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ALKALI METAL PHYSICAL PROPERTIES PROGRAM AT
PRATT & WHITNEY AIRCRAFT-CANAL*

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ALKALI METAL PHYSICAL PROPERTIES PROGRAM AT
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S. M. KAPELNER AND R. E. CLEARY

The favorable combination of physical properties such as heat capacity, viscosity, electrical resistivity, thermal conductivity and high temperature liquid range make alkali metals, in principle, among the best heat transfer fluids available for use in nuclear reactor and other esoteric powerplant systems. Unfortunately, many of these properties are not known with sufficient certainty in the high temperature region to permit optimization of design criteria for developing maximum efficiency coolant systems. For this reason, Pratt & Whitney Aircraft-CANEL, have been concerned for some time in extending the physical properties data of alkali liquid metals in the high temperature region. A supplemental program is being initiated to study some of the properties of alkali metals in the gas phase. This information is required for designing systems where the alkali vapor is the working fluid. In addition, programs are under way to study the solubility of noble gases in alkali liquid metals and wetting characteristics of these liquid metals with structural materials.

Electrical Resistivity and Calculated Thermal Conductivities

One phase of the program has been the measurement of the electrical resistivity of the alkali metals (1). This property is important for several reasons:

1. In designing engineering loops heated by I^2R methods.
2. Calibration of electromagnetic flowmeters for alkali metal systems.
3. Study of microscopic properties of metals.
4. Utilizing electrical resistivity data to calculate the thermal conductivity of a liquid metal through the same temperature range.

Due to the corrosive reactions between alkali metals and electrical insulating materials, the electrical resistance of these liquid metals cannot readily be measured directly. Therefore, a method based on measuring the electrical resistance of the liquid metal in parallel with a type 347 stainless steel metal container was employed. The method involves passing a known current through a calibrated stainless steel tube containing the liquid metal at constant temperature and measuring the potential drop across a well-defined length of the tube. This equipment is shown schematically in Fig 1. The resistance is then calculated from the formula for parallel resistors,

$$R_{LM} = \frac{R_T R_{SS}}{R_{SS} - R_T} \quad (1)$$

R_T = resistance of tube full of liquid
 R_{SS} = resistance of calibrated stainless steel tube
 R_{LM} = resistance of the liquid metal.

The resistivity is immediately obtained from equation (2)

$$\rho_{LM} = \frac{R_{LM} A}{L} \quad (2)$$

ρ_{LM} = the resistivity of the liquid metal
 A = the cross-sectional area of the liquid metal
 L = the length of well-defined liquid metal column

The electric current through the tube was obtained from a six volt lead storage battery, rearranged to give a three cell in parallel-two volt battery. The current was determined by measuring the potential across a Weston shunt type 0.001 ohm resistor calibrated to an accuracy of $\pm 1 \times 10^{-6}$ ohm. The circuit is shown schematically in Fig 2.

All tube loading was performed in a dry box under an atmosphere of purified argon. Prior to final welding, the tube was evacuated to 0.1 Torr or less as a precautionary measure to safeguard against build-up of pressure in the closed system. A point worthy of comment is that the tube containing liquid metal had to be heated and held at a temperature of at least 1000F for a period of one hour to insure complete wetting of the inner walls of the container by the alkali liquid. Data have been obtained for lithium (to 865C), sodium (to 853C), potassium (to 764C), rubidium (to 752C) and NaK-56 (to 855C). Measurements were taken going up and coming down in temperature in order to insure reproducibility and to check for any possible effects of corrosion from the inner walls of the container. In all cases the temperatures where resistivity measurements were made were held constant to plus or minus 1 degree centigrade or less.

A least squares fit of the experimental data to a power series was obtained for each system and is shown in Fig 3, where ρ is in microhm-centimeters and t is in degrees centigrade. Maximum deviations of the equations from the experimental points are: lithium 0.9 percent; sodium 1.0 percent, potassium 2.3 percent, rubidium 3.6 percent; NaK (46 weight percent potassium) 1.9 percent.

Figure 4 presents graphically the resistivity of all the alkali metals for comparison and includes NaK alloy (46 weight percent potassium determined by chemical analysis). The resistivity of the alloy is higher than either sodium or potassium at any temperature. This behavior may be expected when we consider the addition of either element as a foreign impurity in the regular lattice structure of the other. Among the alkali elements themselves, with the exception of lithium, the resistivity is proportional to the atomic number throughout the temperature range. Another significant point, is the comparison of the small temperature effect on lithium resistivity compared to the large positive effect on the other alkali metals through the temperature range investigated.

This effect projects itself into the thermal conductivity of lithium which, as shown in Fig 5 increases with temperature while the other alkali metals indicate a negative thermal conductivity temperature slope. The thermal conductivity of lithium was calculated using an average Lorenz number obtained from our resistivity measurements in conjunction with the preliminary thermal conductivity values obtained at NREL. The thermal conductivity of rubidium was calculated using the theoretical Lorenz number with our electrical resistivity data. Fig 6 indicates the discrepancy in reported values of the thermal conductivity of lithium as a function of temperature. Recent values reported by Rudnev (2) indicate an even greater positive slope than we have predicted.

Work is under way at our laboratory to extend the electrical resistivity data for lithium to 1315C and to measure cesium to 870C.

Solubility of Helium in Lithium

The extreme chemical reactivity of alkali metals requires that they be covered with the noble gases for pressuring and for transferring between containers. One is concerned that the gas equilibrated liquid metal in a polythermal circuit would become super saturated with respect to dissolved gas in the reactor core region and the resulting bubble formation cause a perturbation of heat transfer and reactor control properties. Consequently as part of the Pratt & Whitney Aircraft-CANEL liquid metal program, the solubilities of some noble gases in the alkali metals are being determined. The first phase of this program, the solubility of helium in lithium between 650 and 870C has been completed.

The schematic arrangement of the system is shown in Fig 7. Helium at the desired pressure was bubbled through lithium maintained at constant temperature for a period long enough to obtain saturation. After saturation and after allowing time to discharge any possible entrained bubbles, approximately half the lithium (measured accurately by means of a movable probe) was transferred to the second vessel which was maintained at 260C and contained a known quantity of argon. The dissolved helium was then stripped by recirculating the argon through an inert gas sealed diaphragm pump. Helium-argon aliquots were taken and were analyzed by mass spectrometry. Additional samples were analyzed after concentrating the helium by passing the gas mixture through a liquid nitrogen temperature cryogenic charcoal trap which absorbed the argon. Fig 8 presents a tabulation of the experimental data for the solubility of helium in lithium at the temperature and pressure conditions investigated. Fig 9 presents a semi-log plot of the solubility data as a function of reciprocal temperature. The slope of the curve yields a heat of solution of about 4200 cal/mole which can be compared with ΔH of 6200 cal/mole for helium in NaF-ZrF₄ and ΔH of 8000 cal/mole for helium in LiF-KF-NaF found by Grimes and co-workers (3). Fig 10 shows the solubility of helium as a function of pressure. If the system obeyed Henry's Law this should yield a straight line passing through the origin. Although the agreement is not perfect, undoubtedly Henry's Law is obeyed. The apparent deviation may be explained by one or both of the following reasons:

1. One experimental point is at a relatively high pressure, 3 atmospheres, where deviations from Henry's Law may be attributed to non-ideality.
2. The extremely low solubility of this system makes a precision measurement extremely difficult.

