

Electrical conductivity of mercury in the near-critical region

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Electrical conductivity values of mercury, much more accurate than those obtained previously and measured in cells with improved thermostatic control, are reported. The impurity density in the mercury and in the BeO shells is an order of magnitude lower than in previous experiments. The critical parameters estimated from the intersections of the rectilinear 1490 °C [F. Hensel and E. Franck, *Rev. Mod. Phys.* **40**, 697 (1968)] and curvilinear 1510 °C [I. Kikoin *et al.*, *Atomic Energy Inst. Preprint IAE-2310*, (1973)] diameters are contradictory.

The few experimental investigations, by various workers, of the thermodynamic properties of liquid-metal heat-transfer media and of the electrophysical properties of mercury in the near-critical region¹ differ greatly in their results and in the estimates of the critical parameters; the estimated critical temperature T_{cr} , for example, ranges from 1430° to 1510° ± 15 °C.

The electric conductivity of 99.999%-pure mercury was measured in the present study in solidly molded vacuum-tight BeO capillaries located in argon-filled high-pressure chambers. The pressure was produced in the system by a modernized high-speed pistonless gas thermocompressor.

The middle part of the solid ceramic capillary of the cell was heated, in a mercury-filled horseshoe-shaped cavity connected to four channels that led to the cooled upper end of the capillary, by a tungsten heater. The temperature distribution was stabilized by a stainless-steel heater placed near the cooler of the lower end of the capillary. Several sintered BeO insulators were placed in the central part of the hot zone of the cell described in detail in Ref. 2. Small-bulb stainless steel electrodes hermetically sealed to the capillary channels and insulated from one another made contact with the cooled mercury.

The mercury temperature was measured with several different thermocouples, of which the principal ones were made of tungsten-rhenium alloys were calibrated accurate to

3 °C in the high-temperature region. In the four-contact measurements of the electric conductivity, direct current was made to flow through the mercury-filled channels connected to the ends of the inner horseshoe-shaped cavity. Pressure was measured simultaneously by two precision manometers and two piezoelectric manometers, one of them in the form of a single-layer manganin coil annealed in vacuum.

The experimentally proven universal jumplike change of the electric conductivity of simple substances in response to a jumplike decrease in density is the basis of one of the most accurate methods of determining critical parameters of metals. The reason is that in the near-critical region a small change in the density of the material is accompanied by an appreciable change of the electric conductivity. In the present measurements this advantage of the method could be used by reducing to a minimum the effect of impurities in the cells used for the measurements. This was accomplished by using the purest materials in the structural elements of the apparatus in the hot zone, by using pure BeO that has enhanced electric insulating properties and does not interact with the hot mercury, and by avoiding contact between the heated mercury and solid metals whose impurities substantially affect the measured electric conductivity and the critical parameters.

Figure 1 shows anomaly-free near-critical electric-resistivity isotherms, obtained from measurements under conditions better than in the procedures followed previously with thermostatically controlled large mercury mass in cavity segments having rectangular cross sections.

By using pure BeO uncontaminated by other oxides in the capillaries, we found the critical temperature and pressure of pure mercury in this study to be $T_{cr} = 1467 \pm 3$ °C and $P_{cr} = 1513 \pm 5$ atm.

These results were compared with the critical-parameter estimates obtained over many years by Hensel,^{3–5} who used a variety of aluminum-alloy cells and molybdenum structural elements in contact with hot mercury. The comparison has shown that his value $T_{cr} = 1490 \pm 10$ °C obtained from the point of intersection of the binodal with its rectilinear diameter deviates from the experimental results by more than the measurement-error limit.

The measurement errors caused by the molybdenum impurities and by the temperature gradient in the region of

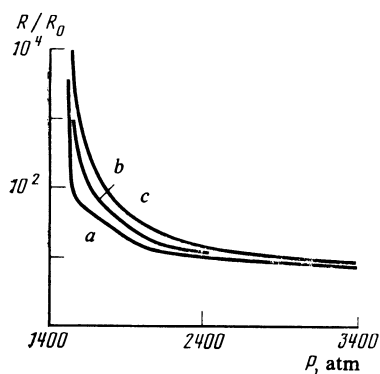


FIG. 1. Isotherms of the electric resistivity of pure mercury as function of pressure in semilog scale: a—subcritical isotherm at $T = 1460$ °C; b, c—transcritical isotherm at $T = 1473$ °C and 1490 °C.

the maximum temperatures in the cells turned out to be larger in Ref. 6, in which the measurements of the expanding volume of heated mercury were made more sensitive by increasing the size of the molybdenum cell with increased cavity surface. The interpretation of the data of Ref. 6, in which the critical parameters $T_{cr} = 1510 \pm 15^\circ\text{C}$ and $P_{cr} = 1730 \pm 30$ atm were determined from the point of intersection of the phase curve with its curvilinear diameter, is made difficult by the larger temperature errors due to absence of thermostatic control in the hot zone and to the difficulty of accounting for the properties of the behavior of the thermal conductivity of mercury at high temperatures.

