is always in the calorimeter. The second option appears unfeasable. A "gulp" calorimeter would have to enclose both the sample and the work coil--an uncertain amount of the sample's energy would therefore be carried away by the water-cooled copper windings; the stability of the sample in the coil during rocket flight is not sufficient to guarantee that the molten metal will float with power off without contacting the coil; the weight and cost of a moving calorimeter would be large; and finally, only one value of the enthalpy at only one temperature could be determined per flight.

The first possibility of ejecting or pushing a sample into the calorimeter appears more realistic. The actual mechanics of ejection could be achieved by using two coils to form the work coil, each wound in one direction only. The sample, which is levitated between the two coils, could be ejected by turning off the power to one coil. This method would require that the "bottom" coil be of a sufficient diameter to allow the ejection of the sample. Assuming that the problem of designing a coil which can both heat and eject a sample could be surmounted, there will still be the problem of the calorimeter receiver itself remaining. So that the calorimeter does not warm while the sample is being heated, it is desirable to have a radiation gate between the two. This would have to be moved prior to ejection.

Then, after the sample is situated in the calorimeter, to keep its heat from escaping, the entry hole must be sealed. These problems certainly could be overcome. The result of such design considerations would be a relatively bulky and massive setup with several moving parts, still capable of producing only one value of the enthalpy at one temperature per flight and no direct data on heat capacity.

After careful and detailed review of the first two traditional drop calorimeter designs, it is the conclusion of this report that the third "cooling or heating" curve method, i.e., a design in which heat is supplied or extracted from, the sample while it is in the calorimeter is the most reasonable approach to the problem. One can either heat a cold sample via a known program of energy input vs. time and detect deviations from the calibration curve caused by the presence of the sample or cool a hot sample by withdrawing some increments of energy, like shutting off a laser beam or an electron beam.

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IV. HEATING AND/OR COOLING CURVE METHODS

This approach is fundamentally different from ~~those~~ the first two mentioned above. For example, the cooling curve method involves heating the sample to some steady-stable temperature above melting, and rapidly cutting power to allow cooling to some lower value of temperature. For a sample cooling isothermally throughout, the rate of cooling $\left(\frac{dT}{dt}\right)$ will be a function of its heat capacity. If one knows the rate at which heat is being lost by the sample $\left(\frac{dH^*}{dt}\right)$ then

$$\frac{M \cdot \left(\frac{dH^*}{dt}\right)}{\left(\frac{dT}{dt}\right) \cdot m} = C_p$$

where M = molecular weight

m = weight of sample

Cp = heat capacity at constant pressure in cal/mole-degree.

The feature of isothermal cooling is essential if this approach is to produce data of sufficient accuracy to warrant its application. If an appreciable temperature gradient were to develop within the melt, then the outer surface would cool faster than an isothermally cooling sphere, and the heat capacity would appear smaller than it really is.

V. EXPERIMENTAL CONSIDERATIONS

A. CHOICE OF MATERIALS FOR STUDY

The feasibility of either the calorimetric or cooling curve experiment will be a function of the substance chosen for the experiment. For the first flight, it is desirable not to modify the available power supply designed for the rocket module. Hence, the ideal substance chosen should have a melting point below 1300°C. A second requirement for the ideal substance is that it have a vapor pressure of less than 10^{-4} atm at the melting point, although higher vapor pressures can be allowed above melting.

An element which fits these requirements is beryllium, with a melting point of 1287 ± 5°C[3]. It was used in the planning and initial flight of the rocket so there is no question concerning whether or not beryllium can be melted. The vapor pressure of 4.3×10^{-5} atm at melting is within usable limits,[4] and liquid heat capacity data are scarce. Although the heat capacity for liquid beryllium could conceivably be investigated on the ground, the supercooling possibilities will allow investigation of the heat capacity over a wider liquid range than normally obtained and the possibility of container contamination can be eliminated.

Another possibility is gallium, which melts just above room temperature, is exceptionally corrosive and has been little investigated at high temperatures. It would be possible to obtain data on liquid gallium from the peak temperature attainable with the power supply down to a temperature at which the pyrometer chosen can no longer see it.