In addition to these programs, Pratt & Whitney Aircraft-CANEL is working on the determination of several other necessary properties of the alkali metals. All of these are either in the equipment check out stage or are under construction and therefore will only be outlined briefly.

Liquid Metal Viscosity

The test program consists in determining the viscosities of all the alkali metals and eutectic NaK alloy (78 weight percent potassium). In Fig 11 the rotating cup equipment is shown schematically. When the cup, loaded with liquid is rotated at constant speed, a shearing force proportional to the viscosity of the liquid causes an angular displacement of the bob wire suspension. Expressed in mathematical terms, this is

$$\eta = \frac{K \theta T}{C (h+E)}$$

- η = viscosities
- K = torsion constant
- θ = angular displacement
- T = period of rotation
- C = constant of system (a function of the geometry)
- h = depth of immersion of the cylindrical bob
- E = end effect connection

Torsion constants have been measured, and end effect corrections have been made with five organic liquids. Preliminary attempts with lithium, however, have revealed some minor difficulties with the system which are being corrected.

Wetting Characteristics

Contact angles between liquid metals and solid interface will be measured by the vertical plate method, as shown schematically in Fig 12. The total force acting on a thin plate will be measured at various temperatures, with the plate immersed at given depths in the liquid. Knowing various constants of the equipment and materials, the surface tension can be calculated. Our first project with this equipment will be to study the advancing and receding contact angles between lithium and columbium-1 zirconium alloy:

Vapor Pressure

A schematic of the apparatus which will be used to measure the vapor pressure of alkali metals to 1650C is shown in Fig 13.

When temperature equilibrium is established in the capsule, the pressure due to the vapor of the liquid metal will be transmitted through the liquid metal line and will be determined by measuring an equivalent argon pressure on the proper manometer or Heise gauge. The vapor pressure of lithium to 1800C will be determined initially.

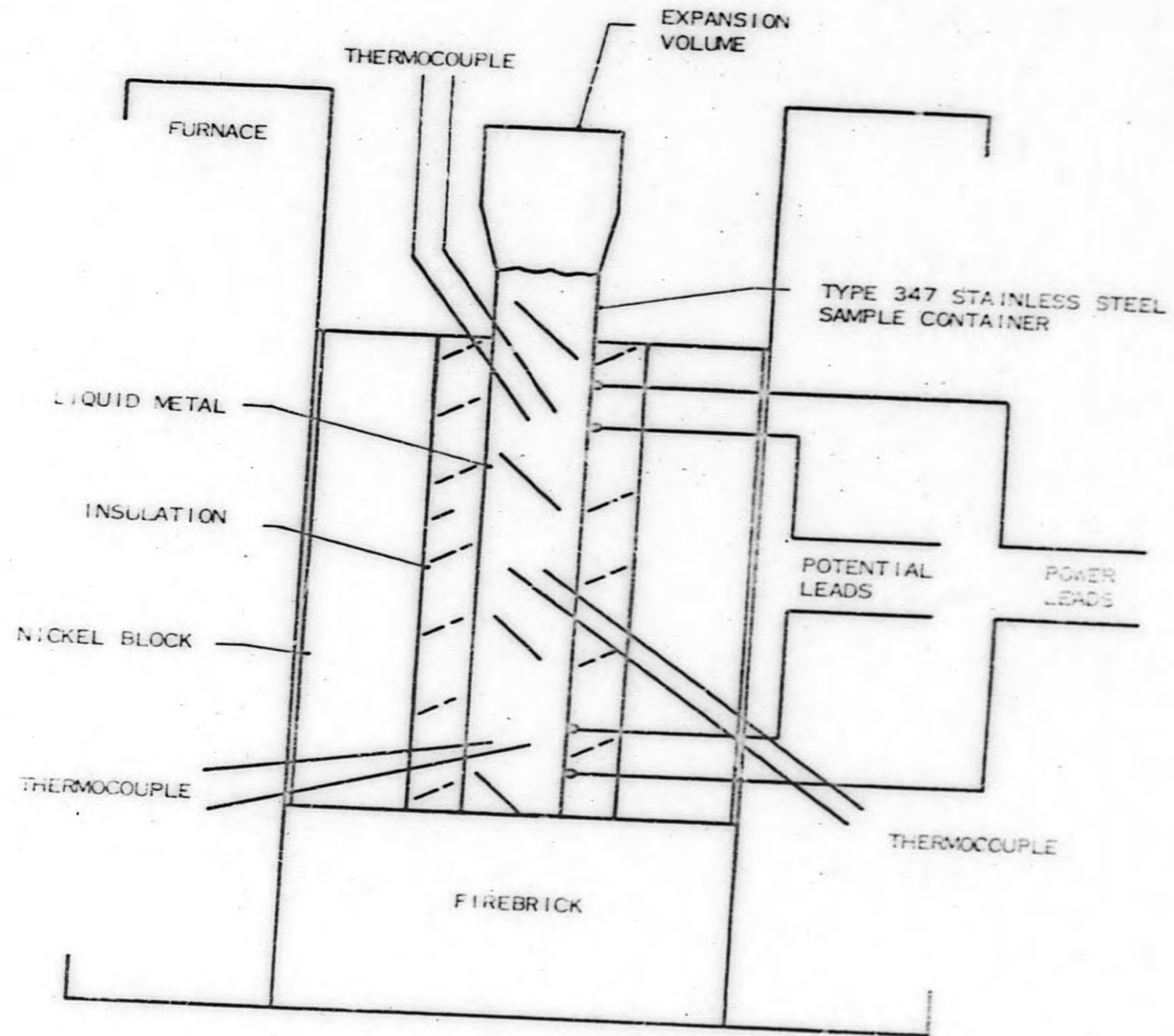
Vapor Density

An apparatus to attempt to measure the vapor density of alkali metals in the gaseous state is also under construction. This apparatus schematically shown in Fig 14, is essentially a modification of the Victor Meyer method adapted to work for high temperature alkali metal systems. In essence: a known mass of alkali metal is dropped into a furnace at the desired temperature. Vaporization of the metal will transmit pressure to an inert gas and the gas pressure in a known volume at room temperature is measured. From these data the apparent molecular weight of the vapor will be determined. The first system to be studied will be rubidium to 870C.

