High Temperature, Vol. 31, No. 1, 1993. Translated from Teplofizika Vysokikh Temperatur, Vol. 31, No. 1, 1993, pp. 40 - 43.

THERMOPHYSICAL PROPERTIES OF MATERIALS

Electrical Conductivity of Dense Cesium Vapors

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Manuscript received August 18, 1992

Abstract – Calculations of the electrical conductivity of plasma of dense cesium vapors are performed within the drop model, in the near-critical region. In doing so, the charged plasma components are included in the equation of state. The results agree with new experimental data. Interpretation is given of the sharp dependence of the electrical conductivity on the density on isotherms and of its weak dependence on the temperature. The theory describes the drop of electrical conductivity on the 61-bar isobar.

Investigations of the electrical conductivity of dense cesium vapor, characterized by its anomalous behavior, have been arousing considerable interest for quite some time. The concept of anomalous electrical conductivity implies rather high values of electrical conductivity near the saturation curve at a temperature comparable with a critical one, as well as a dropping isobaric temperature dependence of electrical conductivity. The measurement of the electrical conductivity of cesium vapors presents a complicated experimental problem; theoretical studies likewise involve considerable difficulties. This may account for the considerable differences between both the experimental data and theoretical estimates. A review of literature is found, for instance, in [1].

New experimental data have been obtained recently by Hensel *et al.* [2]. The values of the electrical conductivity of dense cesium vapors, measured on the saturation curve, proved to be two orders lower than the values previously obtained by the same authors [3]. Values of electrical conductivity very close to those of Hensel *et al.* [2] were predicted by Zhukhovitskii [1] using the drop model in which the cesium vapor was regarded as a mixture of neutral clusters, cluster ions, and electrons.

Zhukhovitskii [1] managed to obtain a qualitative description of both the transition from normal to anomalous electrical conductivity and the equation of state for vapor. At the same time, a strong relationship was observed between the electrical conductivity of superheated vapor and the accuracy of describing the equation of state. Subsequently, a fairly reliable equation of state was derived [4]. In order to refine the model of [1], the fact that the value of surface tension for a small drop differs from that for a plane surface was taken into consideration. Therefore, a dimensional correction to the value of surface tension was introduced in the case of a macroscopic description of small clusters. In addition, more consistently, within a second virile coefficient approximation, allowance was made for the excluded cluster volume. In a number of studies [2, 5, 6], the experimental data on the equation of state in the near-critical region were substantially refined. In this region, as shown by estimates, the degree of ionization is rather high because the contribution of charged plasma components to the equation of state is not negligibly small, as assumed by Zhukhovitskii [4]. In view of the foregoing, it appears to be of interest to include this contribution and to calculate the electrical conductivity using an improved version of the drop model, as well as new data on the equation of state, and to compare the results with experiment.

Section 1 of this paper deals with the equation of ionization equilibrium for dense vapor and Section 2 with the calculation of electrical conductivity while Section 3 describes the calculation results and their discussion.

1. EQUATION OF IONIZATION EQUILIBRIUM

In order to construct the equation of ionization equilibrium, the model of [4] must be generalized to include the charged component of vapor, with the latter treated as a nonideal mixture of cluster ions and electrons (negative ions at high densities are insignificant [1]). To this end, note that, in accordance with the drop model, the size of a neutral cluster coincides with that of a cluster ion containing the same number of ions; the electron size in this model should be made equal to zero. All of the quantities relating to various plasma components are marked by the subscript g (we assume that all of the positive values of this subscript correspond to neutral clusters, all of its negative values, to positive cluster ions, and its zero value, to electrons). Because, according to [4], the nonideality of the system is associated with the excluded volume, the expression for its free energy is derived from that given by Zhukhovitskii [4] by extending the summation over g and j to the zero and negative values:

$$F/T = \sum_{g=-\infty}^{+\infty} [N_g \chi_g(T)/T + N_g \ln(N_g/V)$$
$$+ (1/2n_L)(N_g/V) \sum_{j=-\infty}^{+\infty} N_j (|g|^{1/3} + |j|^{1/3})^3] \quad (1)$$
$$- 4N_1^2/n_L V.$$

