

Metallic Conductance of Supercritical Mercury Gas at High Pressures

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(Received 10 January 1966)

The electrical conductivity of mercury has been measured at fourteen temperatures between 800 and 1700°C and at pressures between 1200 and 2100 bar. From the discontinuities of the conductance observed with increasing temperature at constant pressures, the vapor-pressure curve beyond 800°C has been derived; it has a critical point at $T_c = 1490 \pm 15^\circ\text{C}$ and $p_c = 1510 \pm 30$ bars. The specific conductivity of liquid mercury in the lower temperature range increases only slightly with pressure (at 0°C from 1.06×10^4 to $1.14 \times 10^4 \Omega^{-1} \text{cm}^{-1}$ between 1 and 2100 bar; at 1200°C from 1.6×10^3 to $2.4 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ between 610 and 2100 bar). Beyond 1200°C the conductivity becomes strongly pressure-dependent. At 1520°C the specific conductivity of supercritical mercury increases continuously by more than 4 orders of magnitude from $10^{-2} \Omega^{-1} \text{cm}^{-1}$ to $5 \times 10^2 \Omega^{-1} \text{cm}^{-1}$ if it is compressed from 1580 to 2100 bar. At higher supercritical temperatures the behavior is similar, although the increase of the conductance with pressure becomes less steep. It follows that supercritical gaseous mercury exhibits metallic conductance if compressed to sufficiently high density.

THE electrical conductivity of mercury has been measured at various temperatures between 800 and 1700°C and at pressures up to 2100 bar. The determination of the vapor-pressure curve gave for the critical data of mercury $T_c = 1490^\circ\text{C}$ and $p_c = 1510$ bar.

Two kinds of fluids have so far been studied which exhibit continuous variation of electrical conduction from ionic to an essentially metallic type: metastable solutions of alkali metals in liquid ammonia, amines and polyethers, and solutions of electropositive metals in their molten halides.¹ Compressed metal vapors offer a unique possibility for studying this phenomenon with a one-component system, if the density can be varied continuously over a wide range. This requires experiments at supercritical temperatures.

Very probably the lowest critical temperature of all metals is that of mercury, the only metal for which an experimental determination of this quantity has been attempted. Birch obtained $T_c = 1460 \pm 20^\circ\text{C}$ and reported three approximate conductivity values for supercritical mercury.² Earlier vapor-pressure data, reported in the literature, are reliable only up to 880°C.²⁻⁴ The density of the coexisting gaseous and liquid phases up to 1380°C have been measured by Bender.⁵ Detailed discussions of the coexisting phases of mercury and of the presumed critical properties of other metals have been given by v. Grosse.⁶

A conductance cell was designed and built, which permitted the investigation of mercury at high temperatures and pressures. The cell proper was a cylinder of forged molybdenum with a 3-mm internal diameter containing in its center two adjacent molybdenum rods as electrodes, insulated by tubes of pure nonporous sintered alumina. The cell, together with a surrounding

resistance furnace, was mounted inside a high-pressure vessel filled with purified argon. The argon pressure always balanced the mercury pressure inside the cell. Two thermocouples (PtRh 94/6-PtRh 70/30) were inserted into wells drilled at different positions into the molybdenum wall of the cell. This permitted dependable temperature determination and control of temperature uniformity. The electrical resistance of the mercury was measured either with a transformer-arm bridge or derived from the potential difference across the mercury at various currents.

Vapor pressures have been determined applying the following procedure: At fixed pressures the temperature of liquid mercury was gradually raised and the increasing resistivity observed. At boiling temperature the mercury resistance was abruptly replaced by the high insulation resistance of the assembly. This means that the resistivity of the vapor up to about 1400 bar exceeds $2 \times 10^3 \Omega \text{cm}$. Boiling and condensation temperatures, determined at constant pressure, coincided within one percent. Since no discontinuity of resistance was observed at pressures beyond 1510 ± 30 bar, this value was assumed to be the critical pressure with a corresponding critical temperature of $1490 \pm 15^\circ\text{C}$ (Fig. 1).

The variation of the specific conductivity of liquid and supercritical mercury as a function of pressure is demonstrated by the isotherms of Fig. 2. An extremely steep rise of conductivity within a small pressure range has been observed at slightly supercritical temperatures. Each conductivity value in this range is an average of up to twenty independent determinations. At the higher supercritical densities (1500 to 1550°C, pressure above 1900 bar) the magnitude and pressure dependence of the conductivity approach the properties of liquid mercury. At lower densities (1500 to 1550°C, pressures below 1600 bar or pressures of about 2100 bar up to 1700°C) the conductivity is lower by a factor of about 10^4 . Between these two regions the transition to the "metallic" state occurs.

The specific conductivity of liquid mercury at 0°C is

¹ T. C. Waddington, *Non-Aqueous Solvent Systems* (Academic Press Inc., New York, 1965).

² F. Birch, *Phys. Rev.* 41, 641 (1932).

³ L. Cailletet, E. Collardeau, and C. A. Riviere, *Compt. Rend.* 130, 1585 (1900).

⁴ F. Bernhardt, *Physik. Z.* 26, 265 (1926).

⁵ J. Bender, *Physik. Z.* 16, 246 (1915); 19, 410 (1918).

⁶ A. v. Grosse, *J. Inorg. Nucl. Chem.* 22, 23 (1961).