REFERENCES

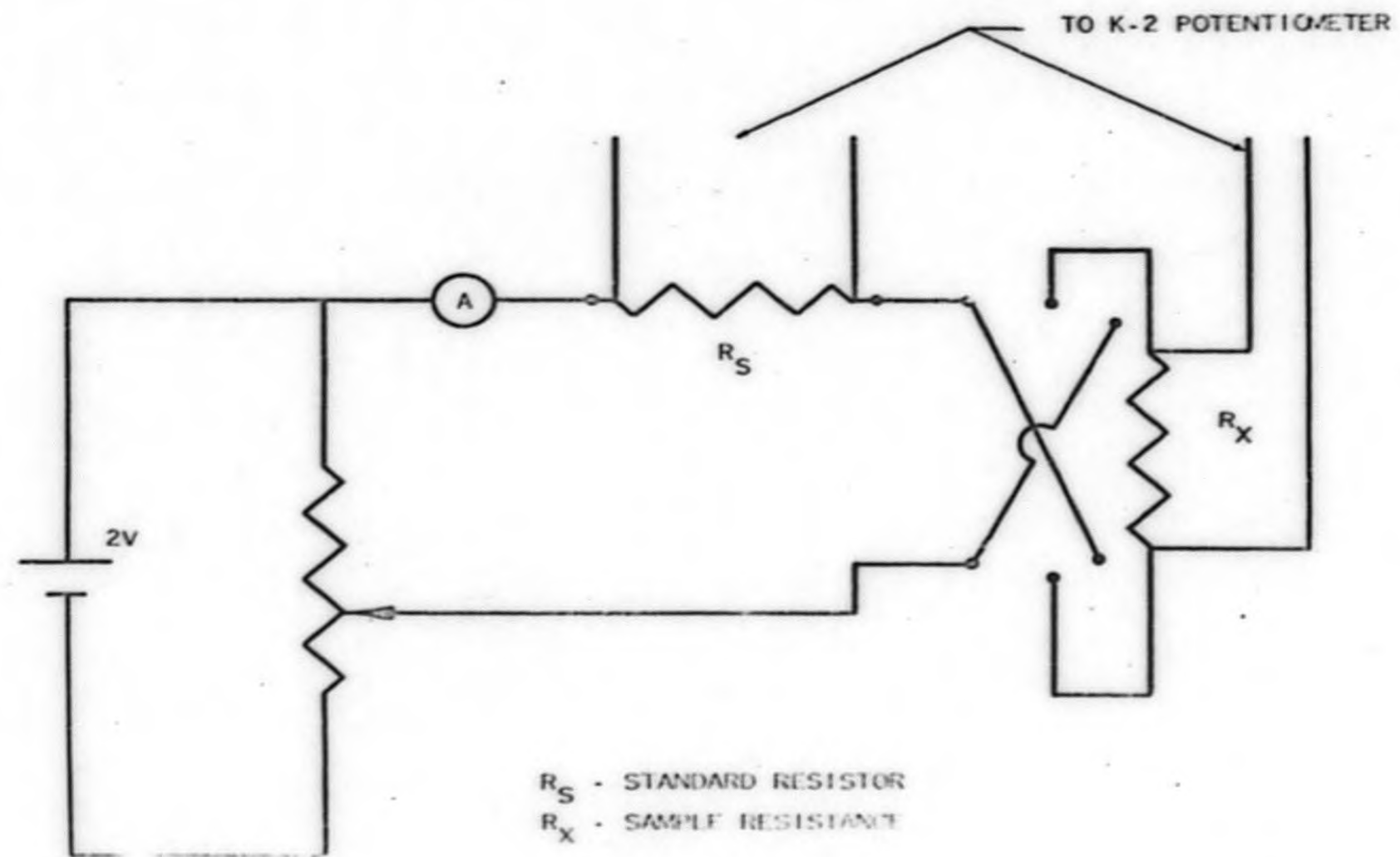
1. Kapelner, S. M., The Electrical Resistivity of Lithium and Sodium-Potassium Alloy, PWAC-349, June 1961.
2. Rudnev, I. I., Lyashenko, V. S., and Abramovich, M.D., Atomnaya Energy; 11:230 (Sept. 1961)
3. Blander, M., Grimes, W., Smith, N. V. and Watson, G. M., J. Phys. Chem. 63, 1164 (1959)