It is by the second criterion that manganese, with a vapor pressure at melting in excess of one torr, fails. Other medium

melting metals--copper, silver, and gold--have already been adequately investigated above their melting point. Little or no data exists for these metals supercooled, however. Silicon is a poor conductor and is hard to levitate at 450 KHz.

There appears to be little advantage to using gallium as a test material. Its low melting point will prevent the possibility of observing supercooling, so it could probably be studied adequately using levitation on the ground. For beryllium, copper, silver, and gold, however, the study of their supercooled states would yield valuable knowledge. In the case of beryllium, all the data above melting would be new and useful. An advantage of using copper, silver, or gold for a first test is that the heat capacities for them are known above melting and a check on the accuracy of the method would be possible. Ideally, at least two elements should be studied, e.g., Cu and Be or Ag and Be or Au and Be.

B. CHOICE OF ATMOSPHERE

Because of the added cost and weight of modifying the capsule for vacuum work, the experiment is best performed in an inert gas, such as helium or argon. Argon, with its lower thermal conductivity, will allow higher temperatures to be achieved by minimizing conduction losses, so it is the gas of choice.

C. TEMPERATURE DISTRIBUTION

In order to determine the temperature distribution within the melt accurately, one must take into account conductive and radiative heat losses, evaporative heat losses, sample geometry, environmental temperature, and any back-radiation that might be present. If one is simply interested in an approximation to the solution, then the problem can be simplified by the assumption that the melt is spherical. This can be insured by controlling for spin, since in the free-fall environment, surface tension of a non-rotating melt will cause the formation of a sphere. Since the experiment is performed in argon, a gas of low thermal conductivity, conductive losses can be neglected when compared with radiative losses. Similarly, losses from evaporation can be neglected in this approximation. The problem thus reduces to the solution of the equation for heat flow from a sphere

$$\left(\frac{\partial^2 T}{\partial r^2}\right) + \frac{2}{r}\left(\frac{\partial T}{2r}\right) = \frac{1}{\alpha}\left(\frac{\partial T}{\partial t}\right) \quad ; \quad 0 \leq r \leq R,\ t \geq 0$$

where r = distance from center of sphere

T = absolute temperature

t = time

$\alpha = \frac{K}{\rho C_p}$ = thermal diffusivity

K = thermal conductivity

ρ = density

with appropriate boundary conditions. Electromagnetic stirring of the melt will insure that initially the sphere is isothermal. There are no sources or sinks within the sphere, and the only

heat losses occur at the surface. Newton's law of cooling cannot be used as a boundary condition because it only holds for small temperature differences between object and environment. Instead, the Stefan-Boltzman T^4-law must be applied. Thus, the boundary conditions are

$$T(r,0) = T_i, \quad 0 \leq r \leq R \quad t = 0$$

$$\frac{\partial T_o}{\partial r} = 0 \quad r = 0, \; t \geq 0$$

$$\frac{\partial Ts}{\partial r} = \frac{\varepsilon_T \sigma}{k} [T_e^4 - T_s^4], \; r = R, \; t \geq 0$$

where T_i = initial temperature of sphere

T_s = surface temperature

T_e = environment temperature

ε_T = total hemispheric emissivity

σ = Stefan-Boltzman constant

For small values of T_e that are likely to be encountered, the quantity $T^4 - T_e^4$ is approximately T^4. Therefore, the problem reduces to that of a sphere radiating into a vacuum at 0°K. This problem has already been solved using the method of finite differences on a computer.[5] In this solution, the assumption that area, emissivity, and heat capacity remain constant is made. These assumptions should certainly be approximately valid over the temperature range to be investigated.

In the analysis dimensionless parameters were employed in the following form:

Temperature T/T_i

Time $\alpha t/R^2 = kt/\rho C_p R^2$

Position r/R

Radiation $N_{RC} = k/\sigma \varepsilon_T T_i^3 R$

It was found that for systems with N_{RC} greater than 30 or time greater than 10, cooling is essentially isothermal; that is T/T_i is constant for all values of r/R at any time.

Evaluation of these parameters requires a knowledge of K, Cp, ρ and ε, quantities for which high temperature data is limited. Thus approximations will have to be made.

