12. L. S. Kotousov, Y. I. Popov, and A. N. Sviridov, "Mesure de la chaleur de mélange de Ar—He et N_2—He dans le domaine de pression: 2-15 bar," C. R. Acad. Sci. Paris, 287, Ser. B, 109-111 (1978).
13. L. S. Kotousov, "Determination of the thermodynamic mixing potential of a binary mixture on the basis of an analysis of the processes in interdiffusion," Zh. Tekh. Fiz., 40, 1994-2004 (1970).
14. L. S. Kotousov and A. N. Sviridov, "Calculation of the excess potentials of binary gas mixtures," Zh. Tekh. Fiz., 47, 1324-1332 (1977).
15. V. F. Bondarenko, "Experimental and theoretical investigation of the caloric properties of compressed gas mixtures," Author's Abstract of PhD Thesis, MÉI, Moscow (1975).

ANALYSIS AND CORRELATION OF NEW DATA ON THE THERMOPHYSICAL PROPERTIES OF MERCURY VAPOR

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The article contains a critical analysis of the experimental data concerning the thermophysical properties of mercury vapor and the coordination on the basis of the simultaneous processing of the data on saturation pressure, viscosity, and heat conductivity.

In the preparation of reference data on the thermophysical properties of mercury vapors for the monograph [1], the properties at temperatures up to 2000°K and pressures of 10 MPa were generalized on the basis of a single potential of interatomic interaction of atoms, chiefly in the 6^1S_0 state. We implemented the method of simultaneous determination of the sublimation temperature ΔH_0^0 and two parameters of the selected potential: the potential well depth ε and the collision diameter d with joint approximation of the experimental data on the saturation pressures P_S–T_S, and also viscosity $\eta(T)$ and heat conductivity $\lambda(T)$ of the rarefied vapor. The main calculations of the reference data were carried out with the aid of the Morse potential ($\beta = 4.5$), and later [2], the Lennard-Jones (L.-J.) potential (9-6) was also successfully applied.

At the same time, the following problems in the investigation of the properties of mercury were discovered.

1. The experimental data on the heat capacity of the solid phase at 4-20°K contain a considerable error, making the principal contribution to the error in determining the sublimation temperature $\Delta(\Delta H_0^0) = 60$ J/mole, and they are, as noted in [2], probably exaggeratedly high.

2. On the basis of a critical analysis of the data on the viscosity and heat conductivity of the vapor, preference was given to the results of Braune, Basch, and Wentzel [3] regarding viscosity in the interval 490-880°K, and this work was the basis for determining the potential. Like any single work, it needed confirmation.

3. In joint processing of the data, it was dicovered [1, 2] that the only results of measuring saturation pressure in the interval 600-800°C [4] claiming very good accuracy were in effect 1.5-2% too high.

At present we are in possession of the results of new measurements of the properties of mercury vapor which, on the whole, confirmed the earlier generalizations [1, 2]. Part of this work [5, 6] was carried out upon the initiative of the Section of Liquid Metals, Scientific Council "Thermophysics" of the Academy of Sciences of the USSR with the object of verifying existing data. Then we give a brief analysis of the new experimental data, a selection of the errors for calculating the weights, an algorithm for and the results of repeated joint processing.

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TABLE 1. List and Brief Characteristics of Experimental Data

Authors, year	Ref.	Temp. range, °K	No. of points	Assumed error, %	Deviation limits, %
Saturation pressure					
Beatty, Blasedell, Kaminski, 1936	[1]	622—636	35	0,02	—0,003—0,009
Blasedel, Key, 1941	[1]	629, 807	1	0,001	+0,001
Spedding, Day, 1955	[1]	534—630	13	0,3—0,1	—0,16—0,025
Ernzberger, Pitman, 1955	[7]	285—326	18	1—0,3	—0,4—1
Shpil'rain, Nikanorov, 1971	[8]	564—883	23	0,7—0,5	—0,8—0,8
	[9]	380—771	115	1—0,02	—0,03—0,04
Viscosity					
Cox, 1885	[1]	546—653	18	4,5	
Braune, Basch, Wentzel, 1928	[3]	492—880	13	1—3	—(1,2—0,3)
Khalilov, 1938	[1]	623—883	27	10	
Frank, Hensel, Tippelskirch, 1975	[10]	1313—1528	15	>10	
Timrot et al., 1979	[5]	625—800	5	3	—1,6—8,8
Lyusternik, 1979	[6]	693—1054	15	3	+(1,3—5)
Heat conductivity					
Zaitseva, 1959	[1]	530—696	5	7	
Erginoz, Bonilla, 1970	[11]	430—717	12	—	
Vargaftik, Yakush, 1970	[12]	606—1183	17	6	+(6—11)
Zarkova, Stefanov, 1976	[13]	978—2273	47	6	—11—6,8
Siegel, Bonilla, 1977	[14]	518—1265		—	