SCHEMATIC VIEW OF ELECTRICAL RESISTIVITY APPARATUS



SCHEMATIC VIEW OF ELECTRICAL RESISTIVITY APPARATUS

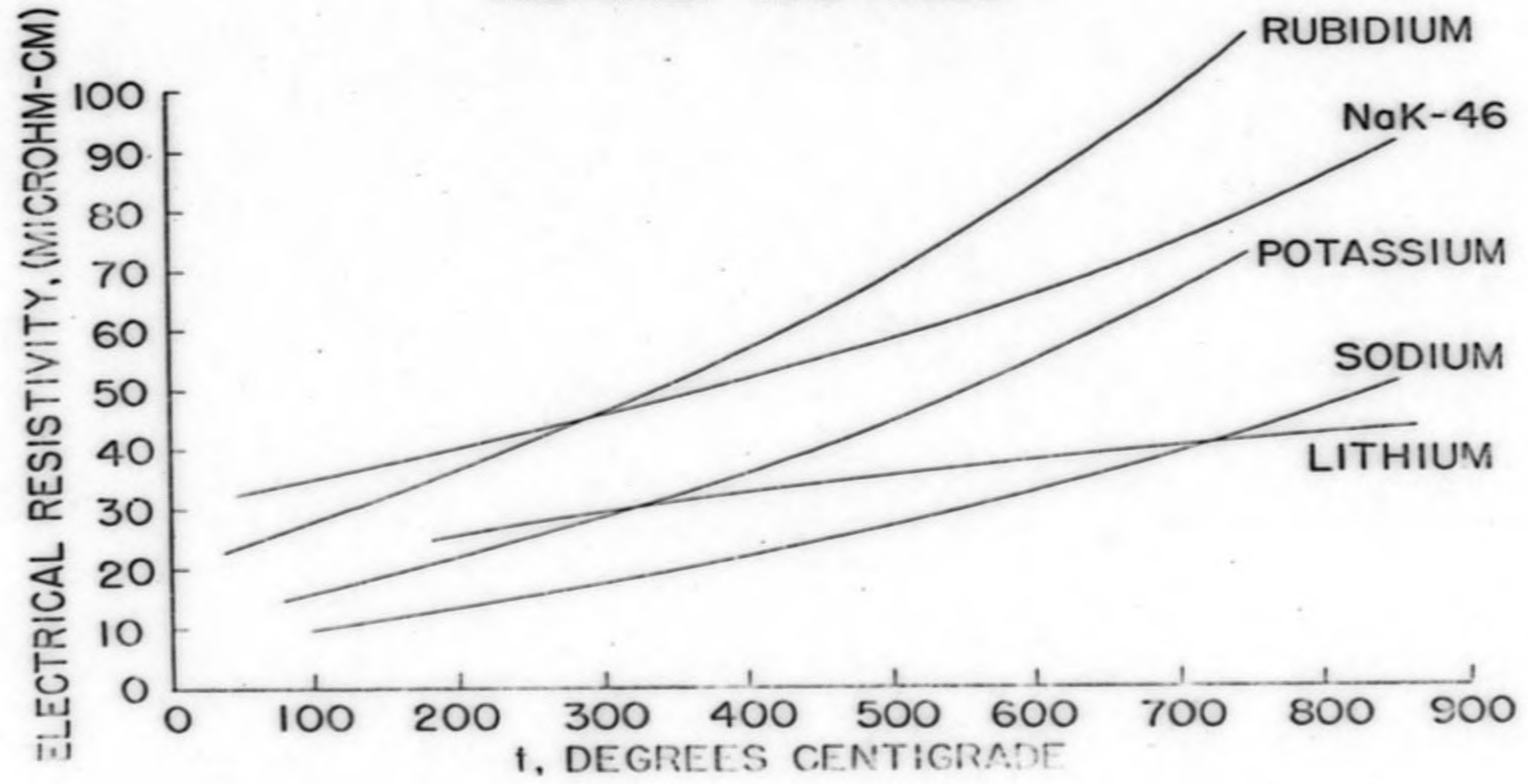
ELECTRICAL CIRCUIT



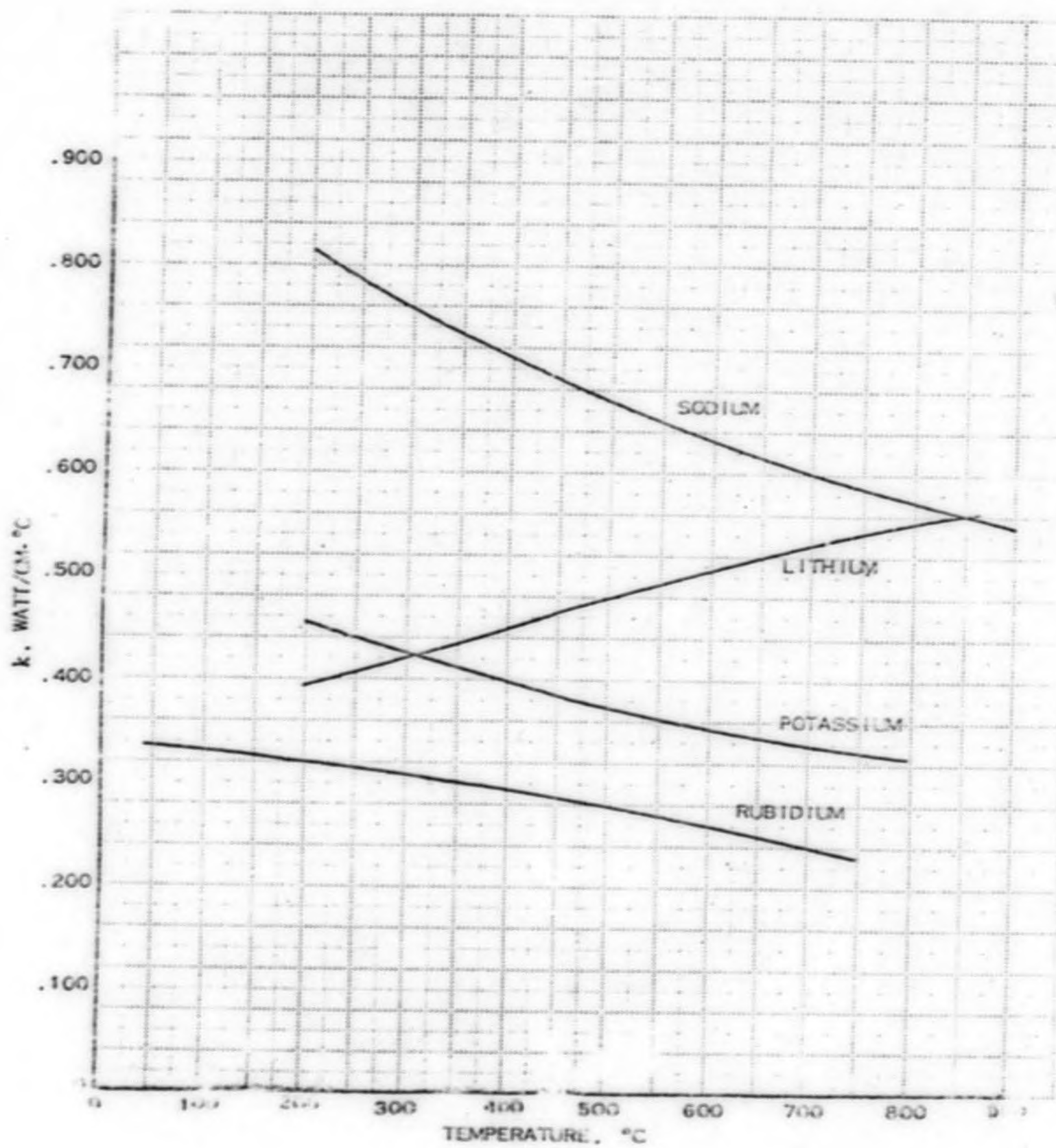
ELECTRICAL RESISTIVITY OF ALKALI METALS

LITHIUM	$\rho = 17.20 + 5.24 \times 10^{-2}t - 4.46 \times 10^{-5}t^2 + 2.28 \times 10^{-8}t^3$ (181.4 - 864.4°C)
SODIUM	$\rho = 5.90 + 3.70 \times 10^{-2}t - 9.36 \times 10^{-7}t^2 + 2.29 \times 10^{-8}t^3$ (98.0 - 852.8°C)
POTASSIUM	$\rho = 10.32 + 5.30 \times 10^{-2}t + 1.56 \times 10^{-5}t^2 + 3.14 \times 10^{-8}t^3$ (79.4 - 764.2°C)
RUBIDIUM	$\rho = 19.52 + 7.89 \times 10^{-2}t + 1.30 \times 10^{-5}t^2 + 5.44 \times 10^{-8}t^3$ (39.2 - 751.7°C)
NaK-46	$\rho = 29.55 + 5.66 \times 10^{-2}t - 2.22 \times 10^{-5}t^2 + 4.70 \times 10^{-8}t^3$ (21.1 - 854.6°C)

