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COMPILATION OF THERMOPHYSICAL PROPERTIES OF LIQUID LITHIUM

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Cleveland, Ohio

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ABSTRACT

A compilation of properties including density, electrical resistivity, enthalpy, heat capacity, surface tension, thermal conductivity, vapor pressure, viscosity, Prandtl number, and thermal diffusivity is presented for temperatures between the melting point and normal boiling point of lithium. Empirical correlations were obtained by statistically fitting a polynomial to experimental data obtained from the literature.

STAR Category 17

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SUMMARY

Liquid lithium is a potential coolant candidate for use in high-temperature nuclear space power systems. It is desirable, based on thermodynamic considerations, to raise the lithium temperature as close to the normal boiling point as possible. Thermophysical property data for liquid lithium at temperatures approaching the normal boiling point are scarce, and some of the data are in disagreement. Empirical correlations relating density, electrical resistivity, enthalpy, heat capacity, surface tension, thermal conductivity, vapor pressure, viscosity, Prandtl number, and thermal diffusivity with temperature have been developed. These correlations, developed from experimental data obtained from the technical literature, were extrapolated to about 1600 K.

The normal boiling point, calculated from the vapor pressure correlation is 1608±6 K. The thermal conductivity predicted from a modified Ewing, et al., correlation suggests a maximum thermal conductivity of about 65 watts per meter-K at 1500 K. The latent heat of fusion calculated from the enthalpy correlations is 4.55×10^5 joules per kilogram.

INTRODUCTION

Reactor designers are considering liquid lithium as a possible coolant for space power systems (ref. 1). Such systems require high operating temperatures to minimize the system size and weight and to ensure best operating efficiencies. Lithium has several desirable features for high-temperature applications such as low vapor pressure, low density, high heat capacity, and low pumping power requirements. If space power systems utilizing liquid lithium as a coolant are to be designed to obtain maximum performance, it is necessary to compile the physical properties of liquid lithium which will be required by the designer. A considerable amount of experimental data for lithium is available in the literature for temperatures between the melting point and about 1000 K.

For space power system application, it is desirable to obtain data up to the normal boiling point (about 1600 K) to increase the flexibility of system designs. Therefore, it is necessary to either perform experiments or extrapolate present data. Some of the present results, however, are conflicting, such as those for heat capacity and thermal conductivity.

The purpose of this report is to correlate the thermophysical properties of saturated liquid lithium as a function of temperature, using both experimental data and theoretical analyses; and based upon these correlations extrapolate the properties to about 1600 K.

The general method of correlating the data with temperature is described first. This is followed by a discussion of the experimental method, correlating equation, and standard and maximum deviation between the correlation and the data for each property. A list of references and a bibliography are included. All of the sources of the experimental data used to develop the empirical correlations are presented in the references. Other sources of work of interest are presented in the bibliography.

SYMBOLS

c_p	heat capacity, J/(kg)(K)
H	enthalpy, J/kg
H_{273}	enthalpy at 273 K, J/kg
ΔH_f	latent heat of fusion, J/kg
k	thermal conductivity, W/(m)(K)
M	molecular weight, g
P	vapor pressure, N/m^2
Pr	Prandtl number
R	electrical resistivity, $(\mu\Omega)(cm)$
T	absolute temperature, K
α	thermal diffusivity, m^2/sec
μ	viscosity, $(N)(sec)/m^2$
ρ	density, kg/m^3
σ	surface tension, N/m

Subscript:

s	solid

CORRELATION OF LITHIUM PROPERTY DATA

Method of Correlation

The experimental data on the properties of liquid lithium were obtained from a literature review. These data were empirically correlated as a function of temperature. Generally, the properties were correlated using the following relation:

$$p = \frac{A_0}{T} + A_1 + A_2 T + A_3 T^2 + \ldots \ldots \ldots$$

where p is either the property of interest or the logarithm of the property, T is the temperature, and A_i are the constant coefficients. The degree of the polynomial was selected (by trial and error) to yield the best correlation. The best correlation is the one which yields a coefficient of correlation closest to 1.0. In cases where there is little difference between correlating equations, the polynomial of lowest degree is selected. To facilitate calculations only polynomials of fourth degree and lower were investigated.

