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Metal–Nonmetal Transition in Dense Mercury Vapor

F. HENSEL, E. U. FRANCK

Institut für physikalische Chemie und Elektrochemie, Universität Karlsruhe, Germany

This article presents the results of conductivity and density measurements of liquid, gaseous, and supercritical mercury up to 1700°C and 2100 bar. Beyond the critical temperature of 1490°C the conductivity varies continuously from 10^{-4} to $10^2\ \Omega^{-1}\ \text{cm}^{-1}$ if the density is increased from 2 to 6 g/cm^3. This variation is an example of nonmetal–metal transition and is discussed accordingly. The activation energy of conductivity in the supercritical fluid decreases markedly with increasing density and approaches very small values around 5 g/cm^3. Conductivity data for dense gaseous mercury–cesium mixtures are given.

I. INTRODUCTION

Since the publication by Mott in 1961, on the transition to the metallic state, the relation between the metallic and thermodynamic properties of a substance has received increased attention.[1–4] Mott presented a treatment based on overlap considerations, which proposed the existence of a critical separation at which a change from metallic to nonmetallic behavior should occur in a system of localized centers.

The experimental verification of this transition, with diverse examples, is an interesting problem. Most of the experimental evidence has been obtained by investigation of nonordered heavily doped solid semiconductors.[5,6] Concentrated metastable solutions of alkali metals in liquid ammonia are another group of nonordered systems well investigated in this respect.[7,8] All of these examples, however, contain two or more components. It is therefore necessary to allow for the influence of the dominant solid or liquid "solvent" on the behavior of the minority component which exhibits the transition to be investigated.

It is certainly desirable to study the transition with a one-component system also. A unique possibility is the observation of the appearance of metallic conductivity in a metal vapor, which occurs if the vapor density is continuously increased to sufficiently high values. Such continuous increase of density is only possible, however, if the formation of a liquid phase by condensation is avoided. This means that the compression of the vapor has to be done beyond the critical temperature which terminates the vapor pressure curve. Figure 1 gives a schematic illustration of the liquid–gas phase behavior of a pure substance. Above the critical temperature T_c the homogeneous supercritical fluid can be compressed to liquid-like densities without phase separation. Thus the mean interatomic distance can be reduced sufficiently so that merging of the individual electronic levels of atoms into common bands is to be expected.

Until recent years very few experimental investigations of dense metal vapors had been made. In almost all cases the substance investigated was mercury, for reasons apparent from Table I. The critical temperatures of metals range from 1500°C to about 20 000°C. Experimental problems arise from the necessity to apply high pressures at very high temperatures, where only very few materials can be utilized.

The first attempt to determine the critical point of mercury was made by Bender[9,10] in 1915. The densities of vapor and liquid (ρ_{liquid} and ρ_{gas}) at saturation pressure were measured to 1380°C using sealed quartz capsules. Figure 2 gives the density of gaseous and liquid mercury according to Bender, together with more recent results.[11–14] The diagram shows that the "law of rectilinear diameters" is approximately valid; that is, the temperature dependence of $\frac{1}{2}(\rho_{\text{liquid}}+\rho_{\text{gas}})$ is almost linear. Using this linearity Grosse[15,16] was able to estimate the critical temperatures of numerous other metals from existing experimental data on liquid densities of these metals at lower temperatures. Recent measurements of the densities of the coexisting liquid and gaseous phases of the alkali metals by Dillon *et al.*[17,18] have provided more reliable numbers for the critical data of these metals.

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[1] N. F. Mott, Phil. Mag. **6**, 287 (1961).

[2] W. Kohn, Phys. Rev. **133**, 171 (1964).

[3] J. Hubbard, Proc. Roy. Soc. (London) **A276**, 238 (1963).

[4] J. Hubbard, Proc. Roy. Soc. (London) **A277**, 237 (1964); **281**, 401 (1964).

[5] H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).

[6] H. Fritzsche and M. Curevas, Phys. Rev. **119**, 1238 (1960).

[7] *Solutions Métal-Ammoniac Propriétés Physicochimiques*, G. Lepoutre and M. J. Sienko, Eds. (W. A. Benjamin, Inc., New York, 1964).

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[10] J. Bender, Physik. Z. **19**, 410 (1918).

[11] D. R. Postill, R. G. Ross, and N. E. Cusack, Advan. Phys. **16**, 493 (1967).

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[15] A. V. Grosse, J. Inorg. Nucl. Chem. **22**, 23 (1961).

