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The Thermodynamic Properties of Solid Mercury at Temperature Intervals of from 0 deg. K to Melting Point at Normal Pressure

ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА ТВЕРДОЙ РТУТИ В ИНТЕРВАЛЕ ТЕМПЕРАТУР ОТ 0 К ДО ТОЧКИ ПЛАВЛЕНИЯ ПРИ НОРМАЛЬНОМ ДАВЛЕНИИ

Termodinamicheskiye Svoystva Tverdoy Rtuti v Intervale Temperatur ot 0 K do Tochki Plavleniya pri Normal'nom Davlenii

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The Thermodynamic Properties of Solid Mercury at Temperature Intervals of from 0 deg K to Melting point at Normal Pressure

In all branches of knowledge a great flow of information (or the lack of it) gives the work of sorting, identifying, and preparing standard reference data a special set.

The Department of Theoretical Foundations of Thermotechnics at the MEI* has prepared thermotechnical tables of mercury characteristics. The properties of saturated and burned out gas are considered up to 1000 degC and 800 bar, and an *i-s* diagram is constructed. (Ref. 1). The results of the experiment, which relate to viscosity and heat transfer are thoroughly analyzed. The possibility of the interaction potential are considered as well as the possibility of error in determining its parameter in relation to viscosity (Ref.2).

The reference table (Ref.3) presents a fairly complete bibliography about the properities of mercury, which were published before 1955.

Two modifications of solid mercury are known: α and β given various crystalline structures. α-mercury is a crystal and has a simple rhomboid nuclear mesh structure with the following parameters: a=2.993Å, α=70 deg 45 min given 78 deg K Ref. 4. β-mercury has a tetragonal volumetrically centralized mesh structure (a=3.995Å, c=2.825Å, $a/c \approx \sqrt{2}$ given 77 deg K Ref. 5). In the lower temperature zone (T<79 deg K) the thermodynamically stabel phase is the β mercury; however, this transformation occurs only when there is plastic deformation or high pressure.

When α=mercury cools below 79 deg K and atmospheric pressure is α-β the transformation does not occur under normal conditions Ref. 6. Beyond this the thermophysical properties of β-mercury remain unexplored and it is only possible to create a table of physical heat properties for α-mercury only.

Translator's Note: MEI = Moscow Institute of Energetics

Both modifications of mercury have super conductive powers, given low temperatures. The transitional temperature T_c of α and β mercury into a super conductive state is 4, 15, and 3, 95 deg K respectively Ref. 7.

In principle, the modern theory of solid matter allows for a thermal and caloric equation of the state of solid matter, if the potential energy of the interrelationships of atoms in the crystalline mesh structure is known. A series of simplifications are introduced with the equation: e.g., - a harmony of atomic oscillation is assumed, thus allowing the problem to be considered from the point of view of determining the spectrum of particles of harmonic vibration of the crystal.

Slutsky and Jelinek (Ref. 8) calculated this vibrative of α-mercury in such a fashion when they took into considertion the fixed intensity of mercury established by Gruneisen and Sckell (Ref. 9). In view of the fact that the fixed intensity was determined for only one temperature ($t = -190^\circ C$) and in the inadequate precision, the determined spectrum corresponds poorly with experiments regarding the thermal capacity of mercury.

Several complicated interrelated phenomena harshly stand out in the properties of solid substances - unharmonic oscillation of the mesh structure (thermal expansion), influence of distant neighbors with the possibility of nonadditivity of interaction (mesh structure and emission of X-rays and neutron streams) an electron-phonon interaction (heat conductivity) formation of defects, etc. Inspite of progress in the solid state physics, there are currently no equalizations which transmit data with experimental precision, even regarding equilibrium in wide intervals of parameters. That is why in considering the properties of solid matter the decisive meaning, as a rule, is only experimentally valid.

As a whole the problem of creating correlated tables of physical heat properties with the aid of theoretical equations should include the determination of certain constants, related to parameters of interrelated potentials; different types of experimental data must be utilized in the process (compression, caloric properties, intensity of radiation, heat conductivity, auto diffusions, etc.). However, at the present time this problem can only be solved for gaseous substances of moderate density.