DISCUSSION OF PROPERTIES

The properties of liquid lithium at the melting point and boiling point are summarized in table I. These properties were obtained from the empirical correlations derived herein. The properties of the saturated liquid are plotted in figures 1 to 11 as a function of temperature. All of the empirical correlations, shown as solid curves, are derived from experimental measurement. The heat capacity data and the thermal conductivity data exhibited considerable scatter. Therefore, heat capacity was calculated using the enthalpy correlation, and thermal conductivity was calculated using a modified version of the correlation proposed by Ewing et al. (ref. 2). Prandtl number and thermal diffusivity are defined functions of the liquid lithium properties. The viscosity data of Novikov et al. (ref. 3), were obtained from a technical translation of work done in the U.S.S.R. There are no tabulations of the experimental data, only graphs. These data were obtained by interpolation from the graphs.

TABLE I. - THERMOPHYSICAL

PROPERTIES OF LITHIUM

Property[a]	At melting point of 453.7 K	At boiling point of 1608 K (b)
Density, kg/m^3	516	401
Electrical resistivity, $(\mu\Omega)(cm)$	25.0	57.6
Enthalpy, J/kg	1.140×10^6	5.952×10^6
Latent heat of fusion, J/kg	4.55×10^5	---------
Heat capacity, J/(kg)(K)	4169	4169
Surface tension, N/m	0.396	0.240
Thermal conductivity, W/(m)(K)	44.0	64.7
Vapor pressure, N/m^2	1.771×10^{-8}	1.013×10^5
Viscosity, (N)(sec)/m^2	0.645×10^{-3}	0.140×10^{-3}
Prandtl number	6.12×10^{-2}	8.65×10^{-3}
Thermal diffusivity, m^2/sec	2.03×10^{-5}	3.86×10^{-5}

[a]All properties obtained from empirical correlations presented herein.

[b]Boiling point at 1 atm (1.013×10^5 N/m^2).

Density

The most often used method of experimentally measuring the density of liquid lithium is the maximum bubble pressure technique. This experiment is based upon the measurement of pressures required to bubble an inert gas from a capillary tube immersed to various known depths in the liquid metal. This technique can be used for determining both the liquid surface tension and density. The experimental data determined by Been et al. (ref. 4), and Cooke (unpublished data obtained by J. W. Cooke of Oak Ridge National Laboratory) are presented in figure 1 as a function of the temperature of liquid lithium. Also shown are the data of Tepper et al. (ref. 5), which were measured with a dilatometer apparatus. This apparatus allows the measurement of the change in volume of liquid with temperature for a known mass of liquid. Tepper's data agree with those of Been and Cooke. These data were correlated using the following linear relation:

$$\rho = 562 - 0.100 \; T \tag{1}$$

Using equation (1), the data are correlated with a standard deviation of ±0.7 percent. The maximum difference between the correlation and data is 2.4 percent.

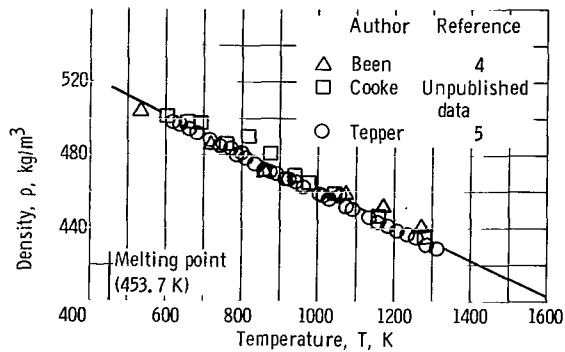Figure 1. - Lithium density (ρ = 562 - 0.100 T).

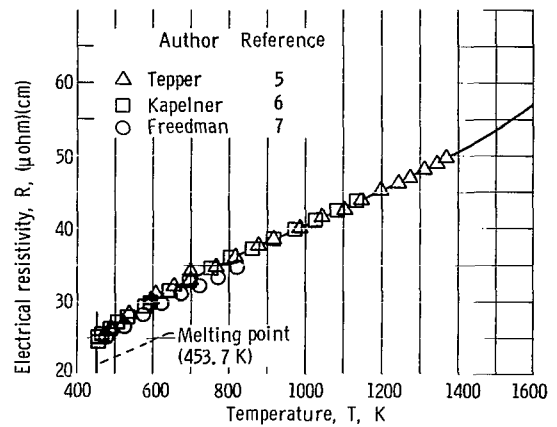Figure 2. - Lithium electrical resistivity (R = 2.256 + 0.06665 T - 4.255×10^{-5} T^2 + 1.398×10^{-8} T^3).