[16] A. V. Grosse, Rev. Hautes Temp. Refractaires **3**, 115 (1966).

[17] I. G. Dillon, P. A. Nelson, and B. S. Swanson, Rev. Sci. Instr. **37**, 614 (1966).

[18] I. G. Dillon, P. A. Nelson, and B. S. Swanson, J. Chem. Phys. **44**, 4229 (1966).

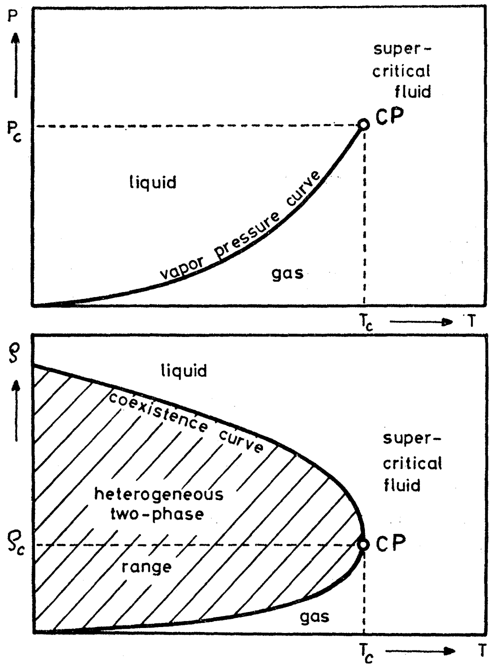

FIG. 1. The liquid–gas equilibrium and the critical point CP, pressure–temperature ($p-T$) and density–temperature ($\rho-T$) diagrams.

Birch[19] in 1931, was the first to demonstrate experimentally the occurrence of metallic conduction in a dense gas using supercritical mercury. He derived critical data for mercury from these conduction experiments which are in good agreement with recent results (viz. Table I). Unfortunately only five conductance values and no densities could be determined at that time. Since 1963 at least three groups have developed new techniques to investigate liquid and supercritical fluid metals at high pressures.

Postill, Ross, and Cusack[11,12] described measurements of the density and electrical conductivity of liquid mercury in the range from 20° to 1100°C and from 1 to 1000 bar. Over this range the conductivity decreases by about a factor 4 and the density changes by about 20% of its room-temperature value. Kikoin and Sechenkov have published two papers[20,21] of measured densities and electrical conductivities as a function of temperature (0°–2000°C) and pressure (1–5000 bars). The conductivity in this range varies from 10^4 to 10^{-1} Ω^{-1} cm^{-1} while the density changes from 13.5 to 1.0 g/cm^3.

TABLE I. Critical temperatures and pressures of some metals. (The values for cesium and mercury have been measured, the other data have been estimated.)

Metal	Critical temperature (°K)	Critical pressure (bar)	References
Cs	2 057	145	17, 18
Na	2 573	350	17, 18
Hg	1 733	1 610	19
	1 753	1 520	21
	1 763	1 510	13, 14
Sn	8 720	2 100	15
Pb	5 400	850	15
W	23 000	>10 000	15

Hensel and Franck[13,14] have measured the electrical conductivity and the density of liquid and supercritical mercury to temperatures of 1700°C and pressures to 2100 bars. Under these conditions the conductivity varies from 10^4 to 10^{-4} Ω^{-1} cm^{-1} and the density decreases from 13.5 to 1.5 g/cm^3.

In the present paper the emphasis is on the intermediate range of conductance between the nonmetallic and metallic states. Therefore, special consideration is given to the properties of mercury at densities between about 20% and 60% of the normal liquid density, that is, at critical or subcritical pressures. This range is not covered by the experiments of Kikoin *et al.* New data are presented and the conductance is discussed as a function of density and mean interatomic distance as well as a function of temperature at constant densities. Activation energies are derived for the conductance of mercury.

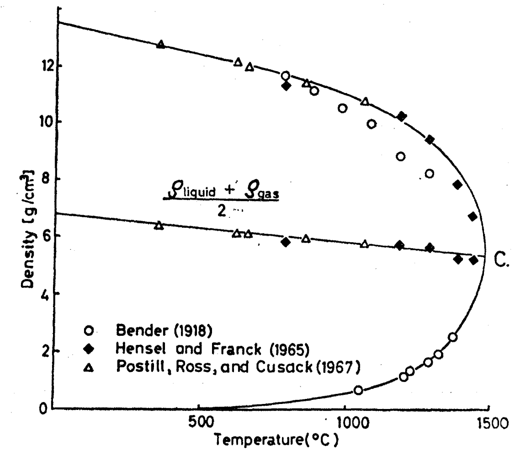

FIG. 2. Density ρ of liquid and gaseous mercury as a function of temperature up to the critical point CP.