Equation (1) in a second virile coefficient approximation allows for the interaction of plasma components associated with the excluded volume, as well as for the attractive interaction of ions; N_g are the particle numbers; the functions $\chi_g(T)$ are determined by their internal statistical sums; V is the system volume; and n_L is the concentration of atoms in the liquid phase. According to the drop model, the internal statistical sum of a cluster does not vary upon its ionization: $\chi_{-g} = \chi_g + I_g$ ($g > 0$), where I_g is the ionization potential of the cluster. For the electron component, $\chi_0 = T[\ln(\lambda_e^3/2) - 1]$, $\lambda_e = (2\pi\hbar^2/mT)^{1/2}$, and m is the electron mass.

On differentiating (1) with respect to N_g, we find the chemical potential of the g-th component

$$\mu_g = \chi_g + T[1 + \ln(n_g \beta_g)],$$
$$\beta_g = 1 + n_L^{-1} \sum_{j=-\infty}^{+\infty} n_j (|j|^{1/3} + |g|^{1/3})^3 - 8\delta_{1g} n_1/n_L, \quad (2)$$

$n_g = N_g/V$. On substituting (2) in the law of mass action $\mu_g = \mu_{-g} + \mu_0$, we get

$$n_0 n_{-g} = (2/\lambda_e^3 \beta_0) n_g \exp(-I_g/T). \quad (3)$$

In (3), summation over g is performed, with due regard for the condition of quasi-neutrality $n_0 - \sum_{g=1}^{\infty} n_{-g} = 0$, to find the electron concentration

$$n_0^2 = (2/\lambda_e^3 \beta_0) \sum_{g=1}^{\infty} n_g \exp(-I_g/T). \quad (4)$$

According to Zhukhovitskii [1], the ionization potential is written as

$$I_g = \begin{cases} W(T) + e^2/2R_g, & g > g^* \\ W_0 + e^2/2g^{1/3} r_0, & g \le g^*, \end{cases} \quad (5)$$

where $W(T)$ is the electron work function dependent on temperature, R_g is the radius of a cluster containing g atoms, $r_0 = 3.45$ Å is a numerical parameter, $g^* = 0.238 e^2 n_L/\gamma$, and γ is the surface tension.

Using (1), one can derive the equation of state (or compressibility factor). In form, it coincides with (3) (or 10) of Zhukhovitskii [4]; however, summation must now extend from $-\infty$ to $+\infty$. In the same limits one should perform summation in Zhukhovitskii's [4] equations (8) and (9) defining the unknowns β_g and n_1, while g and j in (9) [4] must be replaced by $|g|$ and $|j|$, respectively. The quantities $Q_g = n_g/n_1\beta_1$ appearing in these equations are determined as follows: For neutral clusters ($g > 0$), $Q_g = \beta_g^{-1}(n_1\beta_1/n_{1s}\beta_{1s})^{g-1}\exp(-\alpha)$ [4], where the subscript s points to the saturation curve; $\alpha = 4\pi\bar{\gamma}R_g^2/T$, $\bar{\gamma} = \gamma$ at $g > g^*$ and $\bar{\gamma} = A - BT$ at $g \le g^*$; and A and B are numerical parameters determined by matching the calculated values of the compressibility factor with the experimentally found values. For cluster ions and electrons ($g \le 0$), Q_g can be found with the aid of (3) and (4)

$$Q_g = \frac{Q_{-g}}{\left[(\lambda_e^3 \beta_0 \beta_1 n_1/2) \sum_{j=1}^{\infty} Q_j \exp(2I_{-g} - I_j)/T\right]^{1/2}}, \quad (6)$$

$$Q_0 = \left[(2/\lambda_e^3 \beta_0 \beta_1 n_1) \sum_{g=1}^{\infty} Q_g \exp(-I_g/T)\right]^{1/2}. \quad (7)$$

Since $n_0 = n_1\beta_1 Q_0$, (7) is the equation of ionization equilibrium that we sought.