Although this correlation could be improved slightly using a cubic polynomial, the resulting correlation exhibits a minimum at about 1600 K. Because there is no apparent way to justify an increase in density of a monatomic liquid at its boiling point, the linear form of the polynomial was selected to represent the density.

Electrical Resistivity

Kapelner (ref. 6), Tepper (ref. 5), and Freedman and Robertson (ref. 7) measured the resistivity of liquid lithium using the method of parallel resistors, and their data are plotted in figure 2. This method is based upon the application of a known potential across a container holding liquid lithium, measurement of the current through the system, and determination of the overall resistance of the system. When this is compared with the predetermined resistance of the container alone, the resistance of the lithium can be calculated.

The data were correlated to within a standard deviation of ±1.7 percent and a maximum deviation of -3.9 percent using a third-degree polynomial. The correlating polynomial is

$$R = 2.256 + 0.06665\ T - 4.255 \times 10^{-5} T^2 + 1.398 \times 10^{-8} T^3 \qquad (2)$$

Enthalpy

The enthalpy of liquid lithium was measured by Douglas et al. (ref. 8), Bates and Smith (ref. 9), Cabbage (ref. 10), and Achener and Fisher (ref. 11) using the drop method. The lithium is encapsulated, heated to a known temperature, and dropped into an ice calorimeter. The heat evolved from the capsule is measured. The same experiment is done with an empty capsule, and the enthalpy of the lithium is calculated from the difference between the values of the heat evolved.
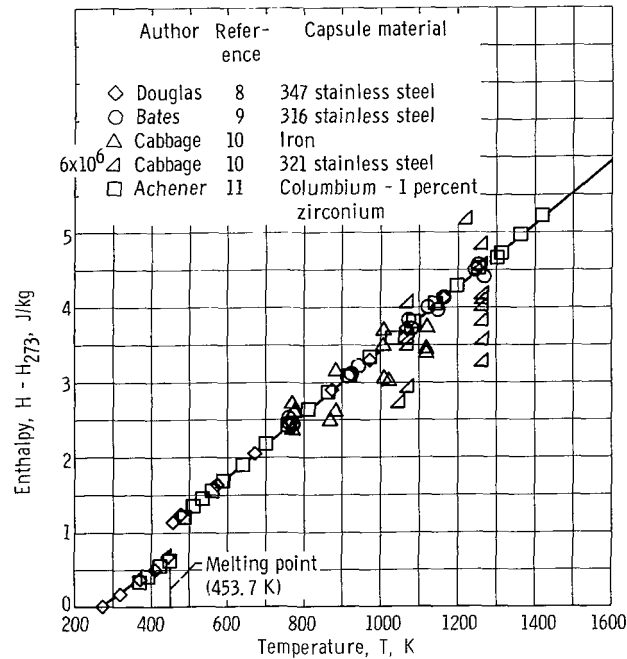

Figure 3. - Lithium enthalpy relative to 273 K (H - H_{273} = -7.519x10^5 + 4169 T).

The enthalpy data of Douglas, Bates, and Achener were presented relative to 273 K, but Cabbage presented his data relative to 298 K. The enthalpy change shown in figure 3 is relative to the enthalpy of solid lithium at 273 K. Cabbage's data have been corrected to 273 K by linear extrapolation.

The enthalpy data presented in figure 3 were correlated using a linear equation in temperature:

$$H - H_{273} = -7.519 \times 10^5 + 4169T \tag{3}$$

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The data of Cabbage were not included in this correlation because of the considerable scatter compared to that of the other experimenters. Equation (3) correlates the data with a standard deviation of ±1.6 percent and a maximum deviation of -5.8 percent when Cabbage's data are excluded. Although a cubic polynomial correlates the data slightly better than the linear equation, the linear equation is recommended because of its simpler form.

Douglas and Achener also presented enthalpy data for solid lithium. These data were correlated with a standard deviation of ±3.6 percent and a maximum deviation of -6.5 percent.

$$H_s - H_{273} = -1.03 \times 10^6 + 3780T \tag{4}$$

Latent Heat of Fusion

The latent heat of fusion was calculated by substracting liquid and solid enthalpies at the melting point obtained from equations (3) and (4).