A list of the experimental data used in the joint processing and their brief characteristics are presented in Table 1. The works published up to 1969 were already dealt with in detail in the monograph [1]. There, among the works on saturation pressure, the unique work by Ernzberger and Pitman [7] was omitted; this presents the experimental P_S–T_S data in the range $(1\text{-}10)\cdot 10^{-6}$ mm Hg obtained by the piston method. The piston in the form of three mica lobes with an area of $\sim$10 cm^2 was suspended from a quartz thread with a sensitivity of $\sim 10^{-8}$ mm Hg. Possible sources of errors were carefully investigated, including the major source, viz. leaks through the gaps between the piston and the cylinder. This last error is $\leq 0.3\%$, and according to the authors' estimate (with which we agree), the total error is $\leq 1\%$.

Shpil'rain and Nikanorov [8] determined the P_S–T_S of mercury largely in order to check the accuracy of their device operating by the boiling-point method and intended for measuring the saturation pressure of alkali metals. These authors refined the measuring method for a long time, and in the region >1 atm the error of their results was $\delta P_S \leq 0.5\%$. With lower pressures the error of the P_S–T_S data increases on account of poorer boiling regimes and the difficulties in calibrating the thermocouples PP, and we took it as $\sim$0.7%.

In principle, it is important that the results of [8] concerning mercury confirmed the earlier assumption, based on calculations in [1], that the Japanese P_S–T_S data [4] are systematically exaggeratedly high. In the body of the data of [8], two points were excluded for being far out.

New precision measurements of saturation pressure were carried out in Great Britain at the National Physical Laboratory (NPL) [9]. This work involved chiefly the study of the temperature range 621-636°K, i.e., near the normal boiling point, by the method of comparative ebulliometry. The error of these data was adopted by us as equally high as for the earlier investigation by Beatty et al.: $\approx$ 0.02-0.03% (see Table 1). The same method was applied in studying the region up to 0.8 MPa. For the maximum pressure, $\delta P_S \sim 0.1\%$ was taken. One series was reserved for measurements of low pressures $P_S = 0.5\text{-}40$ mm Hg, also by the boiling-point method. The pressure was recorded with the aid of a mercury manometer. The error of these data (except for the first point) varied between 1 and 0.1%, respectively.

A considerable number of investigations of the saturation pressure were excluded from consideration because in accuracy these works could not compete with the data dealt with above.

Very important are the measurements of the viscosity of vapor carried out at the High-Temperature Institute of the Academy of Sciences [5, 6]; they largely confirmed the reliability of [3].