II. EXPERIMENTAL

In order to study the conductivity and density of mercury and cesium within a not too limited supercritical temperature range it is desirable to extend the measurements to 1800° or 2000°C and to at least 2000

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[19] F. Birch, Phys. Rev. **41**, 641 (1932).

[20] I. K. Kikoin, A. P. Sechenkov, E. V. Gel'Man, M. M. Korsunski, and S. P. Naurzakov, Zh. Eksperim. i Teor., Fiz. **49**, 124 (1965) [English transl.: Soviet Phys.—JETP **22**, 89 (1966)].

[21] I. K. Kikoin and A. P. Sechenkov, Order of Lenin Institute of Atomic Energy, Moskow (1967).

bar with mercury and to about 500 bar with cesium. Pure molybdenum and pure tungsten were found satisfactory materials for the cells to contain the supercritical metals. Thin tubes of sintered, nonporous alumina or thoria were used as insulators for the conductance experiments. Since the molybdenum and tungsten cells could not withstand high internal pressures at high temperatures, they were placed inside an internally heated autoclave, using argon as the pressurizing medium. The pressures of argon and liquid metal were equilibrated outside the autoclave at low temperature within a stainless steel "buret." Resistance heaters surrounded the cell inside the autoclave. Figure 3 shows the assembly schematically. Details are described elsewhere.[13,14,22]

To obtain the conductivity, the potential differences at various currents between two molybdenum electrodes in the mercury were determined. Since specific resistivities of the fluid metal varied from 10^{-4} to 10^4 Ω cm, according to temperature and pressure, several different shapes of cells and electrodes had to be used. A similar cell made from tungsten and with insulating tubes of thoria served for the cesium measurements.

To determine the density of mercury the conductance cell inside the autoclave was replaced by a molybdenum cylinder of 5 cm^3 internal volume, closed at one end and connected by a narrow capillary to the lower end of the buret, mentioned above, which was partly filled with mercury. Since the mercury level in the buret could be determined by the resistance of a thin centrally located platinum wire, the amount of mercury within the heated molybdenum cell could be evaluated. Temperatures were measured by platinum–rhodium or tungsten–rhenium thermocouples inserted into holes at different positions in the walls of the molybdenum and tungsten cells. Pressures were determined by calibrated precision Bourdon gauges connected to the argon-filled branch of the assembly. Usually the pressure was held constant and the temperature changed slowly while the resistances were recorded. Cesium metal was purchased in evacuated glass ampules. After the ampules were cracked under pure argon gas the metal was dropped into the cell, or for preparing amalgams, into the mixing vessel. The concentrations of the amalgams were measured by weighing the amounts of cesium and mercury. A detailed description of the preparation of the amalgams is given elsewhere.[22]

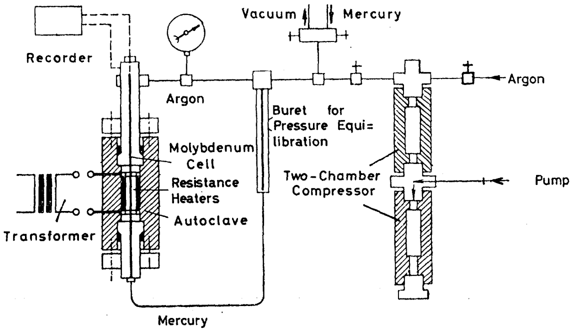

FIG. 3. Assembly for conductivity and density measurements with mercury at high temperatures and pressures.

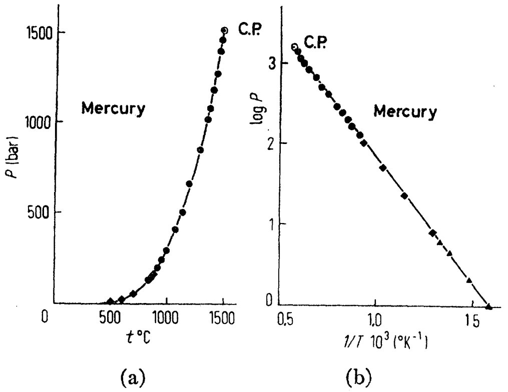

FIG. 4. (a) Vapor pressure curve of liquid mercury up to the critical point. (b) Log p as a function of $1/T$. ● = experimental points, this work. ◆ = values of Cailletet, Collardeau, and Riviere (1926). ▲ = values of Douglas, Ball, and Ginnings (1951).