D. THERMAL CONDUCTIVITY

Thermal conductivity measurements for liquid metals are scarce and subject to large variations. More commonly, data on electrical conductivity are available. When that is the case, one can estimate the thermal conductivity by using the equation[6]

$$k = 2.32 \times 10^{-8}\ \sigma\varepsilon T + .012$$

where σ_E = electrical conductivity

For liquid copper at its melting point, electrical resistivity ρ = 30μΩcm.[7]. Hence $\sigma_E = 33300\Omega^{-1}cm^{-1}$, and $k = 1.06\ °K\ cm^{-1}\Omega^{-1}$ at 1358°K.

For beryllium, an estimate of $0.20°K\ cm^{-1}\Omega^{-1}$ is probably sufficiently accurate.

E. DENSITY

Densities of the liquid metals will be estimated as 10% lower than their room temperature values. Hence:

	ρ, gm^{-1} (25°)	ρ, gm^{-1} (melting)
Cu	8.92	8.03
Be	1.85	1.67

F. HEAT CAPACITY

Copper

Hultgren et al gave a value of C_p for liquid copper as 7.8 cal $g^{-1}K^{-1}$ based on data compiled as of October 1969.[8] In 1970, Chaudhuri et al determined C_p to be 7.89 ± 0.41 cal $K^{-1}m^{-1}$ by the levitation method.[9] In 1974, Stephens, also using levitation, found C_p for the liquid to be 8.0 ± 0.7 cal $m^{-1}K^{-1}$.[10] No data for the supercooled liquid are available.

Beryllium

Data on liquid beryllium are scarce. Hultgren gives the value for C_p as 7.04 cal $m^{-1}K^{-1}$ over the range 1560 - 2200 °K, based on the work of Kantor, Krasovitiskaya, and Kisel.[11] Based on the same work, though, Hausner gives C_p over the range 1560-2200°K as $C_p = 6.079 + 5.138 \cdot 10^{-4}\ T$ cal $m^{-1}K^{-1}$.[12] No other data appear to be available, and there are no heat capacity measurements at all for the supercooled liquid.

EMISSIVITY

For copper, total emissivity is 0.86.[13] The same will be assumed for the total emissivity of beryllium in lieu of data.

G. RESULTS

When N_{RC} is calculated, one finds 402 for copper and 51 for beryllium. Clearly temperature gradients within the melt should not pose a problem during the cooling period. It should be noted that the solution to the problem was done for a solid, i.e., non-convecting sphere. Convection currents, in part caused by residual electromagnetic stirring when power is cut, will tend to further decrease any gradients that may exist.

H. RATE OF ENERGY LOSS

As mentioned previously, it will be necessary to determine the rate at which the sample loses heat in order to calculate C_p. Either a theoretical or an empirical solution is possible. For the theoretical approach, the conductive, radiative, evaporative, and other losses must be considered. Although previously when an estimate of the magnitude of the temperature gradient was needed only radiation losses were considered, such is not the case here if data of high accuracy are to be obtained. Because values for hemispheric emissivity and surface area are likely to have large uncertainties, problems in determining the radiation term will exist. Back radiation from the work coil might also pose a problem, and the boundary condition at the surface will certainly be ambiguous due to the proximity of the coil.

A more accurate approach would involve an empirical determination of the rate of energy imput to the sample, $\left(\frac{dH_a^*}{dt}\right)$. This can be determined through on-ground testing by equipping a sample of known heat capacity with a thermocouple and observing the rate of temperature rise for various power settings. Because the energy input is dependent upon the electrical resistivity of the sample, it will be necessary to carry out tests on samples approximating the electrical resistivity of manganese or beryllium. If test samples can be found which satisfy the requirement of known heat capacity and electrical resistivity similar to that of manganese or beryllium, then measurements to a few percent accuracy can be made.[14]

It is thus possible to write an equation, empirically obtained, relating P to $\left(\frac{dH_a^*}{dt}\right)$. It is necessary though to know the value of

$\frac{dH_r^*}{dt}$, the rate at which heat would be lost if there were no power input, for any value of T in the range investigated. To do this, the sample is heated to some temperature where it is liquid, and the power measured at equilibrium. Since the temperature is constant, $\frac{dH_a^*}{dt} = \frac{dH_r^*}{dt}$, and since the power is known, the value of $\frac{dH_r^*}{dt}$ at that temperature also is known. By heating and cooling the sample over the range of temperatures to be investigated, $\frac{dH_r^*}{dt}$ can be determined as a function of temperature. It would then be possible to cut the power to the work coil. The sample will then cool isothermally, and from the rate of cooling and the rate of heat loss, C_p can be found.