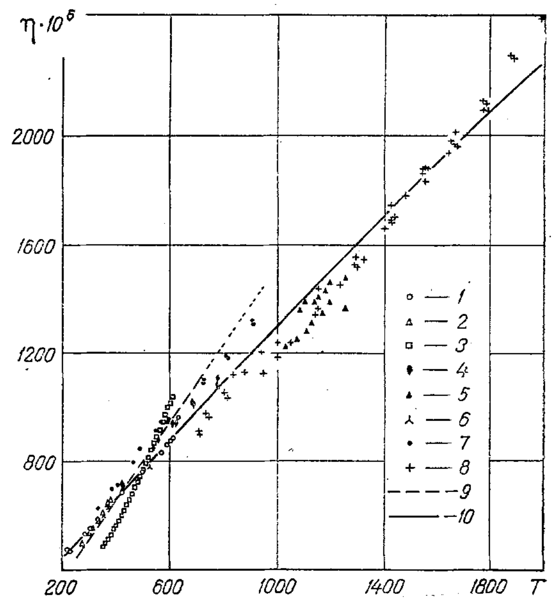

Fig. 1. Viscosity and heat conductivity of mercury vapors: 1) data by Braune, Basch, and Wentzel [3]; 2) Koch [1]; 3) Khalilov [1]; 4) Lyusternik [6]; 5) Tippelskirch et al. [10]; 6) Timrot et al. [5]; 7) Vargaftik and Yakush [12]; 8) Zarkova and Stefanov [13]; 9) by the equation of Siegel and Bonilla [14]; 10) recommended curve for the L.-J. potential. The data on heat conductivity are given in viscosity coordinates. $\eta \cdot 10^6$, P; T, °C.

Timrot et al. carried out measurements by the disk method [5] and obtained 5 experimental points whose error they estimated to be $\sim$1.5% and which lie approximately 1% below the data of [3]. However, their device was designed for work in less viscous media than mercury vapor. The authors therefore managed to observe only two full oscillations of the disk. It is not clear to us with what accuracy they used in such a situation Maxwell's formula, which is correct for periodic oscillations with low attenuation. Somewhat arbitrarily we adopted an error of 3% for these data.

Lyusternik [6] used the capillary method in a device which had been repeatedly calibrated according to the viscosity of steam and which had proved its worth in work with vapors of organic substances. Although the theoretical error of measurement was 1.2%, in the given generalization we used $\delta\eta \sim 3\%$. Here, the discrepancy between different methods of calibrating the viscosimeter constant attaining 2.8-3% and also the noticeable scatter of the data were taken into account. One point, which deviated by more than 5%, was excluded from consideration.

The viscosity of vapors above 1300°K was measured by Frank et al. [10] by the method of torsional vibrations of the crucible. The device was intended chiefly for determining the viscosity of liquid mercury at pressures of up to 100 MPa. Therefore the experiments with vapors in a heavy thick-walled crucible made of the alloy W—3% Re had an error of not less than 10%. For the vapors the data were obtained on the isochores 0.7, 1.05, and 1.37 g/cm^3, and the change in viscosity between the extreme isochores amounts to about 30%. On the other hand, on the basis of the generalized dependence of viscosity on the density of monatomic gases [15], this change must not exceed 4 or 5%.

Among the new works dealing with the heat conductivity of mercury vapors, we must mention in the first place the measurements carried out in 1969 by Vargaftik and Yakush [12] at the Moscow Aviation Institute (MAI) by the steady-state heated-thread method, which in the past was instrumental in adding 500° to the interval in which the kinetic properties of mercury vapor were investigated. In the work, the first thermometer was a platinum thread with 0.1-mm diameter. The second platinum thermometer was wound onto a quartz tube with 2.91/4.02-mm diameter. The authors estimated that the error of the results was 2.8%, but in our opinion it was in reality more than twice as large. The radiative heat losses, which at the highest experimental temperature attained as much as 60% of the conductive heat flux, were not determined experimentally but only on the basis of literature data on the radiant emittance ε_{th} of platinum; moreover, the values ε_{th} used differed from new reference data [16] by from 40% at 400°K to 10% at 1200°K. Consequently, on account of only one indeterminacy of the value ε_{th}, the error of heat conductivity amounts to no less than 6%. In addition to that, the authors did not take radiation into account in estimating the correction for heat losses from the ends of the thread. Still not clear is the cause of the temperature difference when there are nonheating flows between the resistance thermometers, the difference attaining 2°C, i.e., 6% of the total temperature gradient. A corresponding correction was introduced in the calculations but its reliability is open to doubt. Moreover, control experiments with air, which has heat conductivity 5 times higher than mercury vapor, add practically nothing to the verification of the correctness of introducing the correction. It should be borne in mind that on the same device in the same temperature interval the heat conductivity of krypton and xenon was measured, i.e., of heavy gases whose properties are similar to those of mercury vapor. The results of these measurements are 6-7% higher than the reference data [17] obtained in the generalization of the kinetic properties of all inert gases. There are therefore serious grounds for assuming that the data of [12] are systematically exaggerated.