III. RESULTS

A. Vapor Pressure Curves

At fixed pressures the temperature of the liquid metal in the cell was raised and the slowly increasing resistance observed. With subcritical pressures a discontinuous change to very large resistances was recorded at certain temperatures, which was taken as indication for the replacement of the liquid by a gas phase in the cell. The respective pair of values for temperature and pressure were taken as points of the vapor pressure curve. Figures 4 and 5 give the vapor pressure curves for mercury and cesium thus obtained. Boiling and condensation temperatures at constant pressure coincided within 1%. Above 1510±30 bar, discontinuous resistance changes were no longer observed with mercury. This value was assumed to be the critical pressure P_c with a corresponding critical temperature of $T_c=1490\pm15$°C. The values for cesium are $T_c=1750\pm30$°C and $P_c=110\pm10$ bar.[23]

B. Conductivity of Mercury

Figure 6 gives isotherms of the specific conductivity of liquid, gaseous, and supercritical mercury as a function of pressure. Each of the points is an average of five different determinations of temperature and conductivity. Only a part of the experimental points is indicated in the diagram. At slightly supercritical temperatures a continuous but very steep rise of conductance

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[22] R. Schmutzler, thesis, Karlsruhe (1967), Ber. Bunsenges. Phys. Chem. (to be published).

[23] H. Renkert, thesis, Karlsruhe (1968).

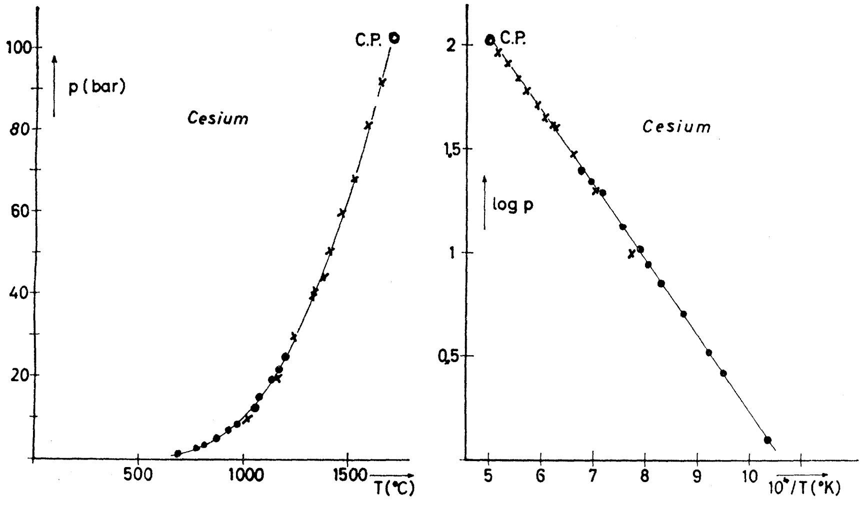

FIG. 5. (a) Vapor pressure curve of liquid cesium up to the critical point. (b) Log p as a function of $1/T$. × = experimental points, this work. ● = values of Stone *et al.*

with pressure is observed. Here every point is an average of up to twenty independent determinations. Among the possible sources of error a conceivable difference in temperature between the thermocouple junctions in the cell wall and the fluid metal within the cell would be important. The agreement, however, of the vapor pressure curve of mercury determined here with earlier, reliable data reported in the literature[24–27] which extend to 860°C for mercury and to 1200°C for cesium should restrict the uncertainty of the temperature values of this work to ±20°C.

C. Density

The variation of the molar volume of liquid and supercritical mercury with pressure is demonstrated by the isotherms of Fig. 7. The dotted line gives the assumed values for the subcritical liquid at equilibrium vapor pressure. In order to interpret the conductance data below about 10^{-2} Ω^{-1} cm^{-1} knowledge of the mercury density below 3.5 g/cm^3 as a function of temperature and pressure are desirable. For the purpose of the discussion following below these density data were obtained by short extrapolations. They were based on an empirical equation of state[22] in polynomial form derived from the supercritical isotherms of Fig. 7.