Equations (6) and (7) further permit us to include the contribution of charged plasma components in the equation of state. This contribution may also be appreciable in the event that the degree of ionization is much less than unity, in view of the fact that the most readily ionizable component of plasma is provided by heavy clusters containing dozens of atoms.

2. ELECTRICAL CONDUCTIVITY

As shown by estimates, the main contribution to the electron collision frequency is made by collisions with neutral particles. In a not-too-dense system, where the free path length exceeds the mean distance between particles, the electrical conductivity is calculated from the formula

$$\sigma = (4/3) e^2 n_0 l / \sqrt{2\pi m T}, \quad (8)$$

where

$$l = T^{-2} \int_0^{\infty} \exp(-\varepsilon/T) \left[\varepsilon / \sum_{g=1}^{\infty} n_g q_g(\varepsilon)\right] d\varepsilon \quad (9)$$

is the free path length of electron and $q_g(\varepsilon)$ is the transport cross-section of scattering of electrons from a cluster containing g atoms.

No theoretical and experimental data are available for $g > 1$. Since electron-atom collisions prevail in the discussed range of parameters of state, assume these cross-sections to be equal to the atom scattering cross-section, $q_g = q_1$. Given the densities of $\rho > 0.1$ g/cm³, when the fraction of clusters is no longer negligibly small, the value of l calculated from (8) becomes very close to the mean distance between particles

$\left(\sum_{g=1}^{\infty} n_g\right)^{-1/3}$, i.e., to its minimum value. With large scattering cross-sections, the long-range parts of interaction potentials overlap to increase the electron mobility. As a result, the free path length of electrons in this range of parameters of state must depend only weakly on the scattering cross-sections.

Within the foregoing assumption, the values of l are determined with the aid of the values of q_1^{-1} averaged over Maxwellian distribution, calculated and tabulated by Gogoleva *et al.* [7] for different temperatures.

The electron concentration n_0 in (8) is found using (7). Its calculation is a self-consistent problem in the process of whose solution one must simultaneously calculate the compressibility factor, concentrations of different components, etc.

3. CALCULATION RESULTS AND DISCUSSION

The system of (8) and (9) of Zhukhovitskii [4], simultaneously with equations (5) - (7) of this paper, was solved numerically. In doing so, parameters A and B were selected in order to provide for the optimum description of data on the density of cesium vapor [2]. Note that the data on the equation of state used by Zhukhovitskii [4] differ strongly (and not just in the near-critical region) from those obtained more recently and listed by Hensel *et al.* [2] and Kozhevnikov *et al.* [5]. As to the latter two studies, their results agree well with each other. In this manner, the values of $A = 44$ dyn/cm and $B = 1.75 \times 10^{-2}$ dyn/(cm K) were obtained. They differ from those given by Zhukhovitskii [4] both because new data are used, and as a result of the inclusion of the state of the contribution by charged components into the equation. This contribution becomes significant at $\rho > 0.12$ g/cm^3 ($T > 1800$ K on the saturation curve); in doing so, the ratio of the number of heavy ($g > g^*$) cluster ions to that of neutral clusters of the same size is of the order of unity.

A good accuracy for the description of experimental density data has been attained; the error does not exceed 10% at $\rho < 0.12$ g/cm^3, $T \leq 1870$ K. With higher values of ρ and T, the disagreement increases, apparently because the limit of validity of the model has been reached, where a number of basic assumptions are violated (zero compressibility of clusters, smallness of the excluded volume). The latter assumption ceases to be valid even at $T = 1870$ K. The concentrations of clusters in the superheated vapor region are steep functions of the quantities n_{1s} and β_{1s} calculated on the saturation curve at the same temperature. Therefore, at $T \geq 1870$ K, calculations away from the saturation curve may have an inadequate accuracy, increasing as the saturation curve is approached. Note that neither Hensel *et al.* [2] nor Kozhevnikov *et al.* [5] give estimates of measuring errors, and the comparison of theory and experiment in this region cannot determine the limit of validity of the model. In the region quite removed from the critical region ($T \leq 1700$ K), the results of this calculation practically coincide with those obtained by Zhukhovitskii [4].