Therefore the adjustment factor of these various experimental data, about thermodynamic properties of solid mercury was negligible in this work and was mainly qualitative in character.

In the process the International System of units was utilized. The atomic weight was 200.59 (1965 data) attributed to mercury. The thermodynamic scale is used in the table in regards to temperature. The difference between the practical temperature scale and the thermodynamic one is included in the percentage of error.

The point of liquefication of mercury in normal pressure is 38.87 deg C, according to the International Temperature Scale or 234.28 deg K allowing a magnitude of error, according to a thermodynamic scale of ±0.005 deg.

Thermal Capacity of Solid Mercury(According to Given Experiments)

The measuring of thermal capacity is taken into consideration when calculating the caloric properties of solid substances that have been experiemntally determined. The heat capacity of α-mercury has been adequately studied, but for β-mercury data are lacking. That is why it is only possible to provide tables for α- mercury.

In the reference material (10), the table indicates the properties of mercury that are based on the data provided by Busey (Ref. 3) and Grauque (Ref. 1). The appearance of more recent experimental data, especially in the sphere of the lowest temperature ranges, allows us to receive more detailed meanings of caloric function - entropy and enthalpy.

In Table 1, the basic knowledge of experiemnts determening the thermal capacity of solid mercury is presented. In all experiements the method of direct heating of the calorimeter exposed to changing temperatures, existing in the isothermal film in conditions close to adiabatic is used. This data embraces temperature intervals ranging from o.1 deg K to the melting point; with their aid we can determine the caloric function of solid mercury.

The experimental data received from the works of Kammerling-Onnes and Holst (Ref. 12), Dewar (Ref. 13), Barschall (Ref. 14) and Koref (Ref. 15) about the average meaning of thermal capacity Cp in different intervals of temperature, is not exact and is, therefore, not examined in detail.

First, the experimental devices were analyzed and the error in calculating the thermal capacity of mercury was evaluated. According to our observations, the estimated degree of error of Pollitzer (Refs. 16 and 17) and Simon (Refs. 18 and 19) is not less than ±(2-2.5)%. The estimated error for Pickard and Simon (Ref. 20), Smith and Wolcott (Ref. 21) is ±2%.

A thorough analysis of Busey and Giauque's method for measuring the thermal capacity of solid mercury (and other works by Giauque) has indicated that their evaluation of the degree of error is basically correct if the given temperature is higher than 35 deg K, then the degree of error is close to ±0,1% if temperature is 20 deg K it reaches ±1% and if 15 deg K thus it approaches ±3%.

When various data were compared they showed that the early works of the German authors (Ref.16,19) gave results that were in accord, within the limit of measured error; however, in the interval of temperature 25 - 80 deg K they exceeded the value calculated by Buge and Jacques by approximately 2,5% (Ref.11).

In the region between 4 and 10 deg K the data of Pecard and Simon (Ref.20) are excessive by comparison to the results of Smith and Wolcott and have an anomalous character, but in intervals from 10 to 20 deg K they are insufficient by comparison to those of Simon (Ref.19). Smiths' amd Wolcott's data correspond with those of Simon in this temperature interval. On ther other hand, the calculations of Smith and Wolcott correspond sufficiently with those of Van der Hoeven and P. Keesom (Ref.23) when the temperature is lower than 4,2 deg K (in the region beyond mercury's heat capacity'.

The results of Phillips' and his co-workers (Ref.24) basically correspond with those of Van der Hoeven and Keesom. The data of Phillips are presented in graphic form and are not taken into consideration in our processing.

In this regard, the more accurate and more agreeable data are taken to be those of Simon, Smith and Wolkott, Van der Hoeven and P. Keesom, and Busey and Giauque. Preference is given to Busey and Giauque in the area between 20deg K to the melting point of mercury because of greater exactness, even though these data don't correspond with the others (Ref.16-18) of T = 25-80 deg K.