This method assumes that there is no change in sample geometry when power is cut. When full power is applied to the melt, the sample will have a geometry which is influenced by the geometry of the coil. When power is reduced, though, the sample will tend to form a sphere, which has a smaller surface area than any other shape. Since radiative losses vary linearly with surface area, there will be a dependence of $\frac{dH_r^*}{dt}$ on the shape of the sample. It would be advantageous then to construct a coil which tended to favor formation of a spherical melt, so that little surface area change would occur when power is reduced.

I. RATE OF POWER REDUCTION

Ideally, when it is time to allow the sample to cool, power should both be reduced instantaneously and to zero power. As currently designed, neither feature is completely achieved. Instead, power is reduced over a one to two second period to a level approximately 2% of peak power. The problem with a slow reaction of power is that the rate of heat loss is given by

$$\frac{dH^*}{dt} = \frac{dH_r^*}{dt} - \frac{dH_a^*}{dt}$$

For times shortly after power turndown has begun, both right hand terms will be large, and their difference subject to a large error. Thus for temperatures close to the initial temperature, values of C_p will be difficult to obtain.

However, it is possible to cut power instantaneously if the sample is not oscillating in the coil. This can be achieved for a well outgassed sample. Thus, by using a sufficiently purified sample, the slow turn-down precaution can be dropped, and values of C_p obtained over the entire range of temperatures.

J. TEMPERATURE DETERMINATION

The temperature of the molten sample is best determined with an optical pyrometer. Because black body conditions cannot be achieved, information and/or assumptions regarding emissivity will be needed. Either a one or two-color pyrometer is suitable for the experimental studies.

(1) One-color pyrometer

Temperature determination with a pyrometer of this type involves the measurement of brightness temperature T_b at fusion. From this measurement, together with knowledge of the true temperature T_0 and the wavelength at which it was measured λ, emissivity ε_λ can be found from the equation

$$\varepsilon_\lambda = \mathrm{EXP}\left\{\frac{1C_2}{\lambda}\left(\frac{1}{T_0} - \frac{1}{T_b}\right)\right\}$$

where C_2 = 2nd radiation constant 1.438cmK, IPTS-68.

By assuming that emissivity is not a function of temperature, an accurate assumption for liquid metals, true temperature can then be determined from the relation

$$T_0 = \left\{\frac{\lambda \ln \varepsilon_\lambda}{C_2} + \frac{1}{T_b}\right\}^{-1}$$

To determine ε_λ accurately, a several second fusion plateau is desirable. Since the melting points of manganese or beryllium are fairly close to the maximum temperature of the apparatus as now designed, it is likely that this will be the case.

(2) Two-color pyrometer

A two color pyrometer operates on the assumption that emissivity varies in the same way at two wavelengths. By determining T_b at two temperatures simultaneously, it is possible to eliminate the

emissivity term, and true temperatures can be determined directly.

Either pyrometer should prove adequate for the job. The main criteria for choosing one should be precision and size. In the temperature range to be studied, pyrometers accurate to better than ± 0.5% are available. Size and weight should be minimized so that the pyrometer will fit into the limited space provided. In order to facilitate data collection, the pyrometer selected must be of the automatic recording type. The pyrometer must have a focal length that will allow focusing on the sample within the small chamber. Its components must be able to withstand the acceleration during takeoff.

Optical pyrometers often make use of filters in order to view a wide range of temperatures. So that there is no discontinuity in temperature recording, the pyrometer used should be one that does not require a filter change in the range studied.