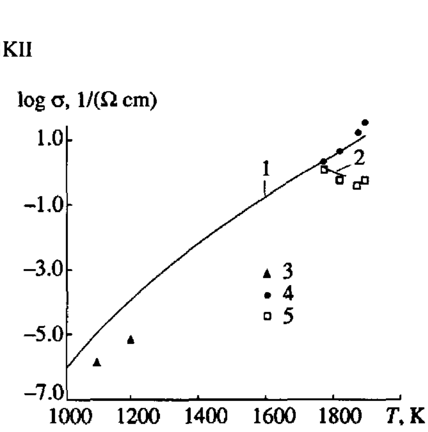

Fig. 1. *The electrical conductivity of cesium vapors on the saturation curve (1, calculation; 3, experiment [8]; 4, experiment [2]) and on the 61-bar isobar (2, calculation; 5, experiment [2]).*

Figure 1 illustrates the electrical conductivity of cesium vapor on the saturation curve. In the case of low densities, negative ions were also included in calculations, as was done by Zhukhovitskii [1]. This curve practically does not differ from that of [1]. Note the good agreement between theory and new experimental data. The extrapolation of the experimental data of Hensel *et al.* [2] to the region of low temperatures is closer to the calculated curve than to the data of Borzhievskii *et al.* [8]. However, no final conclusion can be made because of the absence of assessment of experimental error.

Figure 1 also shows the electrical conductivity on the 61-bar isobar. The $\sigma(T)$ relationship is descending, which illustrates the effect of anomalous electrical conductivity. The descending portion on isobars, as shown by calculations, disappears at $T < 1000$ K (according to Borzhievskii *et al.* [8], it is absent even at $T = 1200$ K). It is this region that should probably be regarded as the point of transition from anomalous to normal electrical conductivity.

Figure 2 shows the electrical conductivity as a function of density at constant temperatures. One can see that the density dependence of electrical conductivity is sharp while its temperature dependence is rather weak. This behavior of electrical conductivity is characteristic of near-critical densities and is attributed to the metal-dielectric transition in vapor. As to the region of lower densities under consideration, the physical reason for this effect is different. Given a temperature rise, the neutral clusters ionize more readily; if the system is far from the saturation curve in the direction of superheated vapor, their concentration decreases. These two factors balance each other.

Although the theory provides a qualitatively accurate description of the decrease of the density depen-

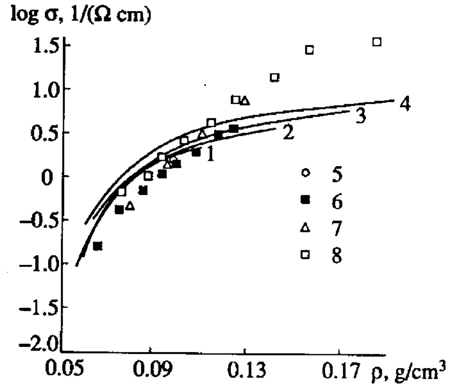

Fig. 2. *The electrical conductivity of cesium vapors as a function of density: 1 - 4, calculation for constant temperatures of 1773, 1823, 1873, and 1893 K, respectively; 5 - 8, experimental data [2] for the same temperatures.*

dence of electrical conductivity at high densities (curve 4 in Fig. 2), in this region the calculation yields a lower value of electrical conductivity as compared with experimental values. This is apparently because of the emergence of a new, metallic mechanism of electrical conductivity. In the region of lower densities, as on the 61-bar isobar, theory and experiment adequately agree, which is a result of the consistent description of the equations of state and ionization equilibrium.

The agreement observed between the experimental data obtained at high [2] and low [8] temperatures, and the calculation results (Fig. 1) reveal a certain clarity of the situation with the electrical conductivity. At the same time, both the theoretical and experimental accuracy is still not high enough. This adds urgency to the need for new measurements of electrical conductivity under conditions of intermediate temperatures and densities ($T \sim 1500$ K, $\rho \sim 0.04$ g/cm^3), where the anomalous properties of cesium vapor plasma must show up most vividly. One should also expect theory to yield the most exact results in this region.

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