It is important to indicate that the analysis of this experimental data, by the authors of the sxperiments or by those who created the tables, was not able to reveal experimental errors close to the numerical value of the sensitivity of the apparatus, and only repeated measuring could verify a high degree of accuracy. That is why it is imperative to conduct additional measuring experiments of mercury's heat capacity in the interval between 25-80 deg K within the limit of error ≤0,1%.

In analyzing data regarding heat capacity of solid substances the character of heat activity near the melting point is important.

According to special experiments with mercury by Kostriukov and Strelkov (Ref.25) it has been demonstrated that great pre-melting effects, that are expressed in increase of heat capacity (C_p) up to tens and hundreds of percents, are not necessarily present. The results in (Ref.11) show that even a small amount of additives varies heat capacity sharply if the temperature is 3-4 degrees below the melting point. A similar effect can be observed if temperature is not even throughout a given substance.

Carpenter and Oakley also measured heat capacity of mercury near the melting point. The mercury was thoroughly purified beforehand. The dispersion of points in relation to a curve medium lay within the limit 1%. On the basis of the curves form the authors of the work (Ref.22) concluded there is an anomaly of heat capacity of solid mercury near the melting point, where it increases to a degree not greater than the dispersion of experimental data.

The points do not disperse systematically near the melting point and, therefore, such a conclusion by the authors is difficult to explain. Apparently, a correct manipulation of Carpenter's and Stoodley's data would give us a smooth curve without twists which would approximate a straight line, even to the melting point.

The values of mercury heat capacity found by Carpenter and Stoodley are 1% lower in the average to those of Busey and Giauque (Ref.11) and are not processed by us.

It should be noted that the sources of systematic error in measuring heat capacity with low temperature, may be due to gas absorption, the appearance of thermal pressure in the substance and in resistance within the thermometer. If heat capacity is insignificant and temperature is low the smallest vibration limits increased heating of the specimen . That is why it is important to perform additional experiments that will agree with previous ones.

Let us note, that a more detailed analysis of experimental settings, tables of resulting data, etc. is presented by the authors in tables (Ref.26).

Calculation of caloric functions of solid mercury

In order to calculate entrophy, enthalpy, isobaric and isothermal potential; and to create a heat-capacity table, it is necessary to choose a function that describes best the experimental data regarding the heat capacity of solid mercury.

Usually in describing the isochoric heat capacity of solid mercury Debay's formula is used:

$$C_v = 9Nk\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^4 e^x}{e^x - 1}\,dx, \qquad (1)$$

(1) where θ is the characteristic temperature.

However, C_v calculated according to equation (1) cannot be greater than 3R - this does not correspond to our data. That is why we must correct elements relating to disharmony, formation of holes (gaps), and the term that considers the difference between C_v and the value of C_p determined in our experiments.

$$C_p - C_v = \frac{\alpha^2 VT}{\varkappa_T}, \qquad (2)$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \text{ и } \varkappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T.$$

(2) All this complicates the equation that is useful in approximating our data.

In order to describe the dependency of heat capacity on temperature, we can utilize the equation based on a more definite dynamic theory of crystalline mesh structure

$$C_v = 3Nk\int_0^\infty E\left(\frac{h\nu}{kT}\right)\rho(\nu)d\nu, \qquad (3)$$

where

$$E(x) = \frac{x^2 e^x}{(e^x - 1)^2} -$$

Einstein's formation for harmonic oscillators and

$$\rho(\nu) -$$

is the function of mesh oscillation depending on frequency. The function $\rho(\nu)$ for mercury was calculated by Slutsky and Jelinek (Ref.8); however, the heat capacity C_v, calculated with the aid of equation (3) poorly coincides with experimental dependency $C_v(T)$ of mercury, even with low temperatures (up to 50 deg K).

In principle (Ref.27-29) it is possible to discover function $\rho(\nu)$ by referring to experimental data regarding heat capacity with the aid of integral transformative functions (3). In this way we can find an analytic dependence $C_v(T)$ which, however, will not be free of limitations existing in equation (1).