D. Amalgams

It is interesting to study the influence of the small addition of an element with a low ionization energy on the conductivity of a dense metal vapor. Figure 8 shows

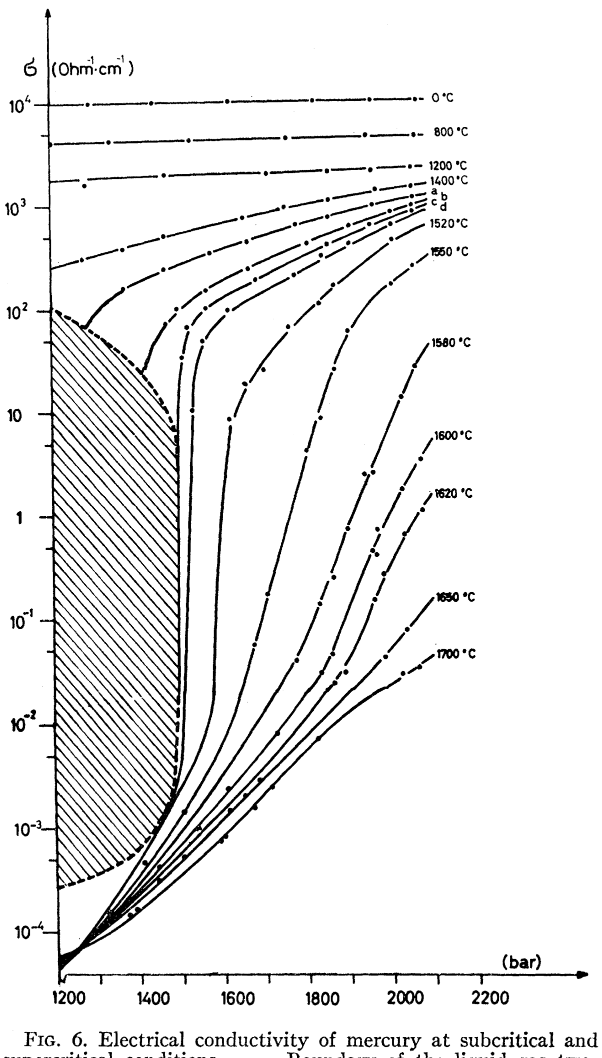

FIG. 6. Electrical conductivity of mercury at subcritical and supercritical conditions. --- Boundary of the liquid–gas two-phase region (a = 1450°C, b = 1480°C, c = 1490°C, d = 1500°C).

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

[25] T. B. Douglas, A. F. Ball, and J. Ginnings, J. Res. Natl. Bur. Std. **46,** 334 (1951).

[26] C. F. Bonilla, D. L. Sawkney, and M. M. Makansi, Trans. Am. Soc. Metals **55,** No. 3, 877 (1962).

[27] J. P. Stone, C. T. Ewing, J. R. Spann, E. W. Steinkuller, D. D. Williams, and R. R. Miller, J. Chem. Eng. Data **11,** 315 (1966).

the effect of small additions of cesium on the conductivity of supercritical mercury at 1600°C as a function of the density of pure mercury. These data were obtained by using the same experimental arrangement and method that has been described for measuring the conductivity of pure mercury. The concentrations in Fig. 8 are those of the liquid amalgams at 25°C. With the experimental conditions prevailing, this composition is certainly not maintained in the fluid phase in the cell at 1600°C. The actual cesium concentration must be lower. It is quite evident, however, that the addition of a small amount of cesium to supercritical mercury can increase the conductance by a factor of 10 to 100.

IV. DISCUSSION

The results presented in the last section demonstrate that by compression a metal vapor which is an insulator at low pressure can be transformed continuously into a dense, fluid, disordered system exhibiting metallic conductance. This requires a simultaneous change of the interatomic forces and the interatomic cohesion. It is of interest to examine the macroscopic thermodynamic properties of the fluid in the same range of conditions.