It can be noted from our resistivity isotherms measured directly below the critical point using cells with improved thermostatic control that the structural disordering of mercury takes place in the liquid phase, and that the resistivity jump at values close to Mott's minimum metallic conductivity for metal-nonmetal transitions is clearly pronounced.

The variations in the electrical conductivity of mercury measured in the near-critical region is particularly large, and is explicable to a considerable degree by the influence of the impurities in the cells used by other workers, distorting the measured electrical conductivity and also causing changes in the values of the critical parameters.

The experimentally determined critical temperature T'_{cr} of mercury differs from the true T_{cr} because the temperature shifts in the Eq. (1) are arranged in increasing order of the influence of the various factors in the actual measurement cells (the quantities compared are successively simpler to determine in experiment):

$$T_{cr}' = T_{cr} + \delta_i T + \delta_H T + \delta_E T + \delta_{\bar{H}} T + \delta_g T + \delta_a T + \delta_{imp} T, \quad (1)$$

where the isotope shift $\delta_i T$ and the action of the electric field that decreases T_{cr} are connected by the relation $\delta_i T \ll |\delta_E T|$. The influence of the constant and alternating magnetic fields is taken into account through the quantities $\delta_H T$ and $\delta_{\bar{H}} T$, the changes due to the gases and impurities are accounted for in $\delta_g T$ and $\delta_{imp} T$, and the influence of the other apparatus effects is included in $\delta_a T$.

Note that the T_{cr} estimated from results from which the interaction of the mercury with heated metallic structural

elements was not excluded are higher than the T_{cr} determined by various workers who excluded the interaction of mercury with other metals. In our investigation the value of $\delta_g T + \delta_{imp} T$ was reduced to a minimum compared with the values obtained by all other workers.

The last term of Eq. (1) takes into account the cell-structure features that influence the oscillation propagation conditions, the nucleation properties, and the system properties that influence the kinetic phenomena.

The accuracy of the high-temperature experiments is determined to a considerable degree by the temperature-measurement accuracy, which was 3–4 times better in the present study than in all others. The absolute measurement accuracy at temperatures close to critical was on the order of 2°C , owing to the use in the cells of several better-calibrated thermocouples when the electric conductivity of mercury was measured (stabilized and slow-aging thermocouples of four types, including the VAR 5–VAR 20 couple, not used by others, made of stabilized alloys based on W and Re, and checked in four different metrology laboratories). A number of other advantages of our procedure were noted in Refs. 1 and 2. The accuracy with which the thermoelectric power of the thermocouples was measured and the temperature was stabilized in our measurements of the control isotherms of the mercury conductivity was on the order of $10^{-4}\%$ and better. The procedure so tested permitted an experimental analysis of the terms of Eq. (1).

The method used to determine the critical parameters from the rectilinear diameter of the phase curve was confirmed by experiment not only for simplest dielectric liquids with low-temperature phase transitions, and in many compounds. The phase curves of substances with high-temperature phase transitions (all alkali metals, S, Pb, Ag, and Sn) have rectilinear diameters. A rectilinear diameter of the phase diagram was observed for mercury in most experiments.

Deviation Δd from rectilinearity of the mercury phase-curve diameter has been observed only in two studies, but these deviations exceed the corresponding values δd observed on the phase diagrams of all compound systems by more than a factor of ten $\Delta d \gg \delta d$. The experimental results of various workers are compared with theory in Table I. The

TABLE I.

	[8]	[9]	[3]	[10]	[11]	[12]	[13]	[6]	Present work	[14]
	Theory		Experiment							
$d_c, \text{r/cm}^3$	3,77	3,56	4,2	4,5	4,7	5,3	5,7	5,9	4,9	5,0
$T_c, ^\circ\text{C}$	—	1677	1490	1460	1460	1495	1480	1510	1467	1460
Features						Float made of Mo and alloys		Mo ampoule		
								$t_{13} < t_6$		
Rectilinear phase-curve diameter			+	+	+	+	—	—	+	+
Curvilinear phase-curve diameter			—	—	—	—	+	+	—	—

Note. The value of T_c from Ref. 13, corrected by extrapolation of the critical exponents determined in the present paper, is $\approx 1425^\circ$.