With all this in mind we decided to approximate the experimental data regarding isobaric heat capacity of simple analytical dependency in terms of multiple algebraic terms, which allow us to get simple correlations for calculating caloric function

$$\left.\begin{aligned} I - I_0 &= \int_0^T C_p dT \\ S - S_0 &= \int_0^T \frac{C_p}{T} dT \\ \Phi &= I - TS \end{aligned}\right\}, \qquad (4)$$

where I-enthalpy; S-entropy and ϕ-the isobaric-isothermal potential.

In so far as it was difficult to approximate C_p by one multiple term, in the entire temperature interval 0 deg K to melting point, we broke up the interval into several parts; for each of these we selected a multiple term by the method of minimum squares, which described the experimental data with derration not exceeding the experimental degree of error. All calculations were made with the aid of an M-20 computer.

In the multiple-term selection process the areas overlapped, with the exception of joint with To, where there is a jump in heat capacity. Experimental points were included in the calculation with weight $W=Vo^2$, where σ is the absolute limit of error assigned experimental value. We also took into consideration relative errors δCp, which are the results of data described above. We selected polynomials of different degrees, beginning with the smallest. We increased the ratio until the quantity of atomic numbers, last in transforming the matriax system of normal equations did not exceed the quantity of atomic figures of mechanical numbers.

We chose polynomials of the needed degree and based our considerations on the following:

1) the sum of squares of deviation of experimental points from the approximating curve must be close to n-m (n is the number of experimental points; m is the quantity of unknown parameters, in this case the quantity of unknown coefficients of polynomials.

2) the absolute measure of deviation must not exceed the limit of error of experimental points.

3) the calculated errors of coefficients must be at least one order of magnitude less than the value of the coefficients.

After a series of efforts experimental dats, C_p, were approximated to the curve, which consisted of three areas, each of which was represented by its own multiple term. At the joints the coincidence of heat capacity value was guaranteed up to five known digits. The products of joints were disturbed, first according to the final differential C_p (table 6). The degree of error of caloric function stipulated by the inaccuracy of the jointed areas is less than their common degree of error by one to two orders of magnitude.

In the transition of α-mercury to a condition of superconductivity and back we observed a jump in heat capacity ΔC about 0,019 J/(mole · deg) (Ref.23) in magnitude. The value of the transitional temperature T_c, in various sources, oscillated from 4,153 (Ref.7) to 4,167 deg K (Ref.30). We took the average value of $T_c = (4.16 \pm 0.01)$ deg K.

Here are the approximating multiple terms

$$C_p(T) = \sum^{m} a_i T^i. \tag{5}$$

Coefficients a_i are presented in table 2.

The caloric functions are calculated by formula (4) containing corrections leading the function to standard pressure $p_0 = 760$ *mm Hg*.

$$\left.\begin{aligned} I^0 - I^0_0 &\approx I - I_0 + V(p_0 - p_s)(1 - T\alpha) - V_0(p_0 - p_s) \\ S^0 - S^0_0 &\approx S - S_0 - V\alpha(p_0 - p_s) \end{aligned}\right\}. \tag{6}$$

The corrections do not exceed the degree of error of calculated functions.

The crystalline formation of the α-mercury mesh structure is not stable in relation to β-mercury, where $T<79$ deg K but it is stable in relation to small deflections from a state of equilibrium - the α-mercury condition can be realized in a regulated structure by one method. With such a system, given absolute zero, we can accept $S_{0,\alpha} = S_{0.3} = 0$ (Ref.31).

In Fig. 1 we show the durations of the experimental value of mercury's heat capacity from the calculated ones; these durations do not exceed calculated ones, for the most part. We do not show on our graphs the data of Pichard and Simon (Ref.20), whose systematic deviations reach up to 30%, and the experimental points of Pollitzer (Ref.16,17) and Simon (Ref.18), whose deviations reach 6-7%, when temperature ranges from 30-70 deg K.

The degree of error of enthalpy and entropy are related to relative error of heat capacity C_p; which is approximately 3% when $T<15$ deg K: ±1% when $T=15-35$ deg K and ± 0.1% when $T>35$ deg K.