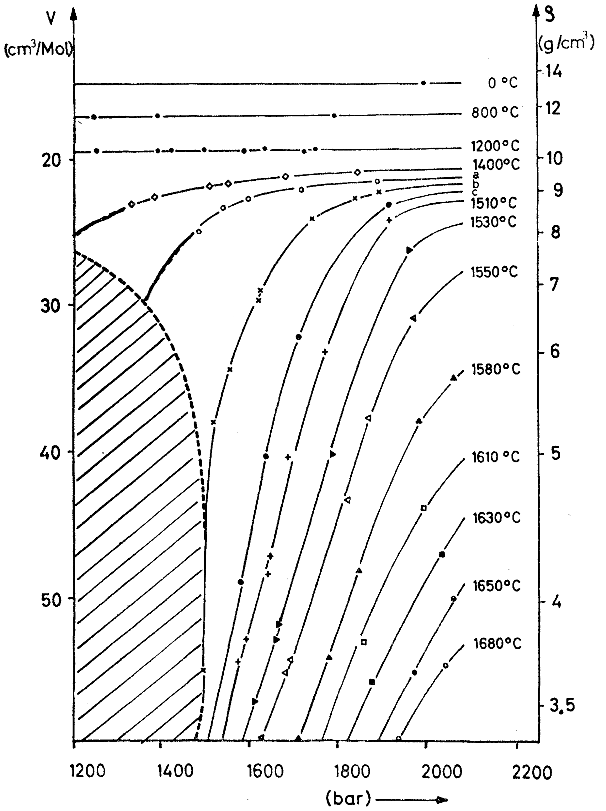

FIG. 7. Volume or density of mercury at subcritical and supercritical temperatures in dependence of the pressure: – – – Boundary of the liquid–gas two-phase region (a = 1450°C, b = 1480°C, c = 1500°C).

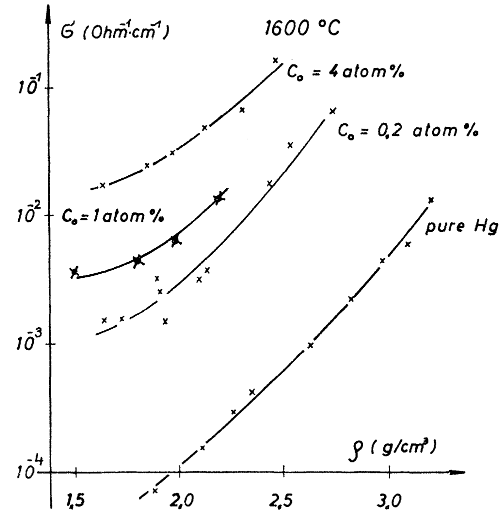

FIG. 8. The increase of the specific conductivity of supercritical mercury caused by small additions of cesium. C_0 = composition of the liquid amalgam at 25°C.

Figures 4 and 5 show that for mercury and cesium, over the entire range of temperature from their melting points to their critical points, the logarithm of the saturation vapor pressure is a linear function of the reciprocal temperature. This is the normal behavior of most substances. From the slopes of the logarithmic plots the enthalpies of vaporization can be derived. For mercury the result is 14.1 kcal/mole and for cesium 15.7 kcal/mole, which is in good agreement with data reported in the literature.[15,18]

The "law of rectilinear diameters" referred to in the introduction has until now been tested only for a few metals[15,17,18] (Fig. 1). Using it Cusack et al.[12] estimated a critical density of 5.3 g/cm³ for mercury, which is higher than the value of 4.2 g/cm³ proposed earlier by the present authors[14] using the same data and another method. The value of 5.3 g/cm³ gives a critical compressibility factor $RT_c/p_cV_c = 2.5$. This value is lower than that for most other substances. It is suggested, however, that this low value may be a peculiarity of mercury, because the estimated values for the alkali metals[18] are much higher.

A comparison of the mercury conductivity and density isotherms of Figs. 6 and 8 demonstrates that large changes in conductivity are primarily caused by variations of molar volume. The data allow a separation of the effects of temperature and volume expansion. Figure 9 shows the conductivity of supercritical mercury at 1550°C as a function of the density. (The upper scale gives the cube root of relative volume per atom.) A change in the density from about 6 to 2 g/cm³ decreases the conductivity by 10^6. This large change in σ is evidence of the metal to nonmetal transition for

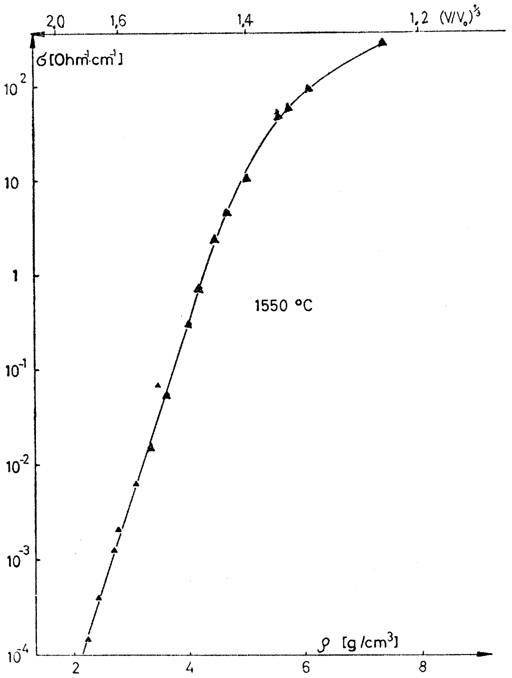

FIG. 9. Specific conductivity σ of supercritical mercury as a function of density ρ or of $(V/V_0)^{1/3}$. V_0=molar volume of liquid Hg at 0°C and 1 bar.

fluid divalent metals described by Mott in 1966.[28,29] This transition occurs in the vicinity of the critical density, as predicted for monovalent metals already by Krumhansl[30] from thermodynamic considerations.

