Metallic Conductance of Supercritical Mercury Gas at High Pressures

E. U. FRANCK AND F. HENSEL
Institut für Physikalische Chemie und Elektrochemie, Technische Hochschule, Karlsruhe, Germany

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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 $T_c=1490\pm15$°C and $p_c=1510\pm30$ 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 1.14×10^4 Ω^{-1} cm^{-1} between 1 and 2100 bar; at 1200°C from 1.6×10^3 to 2.4×10^3 Ω^{-1} 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} Ω^{-1} cm^{-1} to 5×10^2 Ω^{-1} 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 $T_c=1490$°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 $T_c=1460\pm20$°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 2×10^3 Ω 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 ± 15°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).

$1.06\times10^{+4}\ \Omega^{-1}\ cm^{-1}$ at 1 bar and $1.14\times10^{+4}\ \Omega^{-1}\ cm^{-1}$ at 2100 bar.[2] At 1200°C the increase with rising pressure is still small ($1.6\times10^{+3}\ \Omega^{-1}\ cm^{-1}$ at the vaporization pressure of 610 bar and $2.4\times10^{+3}\ \Omega^{-1}\ cm^{-1}$ at 2100 bar). It is only beyond 1200°C that the conductivity becomes strongly pressure-dependent. At slightly supercritical temperatures and at pressure beyond 2000 bars the conductivity is still very close to that of the liquid state around 1200 or 1400°C. The decrease of conductance with temperature at constant pressure, however, becomes very pronounced above 1500°C. This is probably related to the increase of interatomic distances caused by the considerable decrease of density in this region. A quantitative discussion has to be postponed until density data for supercritical mercury are available. An estimation of such density data based on the properties of nonmetallic elements using the principle of corresponding states is not justified.

Thermal ionization of mercury gas at 1700°C and atmospheric pressure at equilibrium conditions can easily be calculated using the ionization potential of 10.4 eV for mercury atoms. Applying an approximate electron-atom collision cross section of 100 square angstroms, a specific conductivity of $10^{-9}\ \Omega^{-1}\ cm^{-1}$ is obtained. The temperature dependence should be positive. The conductivity determined experimentally at 1700°C and 2000 bar is around $2\times10^{-2}\ \Omega^{-1}\ cm^{-1}$, i.e., about 7 orders of magnitude higher than at one bar.

The supposition that this conductivity may originate in insufficient insulation of the alumina parts can be dismissed on the ground of test measurements and also because of the negative temperature dependence

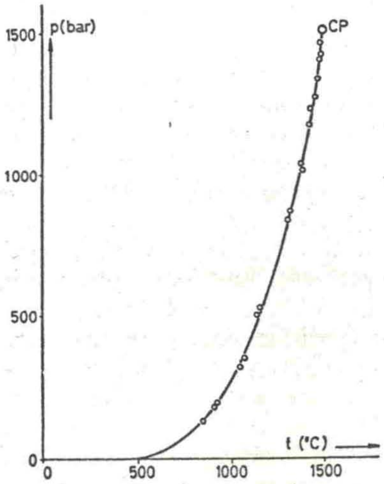

FIG. 1. Vapor-pressure curve of liquid mercury (C.P., critical point; 00, experimental points, this work).

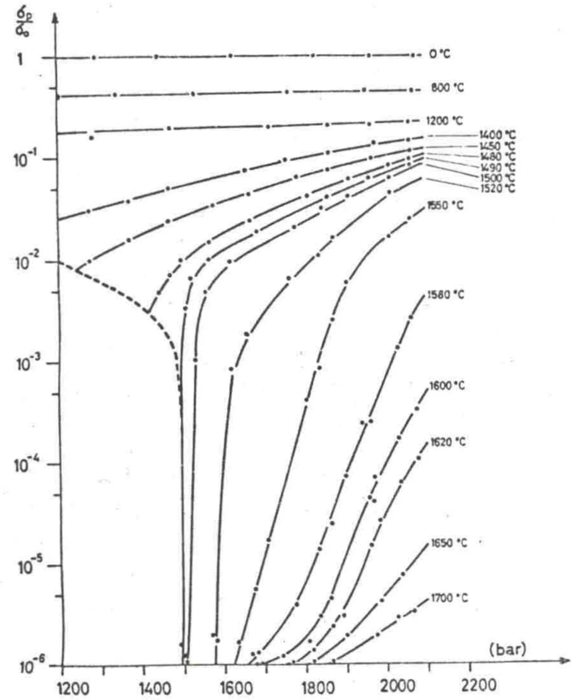

FIG. 2. Relative electrical conductivity of mercury at subcritical and supercritical conditions. σ_p=specific conductivity at temperature t°C and pressure p; σ_0=specific conductivity at $t=0$°C and $p=1$ bar (liquid state); – – – Boundary of the liquid-gas two-phase region.

observed. It cannot be excluded that a certain amount of dimers occur under these conditions, although the dimerization energy of mercury atoms is only about 0.06 eV. It is supposed, that the average interatomic distance is already short enough to cause an appreciable reduction of the barrier impeding the free transfer of electrons.

Quantitative discussion of this phenomenon requires the knowledge of density data. The experimental determination of the mercury density at supercritical temperatures is under way in this laboratory. Details of the conductivity measurements will be published elsewhere.[7]

Note added in proof. Experimental determinations of density of mercury have been completed in the meantime and will be given elsewhere.[7] Recently, similar results have been obtained by I. K. Kikoin *et al.*, Zh. Experim. i Teor. Fiz. **49**, 124 (1966) [English transl.: Soviet Phys.—JETP **22**, 89 (1966)].

[7] F. Hensel and E. U. Franck, Ber. Bunsenges. Phys. Chem. **70**, (1966).