The latent heat of fusion is

$$\Delta H_f = 4.55 \times 10^5 \text{ J/kg}$$

This value is about 6 percent higher than the values quoted by Douglas and Achener.

Heat Capacity

The heat capacity of liquid lithium has been determined by several experimenters. Bates (ref. 9) and Cabbage (ref. 10) measured enthalpies of liquid lithium using the "drop method" described earlier. They calculated mean heat capacities by dividing the measured enthalpy by the temperature interval. Douglas (ref. 8) and Achener (ref. 11) empirically correlated enthalpy data and calculated the heat capacity by taking the first derivative of the enthalpy with respect to temperature. Kutateladze et al. (ref. 12), present correlated results of heat capacity experiments. The data were measured by the method of direct heating of the sample. This method allows the sample to be heated internally while the environment is held at some known temperature. The total internal heat input and temperature rise of the molten metal are measured, and the heat capacity of the liquid is calculated.

The heat capacity correlations recommended by each experimenter are presented in figure 4 as a function of temperature. Kutateladze predicts a linear increase in heat ca-
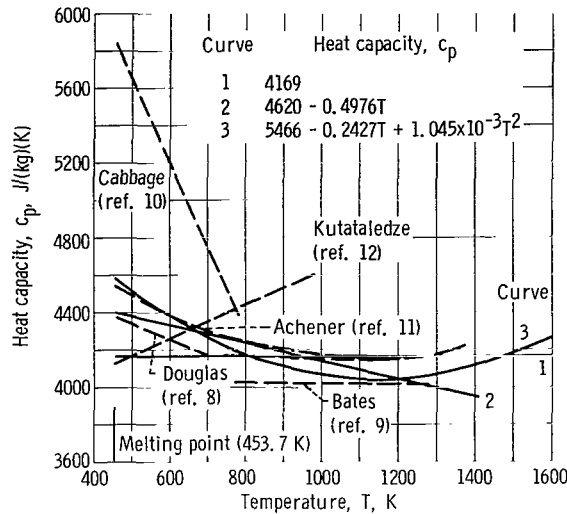
Figure 4. – Lithium heat capacity.

pacity with temperature. Douglas and Cabbage predict linearly decreasing heat capacity with temperature, and Achener predicts a quadratic relation between heat capacity and temperature. Achener predicts a minimum heat capacity occurring at about 1150 K. The mean heat capacity value of 4020 joules per kilogram-K predicted by Bates is also shown.

The results of Cabbage are considerably higher in the low-temperature range than the results of the other investigators. However, as indicated in figure 3, there is considerable scatter in the enthalpy data of Cabbage. Therefore, Cabbage's data were not included in the calculation of the heat capacity of liquid lithium.

The empirical correlation for heat capacity is calculated by taking the temperature derivative of the empirical correlation for enthalpy given by equation (3).

The corresponding heat capacity, shown as curve 1 in figure 4, is

$$c_p = 4169 \text{ J/(kg)(K)} \tag{5}$$

When an empirical correlation for enthalpy is differentiated to determine the heat capacity, the extrapolated value of the heat capacity is affected by the degree of the enthalpy correlation. Three solid curves are presented in figure 4 representing linear (curve 1), quadratic (curve 2), and cubic (curve 3) enthalpy correlations. The temperature derivative of these correlations yields constant (temperature independent) linear and quadratic correlations, respectively, for heat capacity. Although the maximum difference between the enthalpy correlations at 1600 K is 1.7 percent, the maximum difference between heat capacity correlations at 1600 K is 11 percent.

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Surface Tension

Cooke (unpublished data), Achener (ref. 13), and Taylor (ref. 14) measured the surface tension of liquid lithium in the temperature range from 460 K to about 1300 K using the maximum bubble pressure method described earlier (in the section Density). These data are plotted in figure 5. The data were correlated using the following second-degree polynomial in temperature:

$$\sigma = 0.447 - 1.07 \times 10^{-4}T - 1.351 \times 10^{-8}T^2 \tag{6}$$

Using equation (6), the data are correlated with a standard deviation of ±1.9 percent. The maximum difference between the data and the correlation is +5.2 percent.