ELECTRICAL RESISTIVITY OF ALKALI METALS



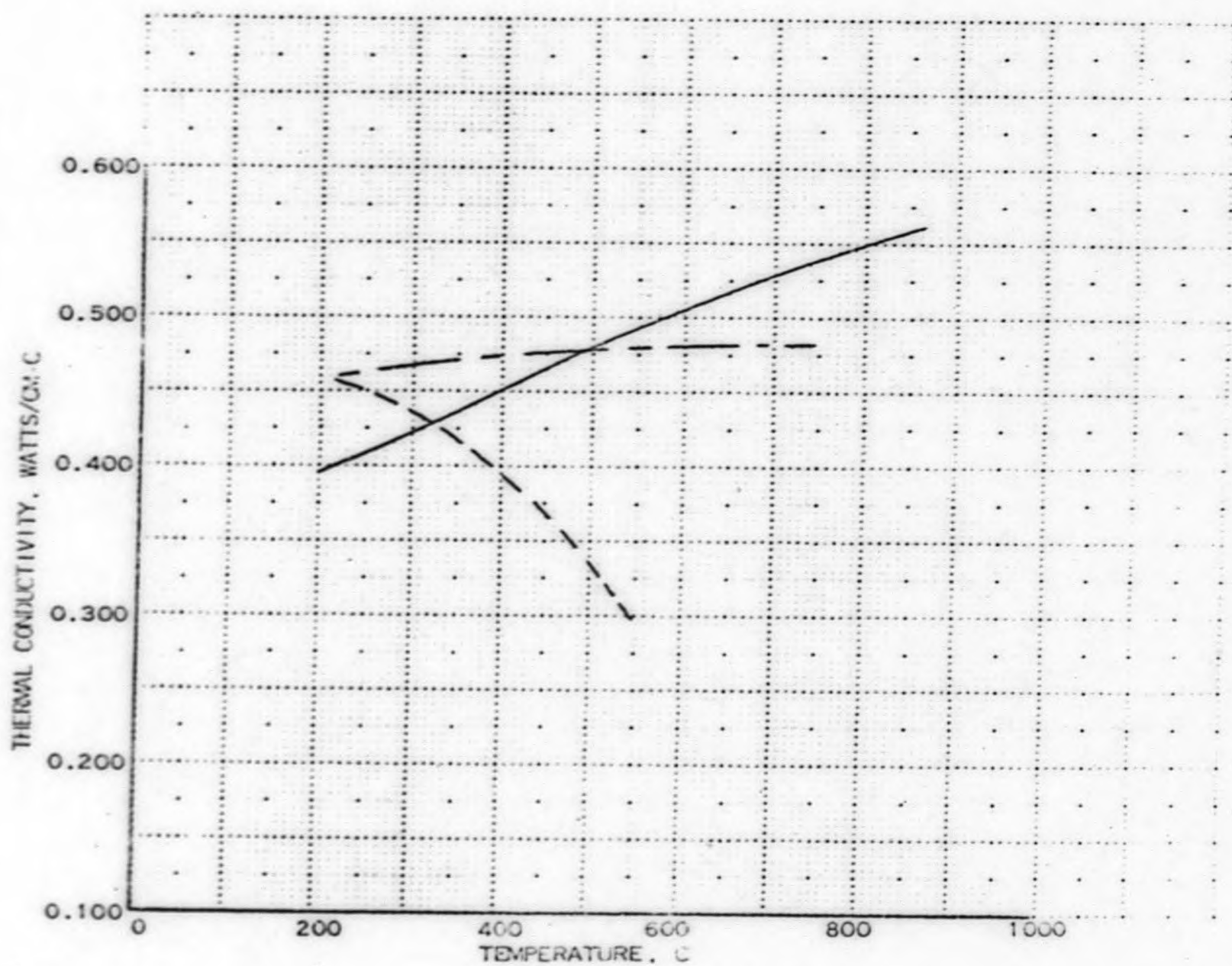
THERMAL CONDUCTIVITY OF LIQUID ALKALI METALS



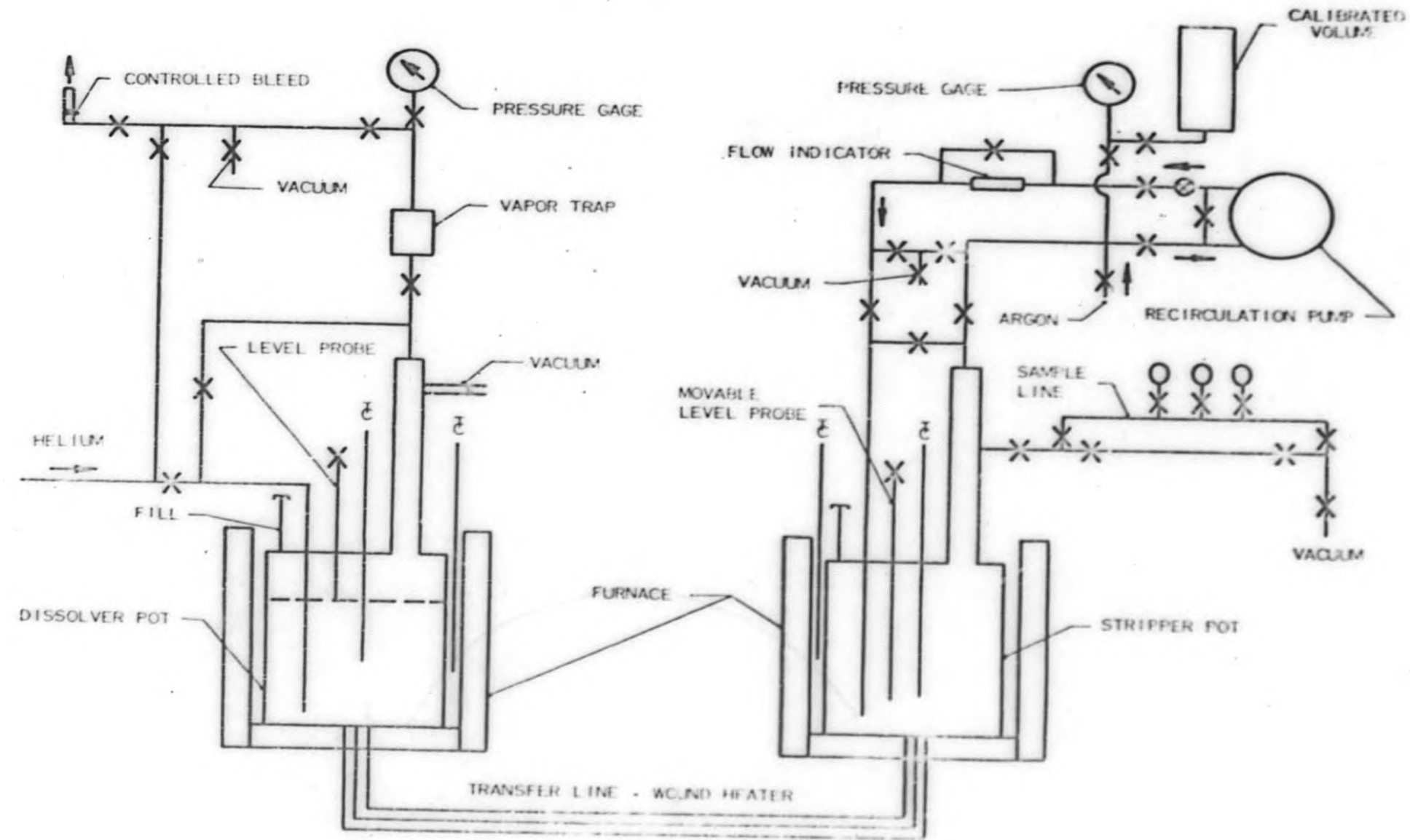
THERMAL CONDUCTIVITY OF LIQUID LITHIUM

LEGEND

- WEBBER, ET AL.
- - - KUTATELADZE, ET AL.