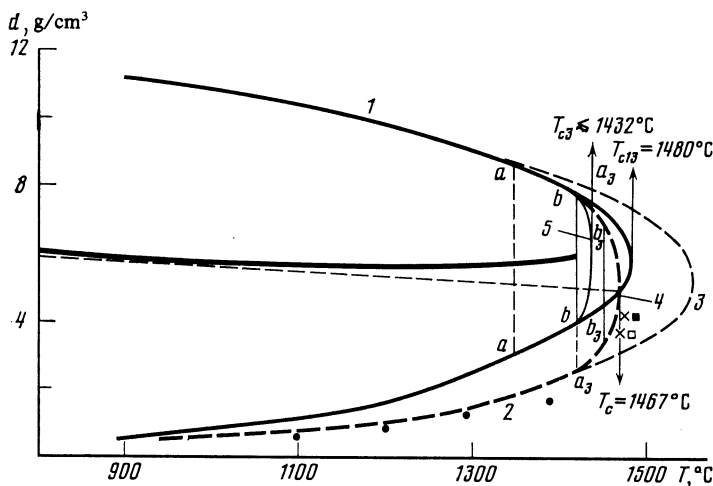


FIG. 2. Schematic representations of the phase curves of mercury, plotted on the basis of the experimental data, and estimates of the critical parameters: 1—data of experiments 13 with curvilinear phase-curve diameter; 2—phase curve corrected by the author on the basis of precise measurements of the electric conductivity of pure mercury, using the cells of Ref. 2; 3—in the extrapolation, the shape of the phase curve was maintained identical with the upper part of curve 1; 4—rescaled phase curve 2 with allowance for the value $T_c = 1467^\circ\text{C}$ determined by the author earlier; 5—possible extrapolation of curve 1 using the critical exponents obtained in the present paper or the experimental law of corresponding states; the points labeled by the same letters but with different subscripts delimit equal values of $d_{\text{liq}} - d_g$ corresponding to the indicated extrapolations, with geometrical similarity of the marked phase-curve segments preserved; \blacksquare and \square —data of Ref. 3, critical point and point on the gas branch of the phase curve; \bullet —points on the phase diagram according to the data of Ref. 10, \times —data of Ref. 20 refined by the authors of Ref. 3.

discrepancies in the estimates of d_c are particularly large. Extrapolation of the curvilinear diameter to its intersection with the phase curve, according to the data of Ref. 13, as a function of the curvature radius of the extrapolated section of the diameter, yields d_c values in the range 6–6.4 g/cm³. Extrapolation to the intersection with the corrected curve 5 in Fig. 2 yields $d_c \approx 6.0$ g/cm³.

Note that the largest experimental critical densities $d_c > 5.3$ were obtained by these workers for cells in which interaction was observed between the heated mercury and the ampoule materials or the auxiliary measuring elements. This explains also the overestimates of the critical temperatures in Refs. 6 and 12. The influence of the impurities was likewise not eliminated in Ref. 13.

The value $T_c = 1460^\circ\text{C}$ in Grosse's paper is confirmed not only by measurements of the mercury density but also by independent viscosity measurements.¹⁵ A value of T_c of the same order was obtained from the data of Ref. 10, but extrapolation of the upper part of the phase curve, with allowance for the experimental law of corresponding states or in accordance with the critical exponents obtained in the present paper, yields a value several degrees lower.

Simultaneous measurements¹³ of the electric conductivity and density of mercury in the transcritical region revealed agreement between the linear section of the $d = f(T)$ curve and the semilog plot of the linear section of relation $R/R_0 = f(T)_p$. A deviation from linearity in the latter coordinates was observed on the mercury electrical resistivity isobar at $P = 1600$ atm and $R/R_0 \approx 10^4$.

The better electrical insulating properties of the ampoules and of the BeO ceramic permitted the electrical conductivity of mercury to be measured more accurately in a resistivity range larger by a factor of ten than that accessible to others. It was found that the corresponding straight sec-

tion of the resistivity isobar, plotted in semilog scale, reaches $R/R_0 \approx 3 \cdot 10^7$. Taking into account the correspondence between the linear sections of $d = f(T)_p$ and $R/R_0 = f(T)_p$ plotted in such coordinates we can state that the density-isobar segment at $P = 1600$ atm, corresponding to the linear section with limit $R/R_0 \approx 3 \cdot 10^7$, should be lengthened. These properties of the variation in the mercury-conductivity and the corresponding deviations from linearity on the mercury-isobar density were verified in a pressure range close to critical, 1600–1800 atm.