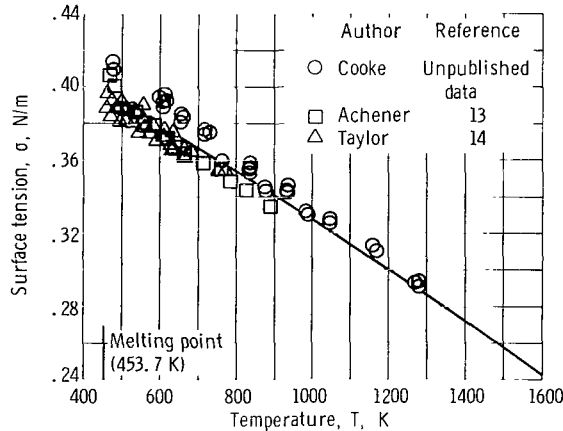| Author	Reference
○ Cooke	Unpublished data
□ Achener	13
△ Taylor	14

Figure 5. - Lithium surface tension ($\sigma = 0.447 - 1.07 \times 10^{-4}T - 1.35 \times 10^{-8}T^2$).

Thermal Conductivity

The thermal conductivity of lithium was measured by Webber et al. (ref. 15), Cooke (ref. 16), and Nikolskii (ref. 17), and the results are plotted in figure 6 for various temperatures. Webber and Cooke determined the conductivity by measuring the temperature gradient in a molten column of lithium subjected to a known heat flow. Nikolskii measured the thermal conductivity by the method of "successive stationary states." This method is similar to that used by Cooke and Webber but no heaters are used to compensate for radial heat losses.

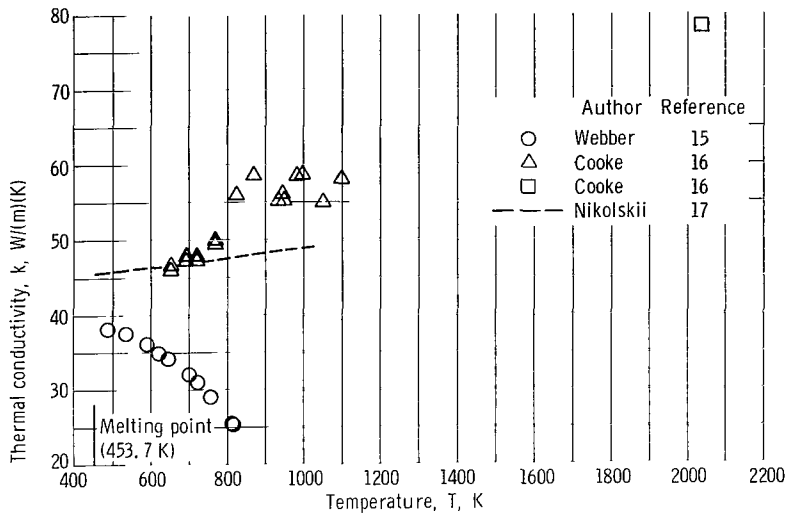The data of Cooke and those of Nikolskii all indicate that the thermal conductivity in-
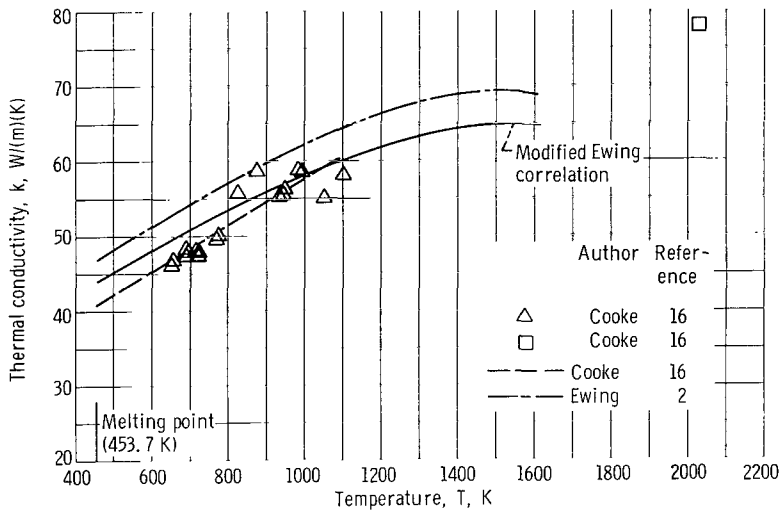
Figure 6. - Lithium thermal conductivity.