- CALCULATED FROM P&WA ELECTRICAL RESISTIVITY DATA



SOLUBILITY OF RARE GASES IN LIQUID METALS

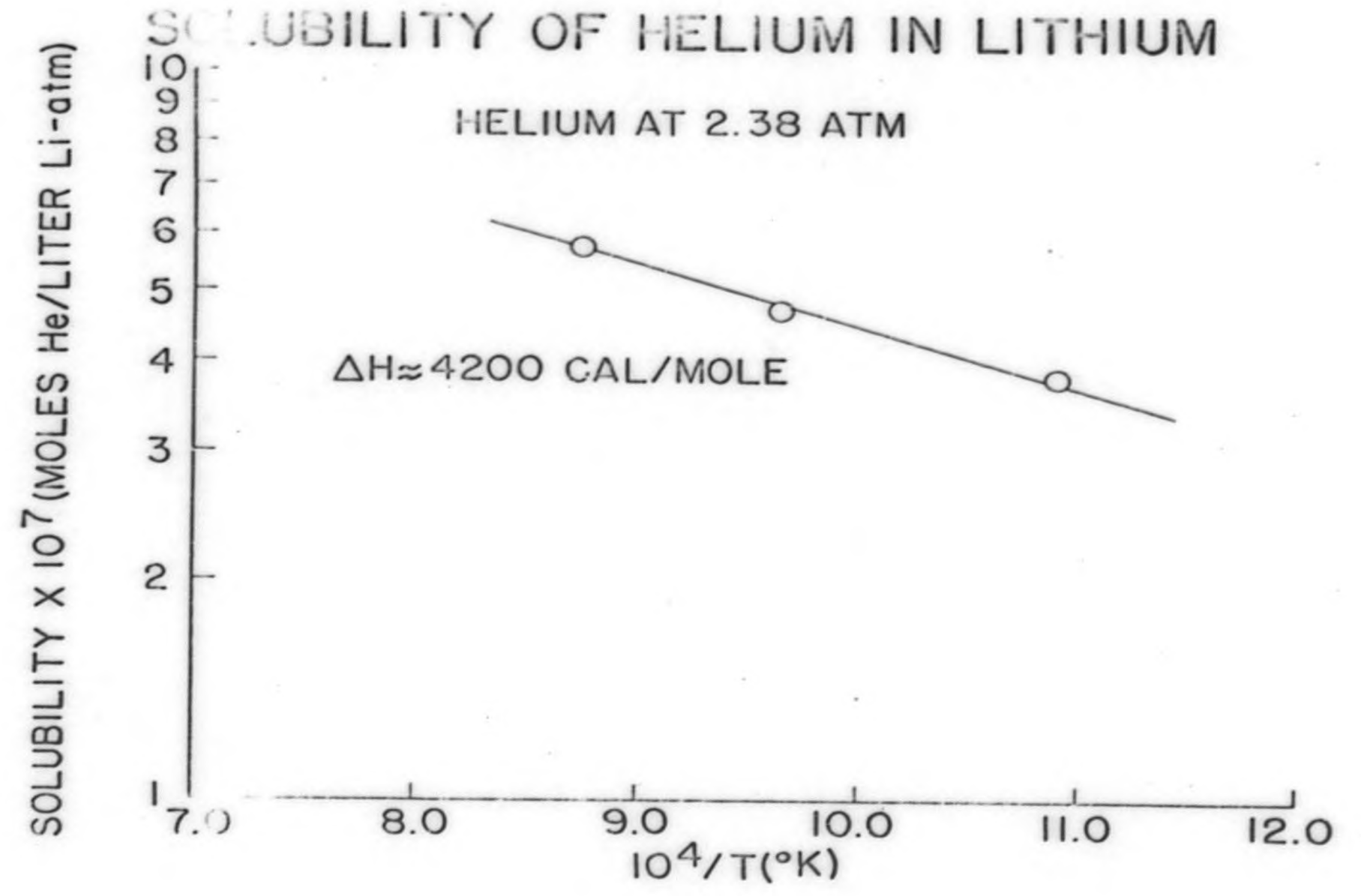


SOLUBILITY OF He IN LITHIUM
AT 2.38 ATM

<u>TEMPERATURE, °C</u>	<u>K(MOLES/LITER-ATM) X 10⁷</u>
648.8	3.8 ± 1.4
760.0	4.7 ± 0.5
871.1	5.7 ± 0.6