It was already noted earlier [1, 2] that the experimental results of [12] are probably higher than the main bodies of experimental data on the kinetic properties of mercury vapor. If the Maxwell coefficient is calculated by the data of [3, 12], then a value is obtained which is noticeably higher than the theoretical value for monatomic gases $f = 2.5$. However, this difference is insignificant. Finally, in the calculations we adopted $\delta\lambda = 6\%$ for the data of [12].

Other new works concerning the heat conductivity of mercury vapor [11, 13, 14] were carried out less thoroughly and are dealt with more briefly than [12].

Zarkova and Stefanov used a modernized steady-state heated-thread method in the variant of Blace and Mann and considerably increased the temperature interval of measuring $\lambda(T)$ [13]. The correction for radiation of the tungsten wire was determined experimentally in vacuum, and at 2000°C it attained 80% of the power supplied, and consequently 400% of conductive heat conduction. The main experiments were carried out at pressures of 44 to 250 mm Hg, and the correction for the temperature jump was introduced by calculation. The mean scatter of the data was ∿1.5%, the overall error, according to the authors' estimate, was 3%. We want to point out that in this work, several points were obtained in the interval 630-930°K, but they are presented only in a figure in [13] and were not used by us in the calculations.

Bearing in mind, in the first place, the enormous proportion of radiation and the fact that the data under examination at 600°C are 5-8% lower than the results of [3, 5, 6], we adopted $\delta\lambda$ [13] = 6%, and generally speaking, with rising temperature this error has to increase.

Bonilla et al. measured heat conductivity by the non-steady-state heated-thread method [11, 14]. A criticism of the low-temperature data of [11] is contained in [18]. Taking the difficulties and the novelty of the method into account, Siegel and Bonilla [14] estimated that the error in their data amounted to 6%. These results are presented only by an equation recommended on the saturation line and in overheated steam up to 1265°K. A certain problem is posed by the conversion of the data of [14] from the saturation line (dashed line, Fig. 1) to the rarefied gas. The limits of the errors in [11, 14] are not clear to us but they are probably not below 6 or 8%, and these results are henceforth not used in the calculations.

The joint approximation of the data was carried out with minimization of the following functional according to the parameters ΔH_0^0, ε, and d:

$$M = \Sigma W_{P_s}[P_s^e(T) - P_s(T,\ \Delta H_0^0,\ \varepsilon,\ d)]^2 + \Sigma W_\eta[\eta^e(T) - \eta(T,\ \varepsilon,\ d)]^2 + \Sigma W_\lambda[\lambda^e(T) - \lambda(T,\ \varepsilon,\ d)]^2, \qquad (1)$$

where the theoretical values of the saturation pressure $P_s(T)$ were found with the aid of the third law of thermodynamics from the condition of equality of the chemical potentials of the liquid and the vapor. The values $\eta(T)$ and $\lambda(T)$ were calculated by the known theory of molecular kinetics for rarefied gas with the aid of the tabulated collision integrals $\Omega^{*(2,2)}(T^{*} = T\varepsilon^{-1})$. This calculation method was explained in detail in [1, 2].

In expression (1) Y^e are the experimental values of the functions. At each experimental point the weight is calculated by the relation $W_Y = (\delta \cdot Y^e)^{-2}$, where the values of the relative errors δ adopted by us are given in Table 1 and were to some extent discussed above.

First we sought in the body of data $\{\eta, \lambda\}$ the optimum function of interatomic interaction in the class of potentials m-6-8 [19]. For whole m in the interval m=8-18 and $\gamma = (0\text{-}2.5)M_{min}$, we obtain for the potential 9-6-8, $\gamma = 0$ with the parameters $\varepsilon = 931°K$ that $d = 2.716$ Å. For the continuous function M(m), the minimum lies at m somewhere between 8 and 9. A similar result for m, but with completely different parameters ε and d, was obtained in [13].