Figure 7. - Lithium thermal conductivity.

creases with temperature, while the data of Webber show a reduction in conductivity with increasing temperature. Cooke (ref. 16) suggests that Webber's data are in disagreement with those of other experimenters because of contamination of the lithium with iron from the sample container and with cement which was used as an electrical insulator. Cooke also suggests that the large scatter in the data of Nikolskii (40 percent of the data deviate from the mean by more than ±5 percent) may be due to contamination of the lithium and radial heat losses. Therefore, the data of Cooke were assumed to be most reliable experimental data available.

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The thermal conductivity of metals can also be calculated as a function of temperature, electrical resistivity, heat capacity, and density using the relation proposed by Ewing (ref. 2):

$$k = 2.61 \frac{T}{R} - 8.37 \times 10^3 \frac{\left(\frac{T}{R}\right)^2}{\rho c_p} + 2.31 \times 10^{-6} \frac{c_p \rho^2}{MT} \tag{7}$$

The empirical correlations between temperature and electrical resistivity (eq. (2)), density (eq. (1)), and heat capacity (eq. (5)) were used to calculate thermal conductivity as a function of temperature. The thermal conductivity calculated from equation (7) is plotted in figure 7 as a function of temperature. The data of Cooke and Cooke's proposed empirical correlation between thermal conductivity and temperature are also shown in figure 7. The conductivity based on Ewing's correlation are consistently higher than the data of Cooke. The standard deviation between Ewing's correlation and Cooke's data is 12 percent. The coefficient used in the first term of Ewing's correlation is, however, about 7 percent higher than the value which was derived by Sommerfeld (ref. 18). Sommerfeld's coefficient was used in the correlation of Ewing to yield the following:

$$k = 2.45 \frac{T}{R} - 8.37 \times 10^3 \frac{\left(\frac{T}{R}\right)^2}{\rho c_p} + 2.31 \times 10^{-6} \frac{c_p \rho^2}{MT} \tag{8}$$

The thermal conductivity calculated using this correlation and empirical correlations for R, ρ, and c_p, is also shown in figure 7. The standard deviation between Cooke's data and the predictions of this correlation is 5.6 percent. The maximum deviation is 8.3 percent. The thermal conductivity based on this correlation exhibits a maximum value of 65 watts per meter-K at about 1500 K. Cooke estimates a maximum value of about 78 watts per meter-K at 2033 K, as shown in figure 6.

Thermal conductivity is not easily calculated from equation (8), so equation (8) was approximated with the following polynomial:

$$k = 21.874 + 0.056255 \, T - 1.8325 \times 10^{-5} T^2$$

The maximum difference between thermal conductivity calculated with this equation and that calculated from equation (8) is 3 percent at 800 K.

Vapor Pressure

Experimental data relating the vapor pressure of liquid lithium to temperature are shown in figure 8. Hartmann and Schneider (ref. 19) measured the boiling temperatures of lithium for various measured values of pressure. An inert atmosphere of argon was used to control the pressure over the liquid lithium. Rigney et al. (ref. 20), measured the pressure with a bellows-activated pressure transmitter which was balanced by an inert gas pressure. Rigney's data were obtained over a temperature range from about 1300 to 1800 K. Achener and Fisher (ref. 21), used a "constant volume method" to measure vapor pressures between 1300 and 1500 K. The lithium was held in a sealed capsule and the pressure was measured by balancing the internal capsule pressure against a null-type diaphragm with an equal external pressure of an inert gas. Maucherat (ref. 22) determined vapor pressures between 800 and 900 K by measuring the flow of an atomic jet through an orifice. The lithium was heated in a crucible under vacuum. A stream of heated lithium was allowed to flow through an orifice for a measured time. The vapor stream was condensed on a target, and the total quantity of lithium collected was measured.
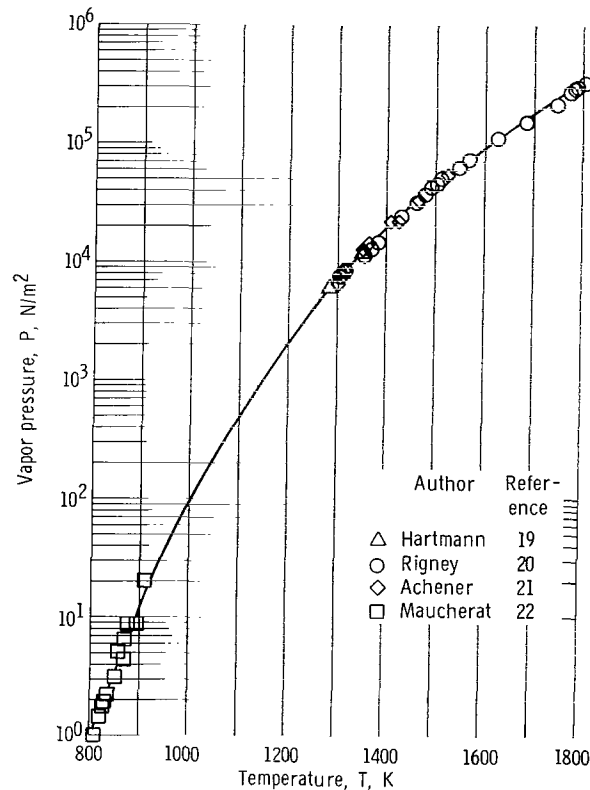
	Author	Reference
△	Hartmann	19
O	Rigney	20
◇	Achener	21
□	Maucherat	22