Because rapid cooling of the molten sample can be expected, the pyrometer chosen should have a fast response time. The cooling kinetics approach will require accurate knowledge of temperature as a function of time, so it is essential that the exact time at which a sample was at a given temperature can be determined.

K. MASS DETERMINATION

In order to determine the heat capacity on a per mole or per gram basis, the mass of the sample at the time of a reading must be known. For short levitation times, the mass would be relatively constant. However, over a 300 second heating period the mass loss from evaporation might be significant. To determine mass as a function of time, the sample must be weighed both before and after the flight. By assuming that the mass loss is linearly related to time, one can write an equation that will give the mass time t.

Let t_i be the time at which the temperature of the sample first reaches a point where the vapor pressure becomes significant. Then at that time the mass is m_i. Let t_f be the time at which the sample cools off to this same temperature at the end of the flight, and let m_f be the final sample mass. Then the mass m at any time t is given by

$$m = m_i - \left(\frac{m_i - m_f}{t_i - t_f}\right) (t - t_i)$$

L. TIME OF EXPERIMENT

The experiment length is of course limited to the 300 seconds of free fall time. Within that period three things must be done:

1) Sample melted
2) $\frac{dH_r^*}{dt}$ determined at several temperatures (i.e. power settings)
3) Sample allowed to cool at least once.

The precise time for parts one and two will be dependent upon the coupling of the coil with the sample, the sample's electrical resistivity, its melting points, and the emissivity. Based on figure 3.4 in Exhibit "A" for Contract NAS8-32030, an estimate of 150 seconds to melt the sample is reasonable.

To determine the time for the sample to cool, again only radiative losses will be considered. Then the equation

$$t = \frac{\rho V C_p}{3A\varepsilon_T \sigma}\left(\frac{1}{T_n^3} - \frac{1}{T_i^3}\right)$$

where V = volume of melt

A = area of melt

T_n = nucleation temperature

T_i = initial temperature

gives the time needed to cool from T_i to T_n for a sample cooling isothermally.[15]

For copper, let T_i = 1500°K, and let T_n = 1154 °K, corresponding to supercooling to 85% of its melting temperature. Then for a 0.9 cm sphere, using the values of emissivity, density and heat capacity listed above, t = 30 seconds.

For berryllium, let T_i = 1573 °K, and let T_n = 1326 °K, again assuming 85% supercooling. Then t = 20 seconds.

Hence, for one complete cooling curve, approximately one half minute is required. Of this time, the first ten seconds are sufficient to cool to the melting point for copper, and even less for beryllium. If 80 seconds are allotted for cooling, a time which should be sufficient to perform two partial and one complete cooling curve, then approximately 70 seconds are left in which $\frac{dH_r^*}{dt}$ must be determined. A savings in time at either of the first two steps means that part of the cooling portion of the experiment can be repeated.

Because the time for the sample to be remelted after fusion has occured is likely to be long, the experiment is probably effectively over after solidification has occured due to a shortage of time. Thus, if two or more cooling curves are to be performed, the sample should be reheated sometime before the first curve is completed. Similarly, when $\frac{dH_r^*}{dt}$ is being determined at various temperatures, it would be best not to supercool too near the expected nucleation temperature. Because the probability of nucleation increases with decreasing temperatures, it would be best to measure $\frac{dH_r^*}{dt}$ somewhat above T_n and extrapolate.

M. CONTROL OF HEATING PROGRAM

Two approaches to the problem of controlling the experiment are possible. In one, the power to the induction heater is changed at predetermined times. The other approach involves coupling the induction heater to the pyrometer so that when the sample reaches some predetermined temperature, power is changed. The first method does not make the most effective use of available time. The second approach however guarantees that no time is wasted, since as soon as a sample reaches the desired temperature, the next step in the experiment can begin.

Some on-ground work will be necessary before the programming of the experiment can be made. If a one-color pyrometer is used, then the experiment must be programmed in terms of brightness temperatures, which requires a value of the spectral emissivity. If a two-color pyrometer is employed, this step is not necessary.