Errors of integration in interval 0-15 deg K are $\delta(S-S_0) = \delta(I-I_0) \gtrsim 3\%$, in interval 15-35 deg K ∿ 1%, and in interval 35 - melting point ∿ 0.1%. The calculated errors indicate the limit in so far as it is assumed that all experimental points C_p are displaced systematically to one side relative to real values.

The absolute limits of error thus calculated, determining entropy ΔS and enthalpy $\Delta\ (I^o-I^o_0)$, are presented in table 3.

In this way the limiting relative degree of error of determining entropy with melting point ∿ 0.5%, and consequently the degree of error of entropy ∿ 0.1% calculated by Busey and Giauque is decreased.

According to our calculations, S^o (melting point) = 59,349 J/(mole · deg), which is 0,134 J(mole · deg) less than the value achieved by Busey and Giauque (Ref.11).

According to (Ref.11) the entropy of mercury is 76.11 J/(mole · deg) at 298.15 deg K while according to Douglas, Ball, and Giueiys (Ref.32) it is $S^o_{298.15}$=75.81 J/(mole · deg) for the pressure of condensed gases.

Our calculation $S^o_{298.15}$=(75.98±0.3) J/(mole · deg) lies between the given results and agrees with them, within the limit of possible errors.

The values of errors $\Delta\phi$ in table 3, calculated according to equation, $\Delta\phi=/\Delta I-T\Delta s/$, do not define the limit.

The caloric characteristics β-mercury are difficult to determine when data regarding heat-capacity of Cp is missing.

From Swenson's experiments determining the parameters of transition α-β, we only know that the generation should be ∿122J/mole where p=1atm with the formation of β-phase from α-mercury. We took $S_{0\alpha} = S_{0\beta} = 0$. This allowed us to determine the effectual values of characteristic temperatures (in the Debye approximation) of α and β-mercury in the interval 0-79 deg K corresponding to $\bar{\theta}_\alpha$ = 97 deg K and $\bar{\theta}_\beta$ = 118 deg K. However, the function $\theta_\beta(T)$ and the energy of the crystalline structure of β-mercury with 0 deg K, $I_{o,\beta}$ remain unknown.

The Thermal Properties of Solid Mercury

The Contractability of Solid Mercury

$$\varkappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right);$$

Swenson obtained more complete data about contractibility of solid mercury in 1958 when he experimented with the substance under high pressure. The experiment was conducted, utilizing the method of a mobile plunger (pecton) developed by Bridgman (Ref.34) and adapted for low temperature measurement.

By extrapolating isoterms $V(p)$, Swenson obtained data about isometric contractibility

$$\varkappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

in conditions of atmospheric pressure (Fig.2). Swenson evaluated the degree of error of determination K_T as equal to 5%. However, we can consider the degree of error to be close to ±10% because of the dispersion of data and possible system error. Swenson's experimental data relate primarily to temperatures between 78-200 deg K. At 4.2 deg K we have another experimental point. This is why Swenson's function $K_T(T)$ needs experimental verefication.

Note that Gruneisen and Sckell (Ref.9) recommended earlier that the value of the contractile coefficient is $_{x}t=3.16\cdot 10^{-11}$ m^2/n when T=82 deg K and in the given reference material there was an extrapolation of data regarding liquid mercury.

In sorting the analytical dependence $K_T(T)$, when p=1atm, the following are considered.

1) when $T \to 0 \frac{dK_T}{d_T} \to 0$;

2) a correspondence of derivatives must be realized resulting from conditions of phase equilibrium

$$\frac{d^2p}{dT^2}\Delta V = \frac{\Delta C_p}{T} - 2\left(\frac{\partial \Delta V}{\partial T}\right)_p \frac{dp}{dT} - \left(\frac{\partial \Delta V}{dp}\right)_T \cdot \left(\frac{dp}{dT}\right)^2, \qquad (7)$$

here, ΔV and ΔC_p is an adhesion of specific volume and heat capacity during fusion.