Figure 8. - Lithium vapor pressure ($\log P = 10.015 - 8064.5/T$).

The vapor pressure data were correlated with the following equation:

$$\log P = 10.015 - \frac{8064.5}{T} \tag{9}$$

With this equation the data shown in figure 8 are correlated with a standard deviation of ±3.38 percent. The maximum deviation of -32.6 percent occurred at a vapor pressure of about 6 newtons per square meter. The normal boiling point of lithium, calculated from equation (9), is 1608±6 K. This agrees well with the boiling point (1609±5 K) reported in the Handbook of Chemistry and Physics (ref. 23). Rigney reported (ref. 20) a boiling point of 1613±2 K, while Hartmann and Schneider reported 1609±5 K. Maucherat extrapolated her vapor pressure data from 915 K and reported a boiling point of 1530 K.

Viscosity

The viscosity of liquid lithium was measured by Andrade (ref. 24), Novikov (ref. 3), Rigney et al. (ref. 25), Ban et al. (ref. 26), and Achener and Fisher (ref. 27), and the data are shown in figure 9 as a function of temperature. These experimenters all chose
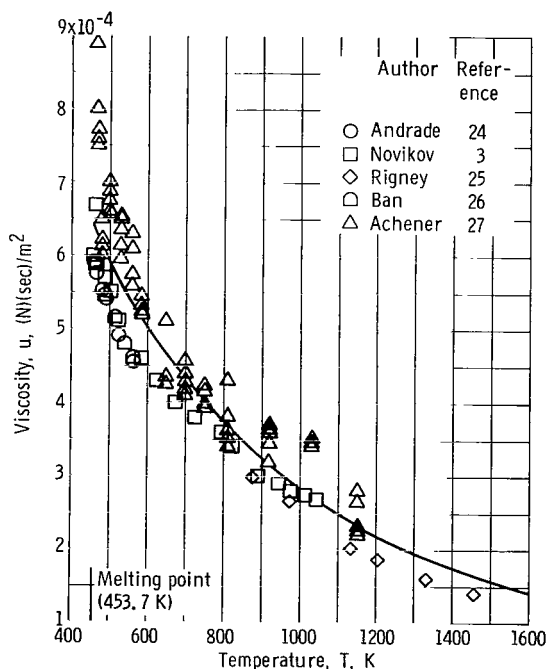

Figure 9. - Lithium viscosity ($\log \mu = -3.080 + [57.63/T] - 5.172 \times 10^{-4}$ T).

the oscillating sphere (or cylinder) viscometer method for measuring the liquid viscos-ity. The viscosity is determined by measuring the period and reduction in amplitude of a torsional pendulum containing the liquid lithium. The reduction in amplitude is caused by the viscous drag exerted by the lithium on the inside walls of the container. The data of Achener are about 25 percent higher than those of the other investigators. His only explanation for the cause of this discrepancy is the possible presence of impurities in the lithium samples.