The upper temperature that can be reached with the equipment must be determined, or else there is the possibility that time might be wasted in attempting to reach an unattainable temperature. So that this latter situation never occurs, there should be a system so that if a desired temperature is not reached within a specified time period, then an alternative procedure is employed. For example, it is conceivable that a systems failure might make temperature above melting unattainable. Thus, without some alternative plan, the entire zero gravity time might pass without a cooling curve ever being performed.

N. TIME LINE

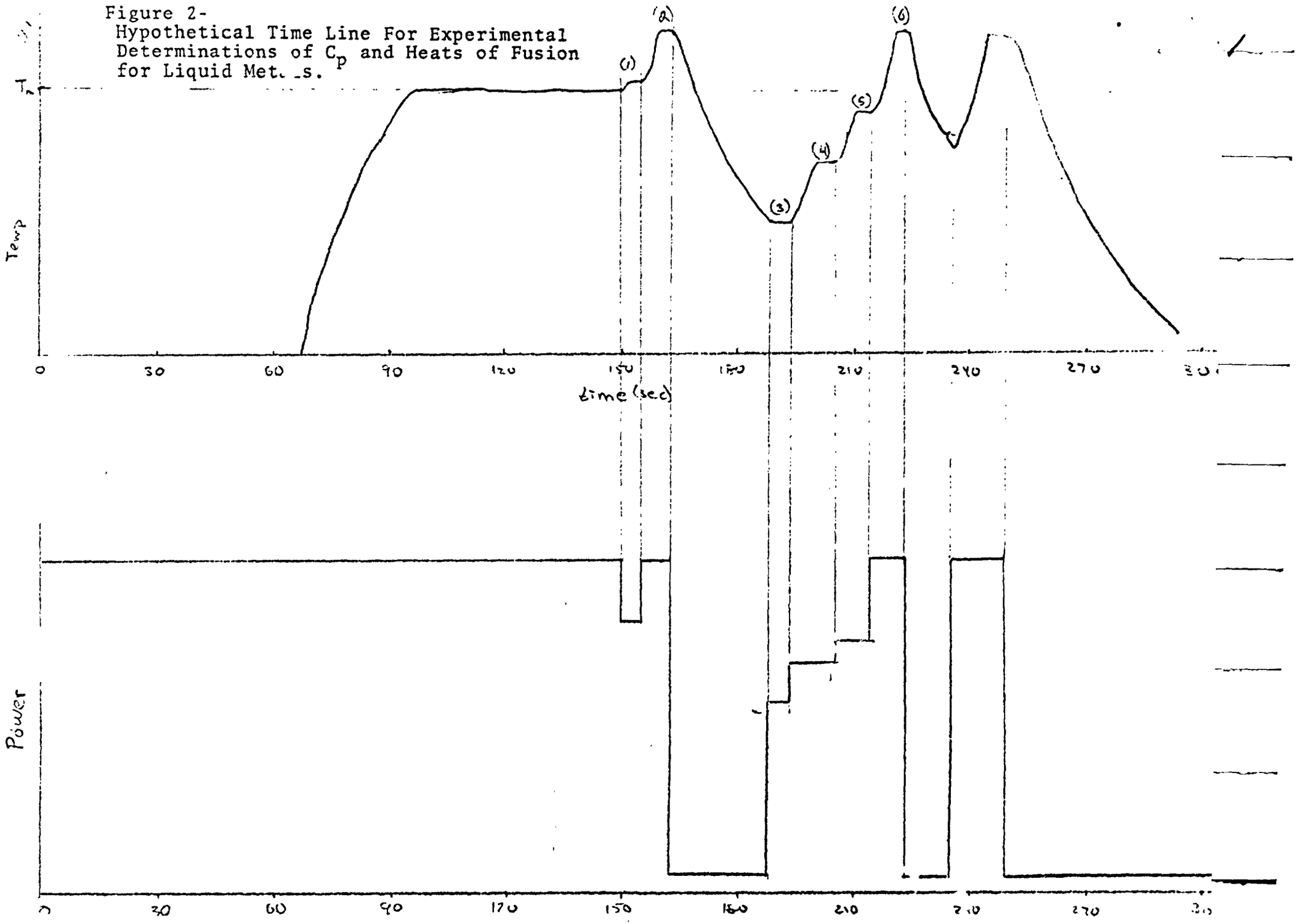
Until on-ground testing with a coil similar to that to be used in the flight is performed, an accurate time line cannot be made. However, a general outline can be drawn showing how the temperature of the sample might be made to change in order to extract data on C_p. (See Figure)