It follows from the works of Busey and Giauque (Ref. 11), Kostryukov and Strelkov (Ref. 25) that the calculations $\Delta C_p = C_p^J - C_p^{TB} = 0$ are within the limit of error.

In extrapolating the data of Bigg (Ref. 35), at the melting point of mercury, we get V^J=14.65064+0.0020 cm^3/mole.

The density of solid mercury has not been satisfortorily investigated. We can discover the specific density of solid mercury at the melting point on the basis of Bridgman's data (Ref. 36), when the volume of mercury is modified during fusion: ΔV=0.5083 cm^3/mole with a degree of error of ±0.0015 cm^3/mole. Then the specific density of solid mercury at the melting point will equal 14.1423 ±0.0035 cm^3/mole.

The preliminary development of the test data concerning the thermal expansion of solid mercury (Refs. 37 and 38) gives us $\alpha^{J}_{234,3}=(18.1 \pm 0.02)\cdot 10^{-5}$deg^{-1}.

On the basis of an extrapolation of Pena's data (Ref. 40) concerning the contractibility of liquid mercury at the melting point, we find: $K_T^J = (3.88 \pm 0.05) \cdot 10^{-11}$ m^2/N.

The equation for mercury's melting curve was provided by Babb in the form given by Simon's equation

$$\frac{p-p_0}{a} = \left(\frac{T}{T_0}\right)^c - 1, \tag{8}$$

where T_0 is the melting temperature with p_0 for atmospheric pressure; $a = 38215 \pm 817$ bar, $c = 1.177 \pm 0.023$ when $p < 10^4$ bar.

By utilizing the listed data with the help of Eq. 8, we can find $K_{234.3}^{TB} = (3.66 \pm 0.4) \cdot 10^{-11}$ m^2/N.

We prefer this value of contractibility even though it makes many assumptions recommended by Swenson (Ref 33) who found $K_{234.3}^{TB} = (3.82 \pm 0.02) \cdot 10^{-11}$ m^2/N in extrapolating his data to the melting point - this is close to $K_{234.3}^J$ and is excessive.

However, Swenson's data gives us some idea about the general progress of $K_T(T)$ and, therefore, its processing together with the above point $K_{234.3}^{TB}$ gives us an acceptable dependability within a limit of error of ±10%

$$K_T = 2{,}807 \cdot 10^{-11} + 1{,}556 \cdot 10^{-16} T^2, \ \text{м}^2/\text{н}. \tag{9}$$

The resulting dependency is shown in Fig. 2 by means of a solid line.

Swenson also measured the contractibility of β-mercury when the temperature varies from 4 to 78 deg K, which turned out to be 20% lower than the contractibility of α-mercury (Ref. 33).

The Thermal Coefficient of Expansion

$$\alpha = 1/V(dV/dT)_p.$$

Experimental data about the actual coefficient of expansion was used in creating the tables regarding the value of thermal mercury expansion.

In 1931, Carpenter and Oakley, and Hull in 1965 performed similar calculations. Carpenter and Oakley (Ref. 37) measured the volumetric coefficient of solid mercury expansion in temperature intervals between 183 - 234 deg K with the aid of a glass dilatometer which consisted of a retort and capillary. The retort (flask) was filled mostly by mercury with the remaining space filled with alcohol. The change in the level of alcohol in the capillary in accordance with a rise in the temperature made it possible to measure the coefficient of mercury expansion. The authors concluded that the error in measurement was $\delta a \leq 3\%$.

The precision of the experimental method and the additional research for evaluating the degree of error systematically verifies the work of Carpenter and Oakley; the degree of error of the data apparently does not exceed ±3%.

Let us note that the anisotropic quality of mercury monocrystal elicits various expansions of mercury according to different axi. When mercury cools, crystallization can occur with a preeminent orientation, which is the chief source of systematic errors relating to the measurement of mercury's coefficient of expansion. Further on we shall consider α to be the "thermodynamic" coefficient of thermic expansion for polycrystals without preeminent orientation.

In this connection, the work of Hill (Ref. 38) is interesting with regards to measuring the coefficients of linear expansion along the main axis of monocrystalline mercury when T=113 - 160 deg K.