An analogy may be taken from solid-state physics for a mercury gas assumed to be held on a lattice: The transformation from insulator to metal passes through semiconducting behavior as the interatomic distance decreases. At low density the insulator has energy bands separated by an energy gap within which no allowed levels exist. With an increase of density the gap should decrease and ultimately go to zero. The gap energy can be measured by analyzing the temperature dependence of the conductivity at different constant densities. Figure 10 shows the temperature dependence of the conductivity of mercury at constant densities and at constant pressures as well.

At high supercritical and at liquid densities the temperature dependence of the conductivity at constant density is positive. This does not necessarily indicate a semiconducting behavior, because a positive $(\partial\sigma/\partial T)_V$ is typical for the divalent metals Zn, Cd, and Hg in the liquid state at low temperature and is qualitatively explicable by Ziman's theory of liquid metals.[31] In the present experiments with mercury, however, with increasing volume the mean free path of electrons calculated from the measured conductivity and free electron theory drops rapidly. At a density of 10 g/cm³ (about 75% of normal liquid density) the calculated mean free path has already fallen to the interatomic distance and the measured conductivity is only about $10^3\ \Omega^{-1}/\mathrm{cm}^{-1}$. According to a proposition of Mott[29] such an order of magnitude of the conductivity should indicate the presence of localized states. At this and at even lower densities it is expected that with rising temperature the conductivity at constant density would be enhanced by the thermal excitation of new conduction electrons. This is what actually occurs at low densities. The temperature dependence for semiconducting behavior is described by a formula of type $\sigma \propto \exp(-\Delta E/kT)$, so that a logarithmic plot of σ versus the reciprocal temperature should be a straight line. Figure 11 shows the $\log\sigma - 1/T$ plot at different densities.

The form of the curves obviously gives evidence for semiconducting behavior. At the lowest density a strong variation with temperature is observed. With increasing density the slope of the curves decreases

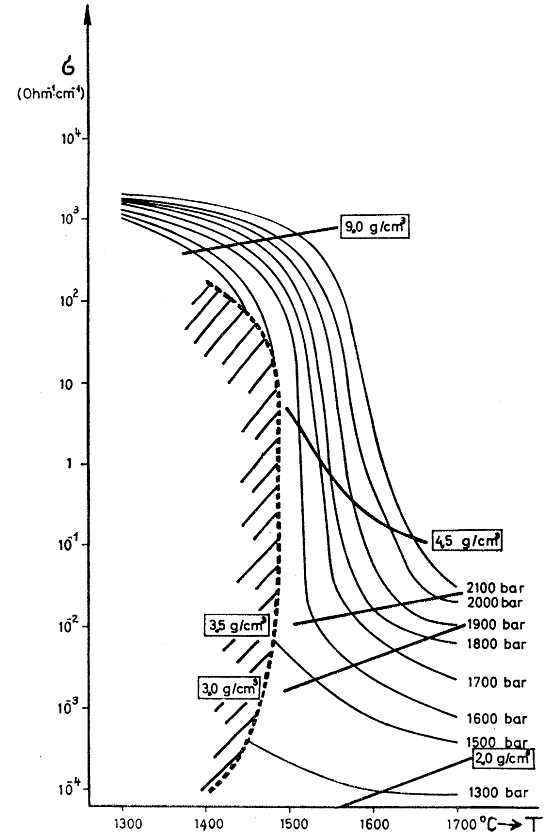

FIG. 10. Temperature dependence of the specific conductivity of mercury at constant pressures and constant densities.

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[28] N. F. Mott, Phil. Mag. **13**, 989 (1966).

[29] N. F. Mott, Advan. Phys. **16**, 49 (1967).

[30] J. A. Krumhansl, *Physics of Solids at High Pressures*, C. Tomizuka, Ed. (John Wiley & Sons Inc., New York, 1966).