As before [1], a comparison of the L.-J. potentials (9-6) and Morse $\beta = 4.5$ according to the value of M did not yield any visible advantage for either of them. The results presented below were obtained for the L.-J. potential (9-6).

In calculating the saturation pressures P_s through the equality of the chemical potentials $\mu'(T) = \mu''(T, P, \Delta H_0^0, \varepsilon, d)$, it is assumed [1] that the values μ' for the condensed phase, which are calculated by integrating the heat capacity of the solid and liquid phases, are known exactly. In reality the values of heat capacity of solid mercury in the interval 4-20°K had up to recently an error of ∿5%; this created an additional indeterminacy in finding ΔH_0^0. Like the authors of [2], we also introduced an additional parameter $S'(T_{mp})$, the entropy of solid mercury at the melting point. The optimum value was found by selection in the minimization of (1). It was found that $S'(T_{mp}) = 59.30 \pm 0.01$ J/mole·°K. This value agrees well with $S'(T_{mp}) = 59.293$ J/mole·°K obtained by I. E. Paukov et al. on the basis of new measurements of the heat capacity of mercury carried out in the interval 5-300°K in 1978 at the Institute of Inorganic Chemistry, Siberian Branch, Academy of Sciences of the USSR [20].

In the joint approximation of the experimental data (n = 331) of Table 1, the minimum functional M = 173.5 was obtained for the following parameters:

$$\Delta H_0^0 = 64{,}550\ \text{J/mole},\ \varepsilon = 987.6\ °\text{K},\ d = 2.673\ \text{Å}, \tag{2}$$

whose errors in the first approximation, with 95% probability, are characterized by the error matrix (EM):

$$\begin{array}{ccc} 0.15 & 8.45 & -0.0056 \\ 8.45 & 530 & -0.38 \\ -0.0056 & -0.38 & 2.9\cdot10^{-4}; \end{array} \tag{3}$$

In the EM, the dispersion 0.15 (J/mole)² relates in fact not to the sublimation temperature ΔH_0^0 but to the magnitude $\Delta H_0^0 - \mu'(T_{mp})$, and the error $\Delta(\Delta H_0^0)$ is determined basically by the error $\Delta\mu'(T_{mp})$. With a view to the relative error $\delta\mu'(T_{mp}) = 0.0015$, the error of determining $S'(T_{mp})$, the variation in the kind of potential, etc., $\Delta(\Delta H_0^0) = 20$ J/mole, i.e., in ten years this error was reduced to one third [1].

If in the approximation of the saturation pressures, we add $S'(T_{mp})$ to the varied parameters, then with the same body of experimental data, the EM, which is analogous to (3), assumes the form (M = 171.8)

$$\begin{array}{cccc} 5.02 & -31.2 & 0.023 & -0.014 \\ -31.2 & 795 & -0.606 & 0.113 \\ 0.023 & -0.606 & 0.47\cdot10^{-3} & -0.84\cdot10^{-4} \\ -0.014 & 0.113 & -0.84\cdot10^{-4} & 0.36\cdot10^{-4}, \end{array} \tag{4}$$

where $0.36\cdot10^{-4}$ is the dispersion $S'(T_{mp})$. It can be seen that when the model is broadened, the estimates of the errors in the parameters and theoretical curves become more realistic.

The scope of the present article does not permit us to analyze in detail the nature of the approximation of each series of data. To some extent this can be judged by the limits of the deviations from the theoretical curve presented in the last column of Table 1. On the whole, the approximation is satisfactory.

In the body of the P_s–T_s data, the results of highly accurate investigations in the region of the normal boiling point agree within the limits −0.017% (Ambrose and Sprake) and 0.01% (Beatty et al.). These data are not contradicted either by the low-temperature [7] or the high-temperature [8] results.

It can be seen in Fig. 1 that for the transfer properties of rarefied vapor we have the body {η, λ} of data from [3, 5, 6, 13] which lies close to the theoretical curve. On the other hand, in view of the importance of mercury as a metrological substance, it is desirable to attain agreement of the experimental data on viscosity within the limits 1-1.5% at 400-1100°K, and to improve the accuracy of measurements of heat conductivity.