These data were correlated with the following equation:

$$\log \mu = -3.080 + \frac{57.63}{T} - 5.172 \times 10^{-4} T \tag{10}$$

Equation (10) correlates the data with a standard deviation of ±19 percent and a maximum deviation of ±29 percent.

Prandtl Number

The Prandtl number Pr is a dimensionless parameter frequently used in heat-
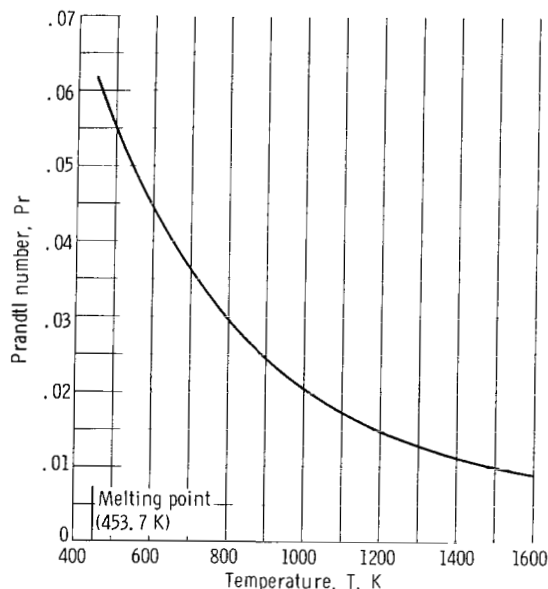

Figure 10. - Liquid lithium Prandtl number
(Pr = $c_p \mu / k$).

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transfer calculations. The Prandtl number is defined as

$$\text{Pr} = \frac{c_p \mu}{k} \tag{11}$$

Values of the heat capacity, viscosity, and thermal conductivity are obtained from equations (5), (10), and (8) and substituted into equation (11). The Prandtl number decreases from 0.0612 at the melting point to 0.00865 at the normal boiling point.

Thermal Diffusivity

Another parameter frequently used in heat-transfer calculations is the thermal diffusivity α. The thermal diffusivity is described by the following equation:

$$\alpha = \frac{k}{\rho c_p} \tag{12}$$

Values of the thermal conductivity, density, and heat capacity are obtained from equations (8), (1), and (5) and substituted into equation (12). The thermal diffusivity is shown in figure 11 as a function of temperature. It increases from 2.03×10^{-5} square meter per second at the melting point to 3.86×10^{-5} square meter per second at the boiling point.
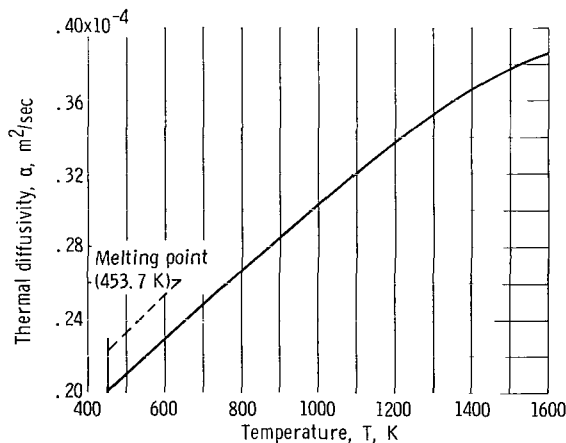

Figure 11. - Thermal diffusivity of liquid lithium $(\alpha = k/\rho C_p)$.

CONCLUSIONS

Physical property data for liquid lithium have been empirically correlated as a function of temperature. The density, electrical resistivity, enthalpy, surface tension, and vapor pressure data have been correlated with standard deviations of 3.5 percent or less. The normal boiling point, calculated from vapor pressure data, is 1608±6 K.

The thermal conductivity data are in poor agreement. Thermal conductivity was calculated as a function of temperature based upon a modified Ewing correlation and the empirically determined relations for electrical resistivity, density, and heat capacity. The standard deviation between this correlation and the experimental data of Cooke is 5.7 percent. The thermal conductivity exhibits a maximum value of about 65 watts per meter-K at about 1500 K. The latent heat of fusion calculated from the enthalpy correlation is 4.55×10^5 joules per kilogram.

Lewis Research Center,
  National Aeronautics and Space Administration,
      Cleveland, Ohio, April 8, 1968,
          120-27-06-17-22.

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