Experiments were performed with monocrystalline mercury, grown in rod shapes, with various orientations of the central axis of the crystal being relative to the end axis. We found the coefficient of linear expansion along the main axis $\alpha_{||}$ and in the perpendicular direction $\alpha_{\perp}$ according to the dependency of the coefficient of linear expansion on the angle of orientation at a given temperature. The volumetric coefficient of expansion was computed by the equation

$$\alpha \quad \alpha_{||} + 2\alpha_{\perp}$$

Hill's error of measurement of α was not evaluated; the dispersion of experimental points of the leveling curve does not exceed 1%. The available data only allow for dependency $\alpha(T)$ in intervals from 110 deg K to the melting point.

$$\alpha = (13{,}631 - 0{,}047636T + 2{,}5973 \cdot 10^{-4}T^2) \cdot 10^{-5}\ \text{град}^{-1}. \qquad (10)$$

Gruneisen's rule is used in extrapolating α from 110 deg K to absolute zero

$$\Gamma = \frac{\alpha V}{\varkappa_T C_v} = \text{idem}, \qquad (11)$$

which is approximately executed for most solid substances.

In order to compute the value of Gruneisen's constant we must utilize the dependence Cp, K_T, and α and also the equation for the mole volume of mercury recommended by Swenson (Ref. 33)

$$V = (13{,}7873 + 7{,}6473 \cdot 10^{-3}T + 1{,}2498 \cdot 10^{-5}T^2 - \\ - 2{,}9021 \cdot 10^{-8}T^3) \cdot 10^{-3}\ \text{м}^3/\text{кмоль при } T = 0 \div 234°\text{K}. \qquad (12)$$

We obtain Γ = 2.22 with 110 deg K, 2.15 at 130, 2.13 with 150 and 170, 2.17 with 190, 2.24 with 210, and 2.06 at 230.

From these values we can see that Gruneisen's rule for solid mercury is executed with sufficient accuracy. The greatest deviations occur near the melting temperature and are probably due to the formation of "gaps" unused bundles in the crystalline mesh structure. The value of Γ at 110 and 170 deg K differs by about 4%. With temperatures below 110 deg K, the deviation from the rule for Γ = idem for mercury, apparently does not exceed 10 - 15%. In further calculations we utilize the value $\Gamma = \Gamma_{T=110} \approx 2.22$.

We calculated the thermal coefficient of mercury expansion with temperatures below 110 deg K with the aid of the relationship resulting from equation (11)

$$\alpha = 2 \cdot \varkappa_T \cdot C_p \Gamma V^{-1} [1 + (1 + 4\varkappa_T C_p T \Gamma^2 V^{-1})^{1/2}]^{-1}. \qquad (13)$$

In this area, the error of determination for α reaches 15 - 10%. The general passage of $\alpha(T)$ is shown in Fig. 3.

The following indicates the comparison between the true calculated value of α and the calculation for the average magnitude of $\bar{\alpha}$. Grummach's values (Ref. 42) are too low: $\bar{\alpha}(195 \div 234$ deg K$) = 12.3 \cdot 10^{-5}$deg^{-1}. So are these by about 10%: (78÷194 deg K) = $12 \cdot 10^{-5}$ deg^{-1} (Ref. 43). The magnitude $\alpha = 12.8 \cdot 10^{-5}$, according to Gruneisen and Sckell (Ref. 9) coincides with the value $\alpha(80 \div 190$ deg K$) = 13.1 \times 10^{-5}$deg^{-1} from Table 5, within the limit of error.

The electron heat capacity is lower than the crystal lattice in the superconductive condition of mercury (T<4.16 deg K); we don't have to take into account the influence of the electrons on the coefficient of expansion. When T<4.16 deg K in the normal state (in the magnetic field), the elctron heat capacity becomes greater than the lattice, and the influence of electron gas on the coefficient of expansion can predomeinate.