[31] C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, Phil. Mag. **7**, 865 (1962).

indicating that the activation energy approaches zero. Unfortunately, because of experimental difficulties with insulation only a relatively small range of temperature was accessible. There are not yet enough data available on the variation of conductivity with temperature at densities above 4 g/cm^3 to determine in what manner and at what density the activation energy vanishes.

Figure 12 shows the activation energy of expanded mercury multiplied by a factor of 2 as a function of the density (in the upper scale vs the cube root of the relative volume). This energy is a measure of the effective energy gap which appears when a disordered mercury lattice is expanded. At zero density the activation energy is half of the ionization energy of the isolated mercury atom with a value of 10.4 eV. From this value the observed activation energy drops with decreasing interatomic distance to 1.0 eV at a density of 3.5 g/cm^3. This is in good agreement with an estimation of Mott[29] which gives an activation energy of 1.1 eV or an "effective ionization energy" of 2.2 eV for this density.

An unexpected behavior is observed in the neighborhood of the critical point. At temperatures near the critical temperature and densities in the range of the critical density the conductivity decreases with increasing temperature, at constant density. It is supposed that density fluctuations associated with the critical range influence the conductivity. In this region the derivatives $(\partial\sigma/\partial T)_p$, $(\partial\sigma/\partial p)_T$, $(\partial V/\partial p)_T$, $(\partial V/\partial T)_p$ have large values indicating that errors in the temperature and pressure significantly affect the values of conductivity and volume.

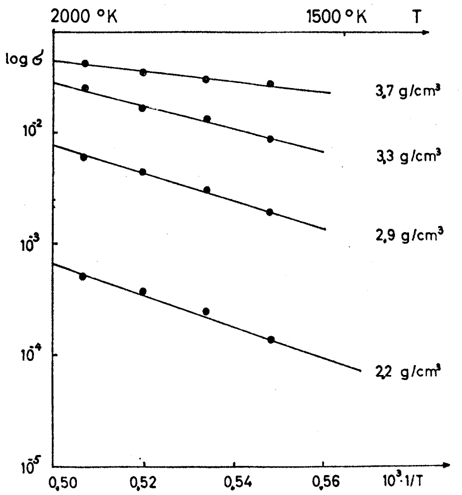

FIG. 11. Temperature dependence of the specific conductivity of mercury at constant densities.

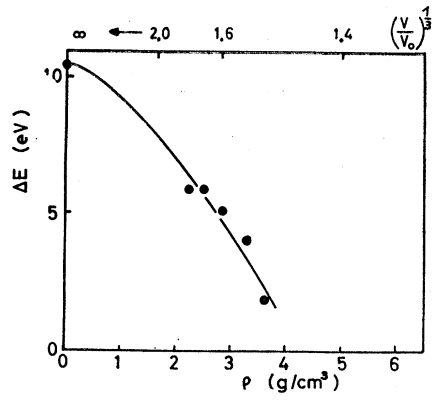

FIG. 12. "Effective ionisation energy" ΔE of mercury as a function of density ρ and $(V/V_0)^{1/3}$. V_0=volume of liquid Hg at 0°C and 1 bar.

Discussion of Hensel and Franck's Paper

M. POLLAK (University of California, Riverside): My question is not really directly related to the Mott transition. I want to inquire about the region where the conductivity decreases with increasing temperature near the critical point. You made a statement that the change might be due to the decrease of the size of the clusters with increasing temperature, and I wonder if you would like to comment on the following question. If the size of the clusters increases then the average separation between the clusters will decrease. One would then offhand think that the conductivity would decrease when the temperature decreases.

E. U. FRANCK: I really cannot give an explanation for this effect. I tried to stress that the experiments in that range were certainly difficult because very slight variations or inaccuracies of the temperature have a very pronounced effect on the density. Actually to investigate that range one should construct a different apparatus which is only used for that particular range and gives accurate results there. Some recent mass spectometry results show that for one of the alkali metals the effective ionization energy (or the energy to free electrons from clusters) is markedly decreased if you proceed from monomers, to dimers, to trimers, and so on. Now, if we should have a considerable amount of trimers, or hexamers, or so, here in the critical range then they may contribute to the ease of setting the electrons free. The size of these clusters should be very temperature dependent and I should think that an increase of temperature should destroy these clusters and thus might have an effect in this range. The energy of interaction of two mercury atoms or two potassium atoms in the gas phase is not very low. These are energies in the order of 10–20 kcal/mole so it may well be that cluster formation should be very temperature dependent. But I should not give too much weight on these results before they have been verified.