The experimental results have made it possible, using the electrical conductivity measured in the present study and allowing for the correspondence of the compressibilities in the gas phase, to rescale the phase diagram of Ref. 13 [curve 1 of Fig. 2, where curve 2 is the corrected one] and to rescale the entire plot of the equation of state. The upper part of curve 2 was plotted allowing for the conditions for the extrapolation of the upper part of curve 1, where the section with equal values of $d_{\text{liq}} - d_g$ (d_{liq} and d_g are the densities of the liquid and of the gas on the phase curve) corresponds to an equal interval $T_c - T_i$, where T_i is the temperature corresponding to equal values of $d_{\text{liq}} - d_g$ on the phase curves being compared (the condition of equal limiting sections).

The estimate obtained in the present study for the critical temperature of pure mercury on the basis of the most accurate known measurements of the electric conductivity in chemically pure ampoules, using the most effective thermal purification of the mercury, such that the impurity concentration was an order of magnitude lower than in the mercury used by all other workers, permitted a more precise extrapolation of phase curve 2 (the upper part is shown as curve 4 in Fig. 2) and yielded, for the first time ever, the critical exponents of the mercury phase diagram. These exponents are compared in Table II with those obtained ex-

TABLE II.

Substance	T_c, K	α	α'	β	γ	γ'	δ	ν	ν'
Hg	1740	—	0,24	0,32	—	1,187	4,71	—	0,586
S	1313	—	0,114 *	0,33	—	1,228 *	4,72	—	0,629 *
CO ₂	304,16	—	0,125	0,3447	—	1,2	4,2	—	0,625 *
SF ₆	318,73	0,14	0,14	0,35	1,6	1,6	4,3	0,62 *	0,62 *
Xe	289,74	0,08	0,08	0,344	1,203	1,203	4,4	0,64 *	0,64 *
³ He	3,3105	≤ 0,3	≤ 0,2	0,361	—	1,15	4,49 *	≥ 0,57 *	≥ 0,6 *
⁴ He	5,1885	0,127	0,159	0,3554	—	1,15	4,69 *	0,624 *	0,614 *

* These critical exponents, never determined before for Hg, as well as critical exponents for other substances which were not reported by the authors of the papers cited, were calculated by the present author.

perimentally for other substances.^{16,17} No critical exponents of the liquid-gas phase diagrams of any metal have been determined to date.

The critical exponents determined in the present paper for mercury agree well with exponents obtained for other liquids. The critical exponent of the order parameter of mercury is smaller than the critical exponents of dielectric liquids with low boiling points or the critical exponents of the magnetic transitions in ferromagnets, but larger than the corresponding critical exponents of phase transitions in binary alloys in certain antiferromagnets. The critical exponents of the order parameters of mercury, sulfur, iron and nickel differ by several percent.^{16,17}

The corrected phase curve 2 of Fig. 2 agrees much better with the data of all other workers than the uncorrected curve 1. Using the results of the experimental law of corresponding states, or using the critical exponents determined in the present paper, it is possible to extrapolate the upper part of the phase curve 1 in accordance with the condition of equal limiting sections of the phase curve, mentioned previously. The result is curve 5 of Fig. 2, which yields, under the assumptions indicated, a critical temperature in the range $T_c = 1422\text{--}1432^\circ\text{C}$.

Comparison of the critical exponents of sulfur and of its compounds shows that the critical exponent δ in the element is larger than in the compounds. The pressure-transmission medium used in Ref 14 was nitrogen, which could interact with the mercury at high temperatures and high pressures. This could decrease the critical exponent of the medium and raise the critical temperature. The value $T_c = 1460^\circ\text{C}$ could therefore be an overestimate.

An analytic equation of state that describes the metal in the near-critical and transcritical regions is known only for cesium—it was determined experimentally for temperatures up to 4727°C in Ref. 18. This equation has been recast in a form that is easier to analyze:

$$\pi = \tau / (3Y - a) - (1 - 2a\tau) / Y^2, \quad (2)$$

where $\tau = T/T_c$, $\varphi = V/V_c$, $\pi = P/P_c$, $Y = Z_c \varphi$, $Z_c = P_c V_c / RT_c$. No analogous equation describes the experimental data for mercury.