At present we are planning to broaden the joint processing with a view to the statistical indeterminacy of the caloric properties of the condensed phase and the variations of the indicator n in the L.-J. potential (n-6). We intend to present revised tables of the thermophysical properties of mercury vapor with an estimate of their reliability in the form of tables of reference data.

LITERATURE CITED

1. M. P. Vukalovich, A. I. Ivanov, L. R. Fokin, and A. T. Yakovlev, Thermophysical Properties of Mercury [in Russian], Standartov, Moscow (1971 (1973)).
2. A. I. Ivanov and L. R. Fokin, "Coordination of data on the thermophysical properties of mercury vapor," Zh. Fiz. Khim., 48, 1048 (1974), Dep. at VINITI, No. 7655-73.
3. H. Braune, R. Basch, and W. Wentzel, "Internal friction of gases and vapors. 1. Air and Br_2. 2. Hg, Cd, Zn," Z. Phys. Chem., A137, 176, 447 (1928).
4. S. Sugawara, T. Sato, and T. Minamijama, "Equation of state of mercury vapor," Bull. JSME, 5, 711-718 (1962).
5. D. L. Timrot, M. A. Serednitskaya, M. S. Bespalov, and S. A. Traktueva, "Measurement of the viscosity of mercury vapors by the oscillating-disk method," Teplofiz. Vys. Temp., 17, 54-57 (1979).
6. V. E. Lyusternik, "Measurement of the viscosity of mercury vapors and analysis of the obtained data," Teplofiz. Vys. Temp., 17, 50-53 (1979).
7. F. Ernzberger and H. Pitman, "New absolute manometer for vapor pressures in the micron range," Rev. Sci. Instrum., 20, 84-89 (1955).
8. É. É. Shpil'rain and É. V. Nikanorov, "Experimental investigation of mercury vapor pressure by the melting-point method," Teplofiz. Vys. Temp., 9, 640-643 (1971).
9. D. Ambrose and C. Sprake, "The vapor pressure of mercury," J. Chem. Thermod., 4, 603-620 (1972).
10. H. Tippelskirch, E. Frank, and F. Hensel, "The viscosity of fluid mercury to 1520°K and 1000 bar," Ber. Bunsen Ges. Phys. Chem., 79, 889-897 (1975).
11. H. Erginoz and C. Bonilla, "Thermal conductivity of mercury vapor," in: Proc. 5th Symp. Thermophys. Properties, New York (1970), pp. 64-71.
12. N. B. Vargaftik and L. V. Yakush, "Experimental investigation of the heat conductivity of mercury vapors," Teplofiz. Vys. Temp., 8, 1182-1185 (1970).
13. L. Zarkova and B. Stefanov, "Measurement of the heat conductivity of gases and vapors up to 2500°K. Cesium and mercury vapors," Teplofiz. Vys. Temp., 14, 277-284 (1976).
14. J. Siegel and C. Bonilla, "The thermal conductivity of mercury vapor," in: Proc. 7th Symp. Thermophys. Properties, New York (1977), pp. 917-925.
15. V. M. Kuznetsov, "Temperature dependence of the second viscosity virial coefficient," Teplofiz. Vys. Temp., 16, 1178-1184 (1978).
16. A. E. Sheindlin (editor), Radiative Properties of Solid Metals (Handbook) [in Russian], Énergiya, Moscow (1974).
17. V. A. Rabinovich (editor), Thermophysical Properties of Neon, Argon, Krypton, and Xenon [in Russian], Standartov, Moscow (1979).
18. N. B. Vargaftik and Yu. K. Vinogradov, "Heat conductivity of mercury vapors," Teplofiz. Vys. Temp., 11, 523-526 (1973).
19. M. Klein et al., Tables of Collision Integrals and 2 VC for the (m, 6, 8) Intermolecular Function, NSRDS—NBS No. 47, Washington (1974).
20. E. B. Amitin, É. G. Lebedeva, and I. E. Paukov, "Heat capacity in the interval 5-300°K, energy of generation, and concentration of equilibrium vacancies of mercury," Zh. Fiz. Khim., 53, 2666-2670 (1979).