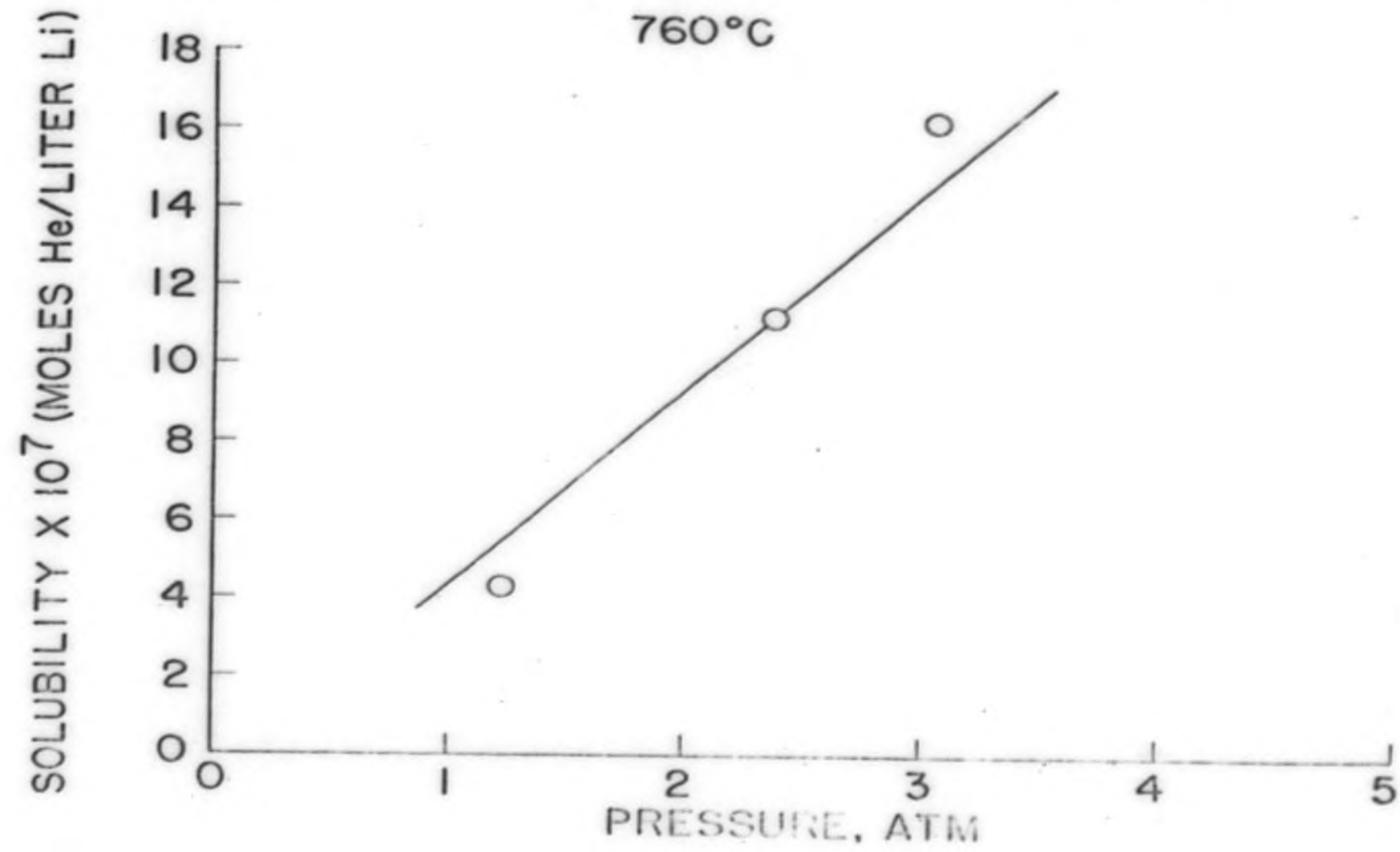
SOLUBILITY OF He IN LITHIUM
AT 760.0°C

<u>PRESSURE, ATM</u>	<u>K(MOLES/LITER) X 10⁷</u>
1.23	4.31
2.38	11.19
3.06	16.22

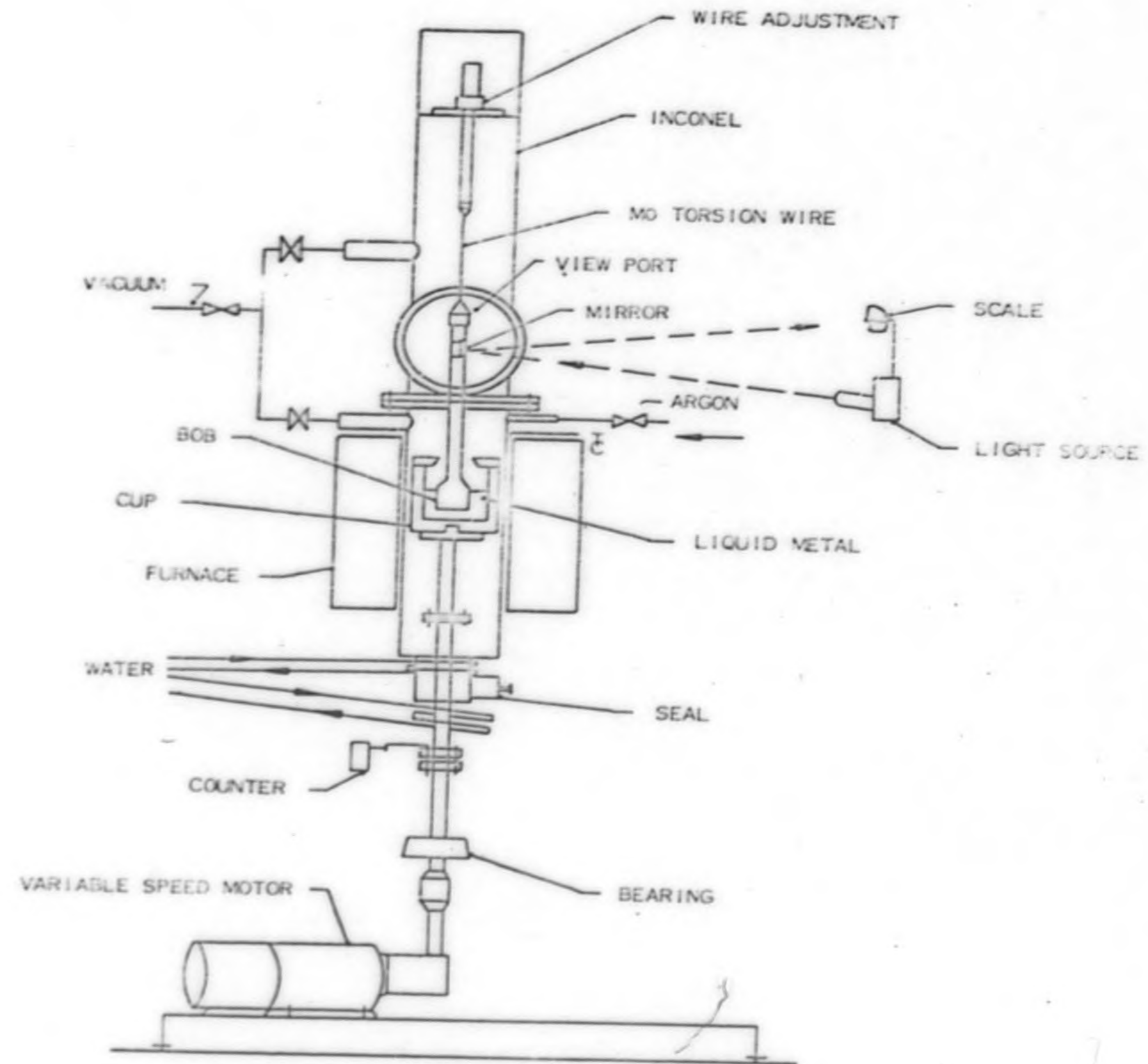


SOLUBILITY OF HELIUM IN LITHIUM

760°C

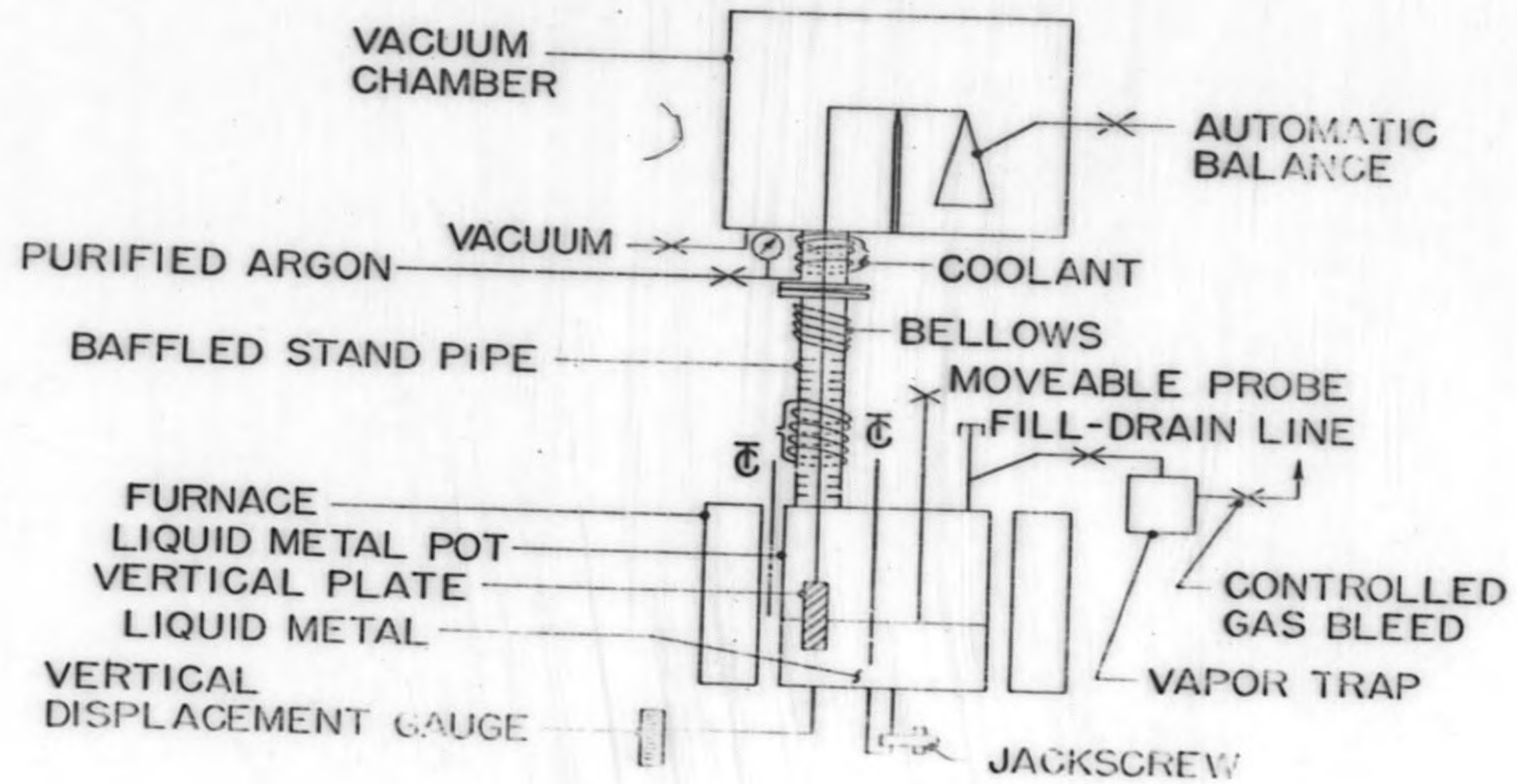