The corrected phase curve of mercury (curve 4 of Fig. 2) is described by the simple equation

$$\pi = (\tau \pm a_i) / B(\tau) b^{\pm 1} \varphi - (1 - b^{\mp 1} \tau) / c^{\pm 1} C \varphi^2, \quad (3)$$

where a_i , b , and c are constants, C remains the same for the phase-curve branches, and the upper and lower signs correspond to the descriptions of the liquid and gas branches of the phase curve.

The precision-experiment results were obtained by null-method measurements using instruments of accuracy class 0.05–0.1, including an R 306 potentiometer, and by recording the isotherms shown in Figs. 1 and 3 with a class-0.5 PDS 21 x-y plotter. The measurement accuracy increased by picking off in each experiment the periodic signals from standard calibrated 0.001, 0.01, 0.1, 1 and 10 Ω resistors in a null circuit.

The better of the set of five standard and piezoelectric manometers were accurate to within 0.2–0.3% of the measured pressure.

The absolute temperature-measurement error was determined in the control experiments with a Pt–PtRh thermocouple and was less than $\delta_T \sim \pm 1^\circ\text{C}$ of the measured value in the near-critical region. When the control isotherm was recorded, the relative temperature-measurement error was much lower, $\delta_{T0} < \delta_T$.

The sensitivity of the thermocouple-emf measurement circuit, of the order of $10^{-4}\%$, ensured a much more accurate temperature stabilization than in Ref. 13.

The approximation accuracy and the features of the mercury-resistance variation in the near-critical region are discussed below and are compared with realistic theoretical

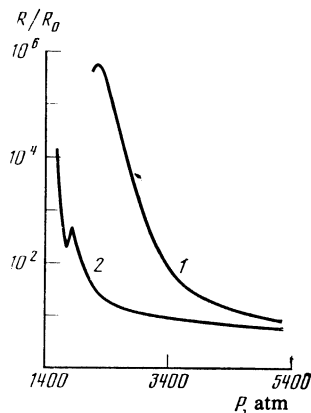


FIG. 3. Transcritical isotherms of the relative resistance of mercury in mercury with a nonmonotonic $R = f(P)_T$ dependence, in semilog scale. Curve 1 – $T = 1703^\circ\text{C}$, 2 – $T = 1506^\circ\text{C}$.

estimates of the critical parameters.

1. The modern theory of phase transitions is based on the similarity hypothesis. The similarity laws permit all the critical exponents to be determined from two independent exponents¹⁹ from the set of equations

$$\alpha + 2\beta + \gamma = 2, \quad \gamma = \beta\delta - \beta, \quad (4)$$

$$\delta = (d_s + 2 - \eta) / (d_s - 2 + \eta), \quad \alpha = 2 - d_s \nu,$$

where

$$c_s \propto |T - T_c|^{-\alpha}, \quad d - d_c \propto |T - T_c|^\beta, \quad (\partial d / \partial P)_{T_c} \propto |T - T_c|^{-\gamma}, \quad (5)$$

d_s is the dimensionality of space, the correlation length is $\xi \sim |T - T_c|^{-\nu}$ for $T_c < T$, with corresponding values α' , ν' , γ' , δ , β —for $T < T_c$. The critical exponents marked by asterisks were undetermined in previous work. The present author obtained these critical exponents from the system (4).

$$d - d_c \sim (P - P_c)^{1/\delta}. \quad (6)$$

The data are listed in Table II.

2. The critical exponent β of sulfur listed in Table II was determined in the cited reference in the range $0.6 < T < T_c$. The critical exponents of mercury were determined in narrower ranges of parameters, the smallest of which was $0.95 < T < T_c$. It should be noted that the critical exponent $\beta = 0.32$ obtained from the rescaled experimental phase curve cited in this paper for mercury should be compared not with the theoretical estimates of the critical exponents of conducting metallic liquids, but with theoretical calculations for liquid semiconductors. There are still no such calculations in a form that permits comparison with the results of experiments with real systems: β was determined from (1) and (3), while α and ν were determined from (4).