Initially, power should be at peak levels so that the sample melts as rapidly as possible. After fusion, the temperature will begin to rise. Power can be turned down slightly so that the steady-state temperature is slightly above T_m, and a value $\frac{dH_r^*}{dt}$ determined from the resulting plateau (1). Power can be turned up to peak value again, the sample equilibrated (2), and $\frac{dH_r^*}{dt}$ found. Power is now cut to its lowest value. Cooling will occur, and data can be obtained. At some temperature sufficiently above the expected nucleation temperature so that the risk of nucleation is small, power is turned up to a level that will reach a steady-state there (3). Power can then be turned up in steps to allow multiple determination of $\frac{dH_r^*}{dt}$ (4), (5). When the temperature has reached its peak value (6), power can be cut and the sample cooled partially. This can be repeated depending on available time. Finally, the sample is heated to peak temperature and allowed to cool until it solidifies.

This sequence has the advantage that two measurements of $\frac{dH_r^*}{dt}$ (1), (2) are made and one cooling curve done before any supercooling is attempted. Thus if nucleation occurs unexpectedly

early, some data will still be obtainable.

Figure 2-
Hypothetical Time Line For Experimental Determinations of C_p and Heats of Fusion for Liquid Met..s.



0. GENERALITY OF APPROACH

The cooling curve kinetics approach should yield data for any system where the value of $\frac{k}{\sigma \varepsilon_T T_i^3 R}$ is greater than thirty.

In general, isothermal cooling is favored by small spheres. Thus, if it appears that temperature gradients may pose problems for a given sample, reducing the radius may eliminate the problem. In cases where this is done, the coil would have to be redesigned for coupling to the small sample. The main limit to reducing size is the viewing area required for the pyrometer, and this problem can largely be overcome through the use of closeup lenses. This method should therefore prove to be general, failing only for those materials which

1) Have vapor pressures appreciably in excess of 10^{-4} atm at melting
2) Exhibit both low thermal conductivity and high melting points.

P. FUTURE PLANS/TASK SEQUENCE

The following is a rough sequence of events anticipated if one is to carry out the determination of heat capacities by a cooling curve approach.

1. Pyrometer obtained
2. $\frac{dH_r^*}{dt}$ vs power equation to be made on ground using a suitable test material
3. Coil designed so that melt is roughly spherical during heating
4. High purity (99.9+ %) copper or beryllium, well outgassed, to be obtained and manufactured into a sphere of size determined by coil.
5. Rocket equipped to hold reagent grade argon
6. Modifications in equipment made so that power to sample can be cut instantaneously
7. Induction heater output coupled to pyrometer so that experiment can be controlled by the temperature of the sample
8. Induction heater modified so that power output as a function of time is recorded.
9. Pyrometer output arranged so that temperature as a function of time is recorded.
10. Heating and cooling rates predicted, and the experiment programed into onboard controls.
11. Experiment performed
12. Sample examined for contamination, mass determined
13. True temperatures as a function of time determined
14. Cooling rate found.
15. C_p calculated as a function of temperature

VI. CONCLUSIONS

Zero gravity determinations of high temperature properties of certain elements, e.g., Mn, Be, and Cu, and conducting compounds, e.g., silicides, sulfides, nitrides, offer some advantages over ground based determinations. Extension of the approach to non-conducting systems is also possible. By avoiding the use of traditional calorimeters and simply observing the rates of heating and/or cooling, the heat capacities of solids or melts can be deduced. In particular, the study of heat capacities of super-cooled liquids should be particularly tractable by this approach. Heats of fusion can also be determined.

Only minor modifications of existing hardware are necessary to implement this technique, making feasibility testing relatively inexpensive. Should the approach prove to yield satisfactory data, then the possibility of a systematic study of the properties of melts in a Skylab or Space Shuttle type facility would become particularly appealing.

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