LIQUID METAL VISCOMETER - HIGH TEMPERATURE

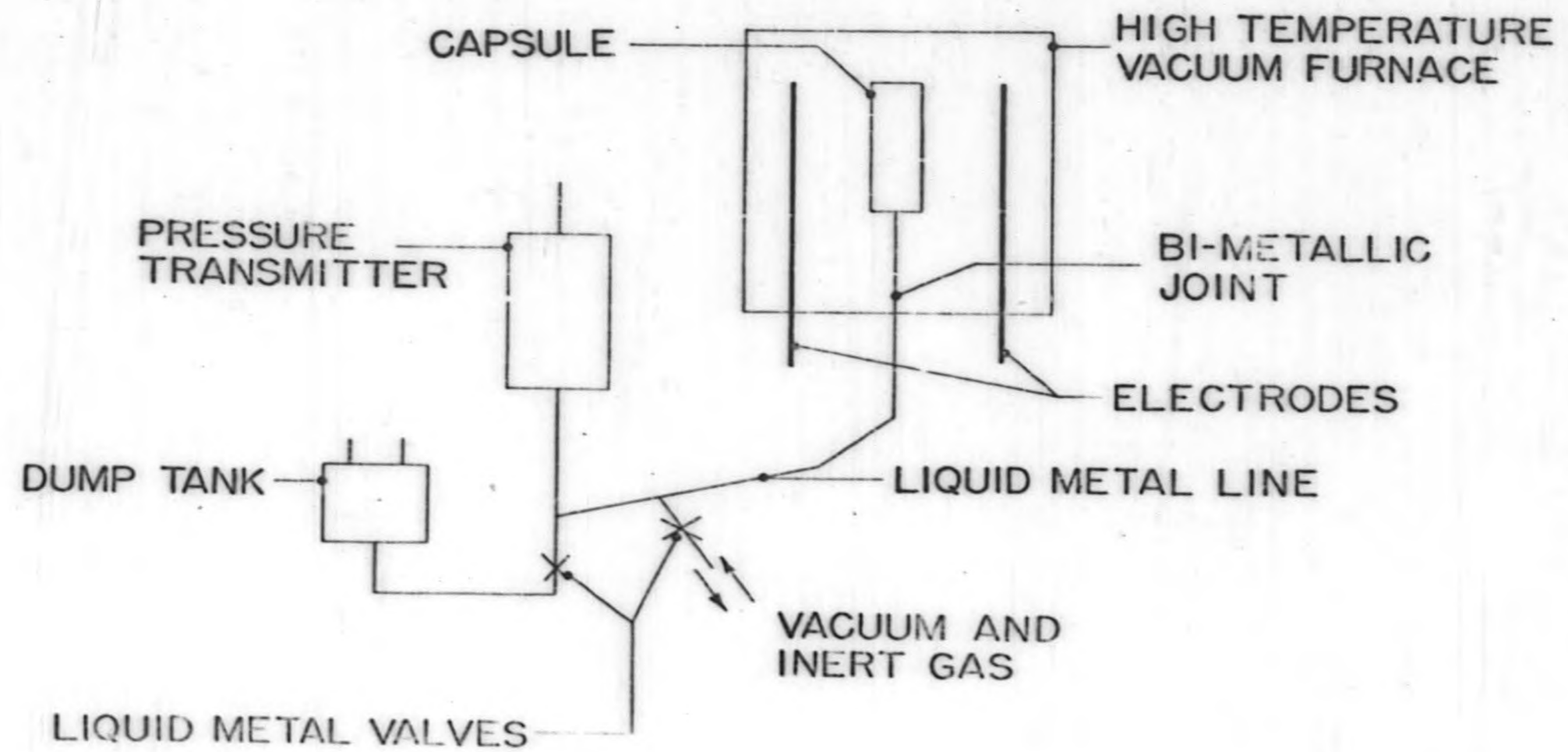


VERTICAL PLATE TECHNIQUE

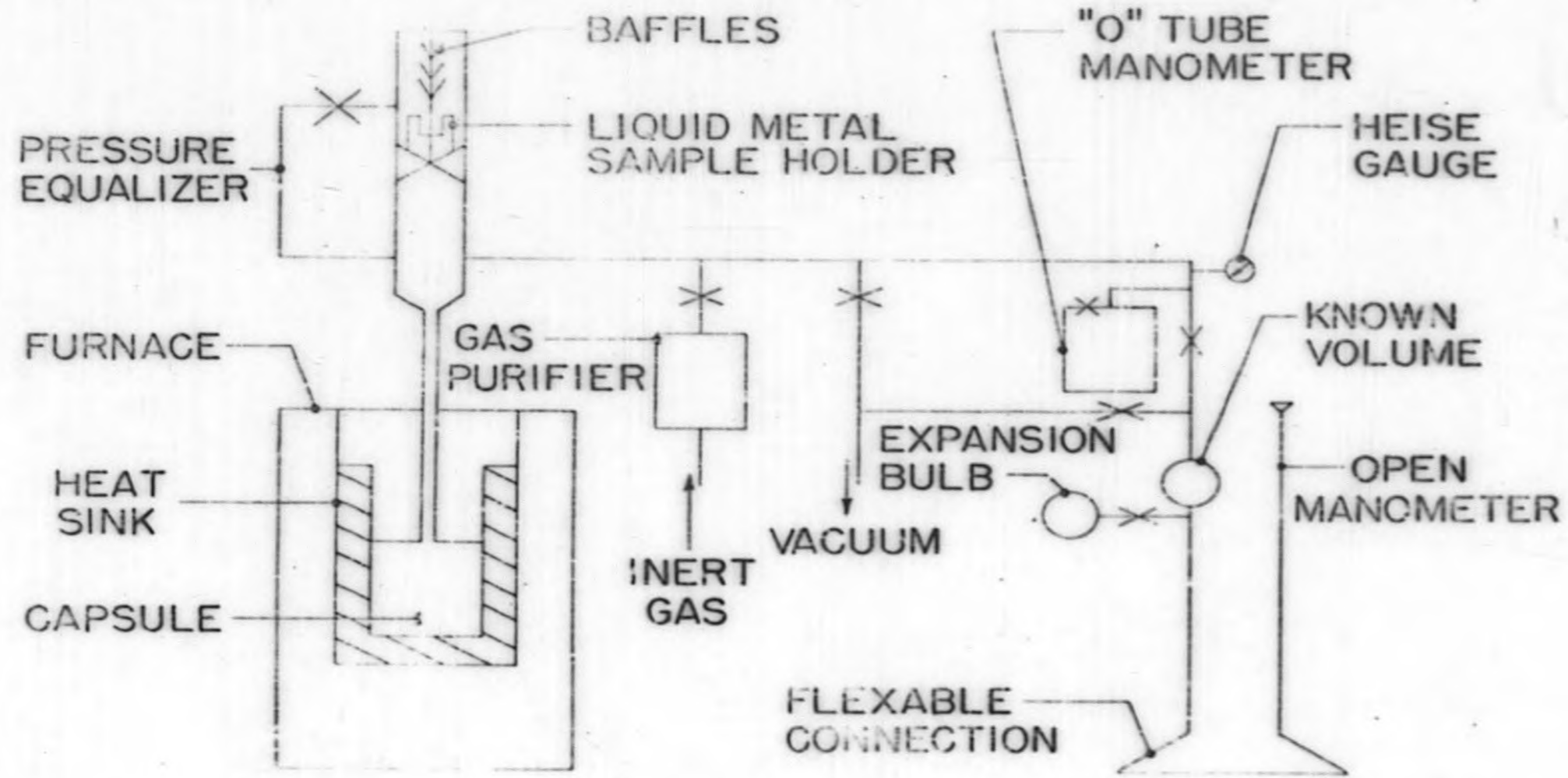
CONTACT ANGLE MEASUREMENT



LIQUID METAL VAPOR PRESSURE APPARATUS



ALKALI METAL VAPOR DENSITY APPARATUS



END