3. The discrepancies among the experimental determinations of the exponent β by different workers for one substance reach 5%, a value exceeding the difference between the critical exponents determined in the present paper for sulfur and mercury. The exponent β was determined from the phase curve of mercury. A number of various approximations, with use of data rescaled in the present paper, averaged data of other workers, and Hensel's data³ rescaled in accordance with his corrected value $T_c = 1477^\circ\text{C}$ obtained from optical experimental data²⁰ (marked by crosses in Fig. 2), give rise to errors less than 1–2% of the value listed in Table II. If γ is determined from (5) then δ is determined from (4); if γ is obtained from (4), then δ is obtained from (6), i.e., the two exponents γ and δ were each determined by two methods.

4. The first realistic theoretical estimates of t_c and d_c , which lead to better agreement with experiment only if d_0 and d^* are varied, are given in Ref. 21, where attention is called to one factor that can bend the diameter of the phase curve, viz., interaction between the order parameters. The calculations are based on representing the thermodynamic potential Φ as a sum whose terms take into account the interaction Φ_{12} of the order parameters and the increment added

by the metallic properties of the substance to Φ_1 of an ideal system:

$$\Phi = \Phi_1 + \Phi_2 + \Phi_{12}, \quad (7)$$

where $\Phi_{12} = -Bdn$ (n is the electron density in the conduction band and B is a constant). By minimizing Φ , the authors obtain $n = f(T, \Delta d)$, where $\Delta d = d - d^*$ and d^* is the mercury density corresponding to the metal-nonmetal transition. The value chosen for the calculation was $d^* = 8.29 \text{ g/cm}^3$. The critical parameters were determined by expansion near the critical point:

$$\Phi_1 = -\mu\varphi_1 + \frac{1}{2}\tau\varphi_1^2 + \frac{1}{3}\lambda\tau\varphi_1^3 + \frac{1}{4}u\varphi_1^4, \quad (8)$$

where λ and u are constants, μ is the chemical potential, and $\varphi_1 = (d - d_0)/d_0$. The chosen value of the critical density of the ideal system, $d_0 = 5.06 \text{ g/cm}^3$, exceeds the corresponding critical densities determined in many experiments (the data listed in Table I, minus the results of Refs. 6 and 12, where the molybdenum impurities and the temperature gradient distorted the measurement results). This is one of the causes of the overestimates of the critical parameters by the authors cited above, who obtained values $d_c = 5.58 \text{ g/cm}^3$ and $T_c = 1517^\circ\text{C}$.

It was noted in Ref. 19 that a thermodynamic potential of type (8) without the φ_1^3 term is possible. This expansion is more accurate the closer the considered parameters to their critical values. This can yield a more accurate expansion and apparently, together with changes in the thermodynamic potential, better agreement between the theoretical estimates and our present experimental results. It seems possible to estimate the critical parameters of mercury by using a similar calculation, if the thermodynamic potential is altered and the terms, including Φ_{12} , are made more accurate by allowing for the microscopic inhomogeneities and the peculiarities of the mercury substructure in the semiconducting state. The qualitative and quantitative conclusions of this theory therefore call for verification and for a more accurate choice of parameters. The choice of the parameter d^* was based on the results of Refs. 6 and 13, whose data have not been corroborated by others and are inaccurate because of the influence of the impurities.

One cause of the bending of the phase-curve diameter and of the inaccurate critical parameters of Ref. 6, on which was based the comparison of the theory discussed above, is that the interaction between the mercury and the molybdenum ampoule increases with rising temperature. Since very different data are given by different workers on the equation of state of mercury at high temperatures and pressures, to choose correctly the value of d^* it is necessary to analyze the procedures of these experiments with the remaining parameters correctly chosen.

5. The electric-resistance isotherms of mercury, shown in Fig. 1, were obtained by plotting the entire isotherm with an x - y recorder. The corresponding control points, including those measured by null methods under static conditions, are less than the thickness of the trace—the experimental errors are comparable with the line width in the figure. The

isotherm at $T = 1460^\circ\text{C}$ shows clearly the start of a resistance jump.

Figure 3 shows in semilog scale transcritical isotherms with a nonmonotonic $R = f(P)_T$ dependence. The observed nonmonotonicity is due to peculiarities of the substructure of transcritical mercury. The peculiarities of the resistance variation on the transcritical isotherm are due to density fluctuations, peculiarities of the kinetic phenomena, and formation of substructure elements such as fluctons, whose dimensions vary with the thermodynamic parameters.

It should be noted that singularities were observed in the variation of a number of physical properties of various substances in a transcritical gas near the critical region. These comprise an extremal variation of the heat capacity, including that of He, an extremal change of the heat transfer, an extremal change of the thermoelectric power of mercury, and an extremal change in the breakdown voltage of He, all connected with the change of the structure factor.

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