Specific Volume of Solid Mercury

Swenson's data regarding specific volumes of mercury under atmospheric pressure is adequately described by equation (12). However, we are not able to determine the true magnitude of the specimen with various temperatures and pressures by using Swenson's methodology; we only measured the changes in the lengths of the sample. That is why Swenson used the data of other efforts on the capacity of capacity of data points to interpret his own calculations of volumetric changes of mercury.

Swenson took the results of Denitz's calculations executed together with Gruneisen and Sckell as the main data points with an 82 deg K temperature: V (82) = 13.865 cm^3/mole.

Swenson's resulting dependency V(T) agreed satisfactorily with the small amounts of other data about the direct changes in density of solid mercury.

In determining analogous dependencies V(T) for solid mercury, Grosse (Ref. 44) used primarily the basic data regarding density by means of X-ray analysis of mercury crystal and also the data about thermal expansion of solid mercury (Refs. 37 and 38). As data points, he accepted Barrett's data regarding the density of mercury (Ref. 4) that were obtained by X-ray analyses with temperatures of 5 and 78 deg K. Barrett's data corresponded poorly with those of Denitz's measurements, and Grosse's results measure substantially higher than those of direct calculation of mercury's density. Barrett himself acknowledges that this points to a systematic deviation of the data subjected to X-ray analyses. That is only why we may consider Swenson's data (Ref. 33) regarding molar volme of mercury to be more reliable

Conducting a correspondence of Swenson's data on the molar volume of mercury with data concerning thermal expansion and with the value $V(T_{\text{boiling point}})$, it is possible to substantially specify the dependence V(T) by means of the equation

$$V(T) = V(T_{\text{пл}}) \exp \left(\int_{T_{\text{пл}}}^{T} \alpha dT \right). \tag{14}$$

Utilizing the values we obtained for α(T) and the molar volume of mercury at boiling point, and also $V(T_{\text{boiling point}}) = 14.1423 \pm 0.0035$ cm^3/mole, according to Equation (14) we computed the dependence V(T) of solid mercury at all temperature intervals. The intergal is taken graphically. We determine the error V_0:

$$\Delta V(T) \approx V_{\text{пл}} \Delta \left(\int_{T_{\text{пл}}}^{T} \alpha dT \right) + \Delta V_{\text{пл}}(T_{\text{пл}}). \tag{15}$$

In as much as $\int_{T_{\text{пл}}}^{0} \alpha dT \approx -0.025 \pm 0.0025$ (the error α(T) is discussed above) we find that the limit of error of the calculated volume when 0 deg K $\Delta V_0 \approx \pm 0.04$ cm^3/mole or $\delta V_0 \approx \pm 0.3\%$. The experimental data 0 V calculated directly are similarly dispersed. The final molar volume of mercury is $V_0 = 13.786 \pm 0.04$ cm^3/mole at 0 deg K.

By these calculations we can determine heat capacity with a constant volume *Cv*, according to Equation (2)

The relative error

$$\delta C_v \approx \delta C_p + \frac{C_p - C_v}{C_p} \delta (C_p - C_v), \tag{16}$$

where

$$\delta (C_p - C_v) \approx 2\delta\alpha + \delta V + \delta \varkappa_T .$$

Errors in obtaining *Cp*, α, *K*, *V* were indicated earlier. From Table 4 we can see how errors δ*Cp* and δ*(Cp - Cv)* influence the degree of error δ*Cv* given various temperatures.

Table 4 shows the calculated limit of error; the probable error would be smaller.

The adiabatic curve of contractibility of solid mercury is determined by

$$K_S = \varkappa_T \frac{C_v}{C_p}. \tag{17}$$

Here we show the obtained values for the characteristic properties of solid mercury of α-phase when p=1 atm with the indicated accuracy of the determination:

Temperature of melting, T_{BP}..............(234.28 ±0.005) deg K
Molar volume, V^{TB} (T_{BP}).................(14.1423 ±0.0035) cc/mole
Coefficient of thermal expansion, $\alpha(T_{BP})$.(16.728 ±0.5·10^{-}deg ^{1}
Coefficient of isothermal contractibility

$K_S = -1/V(\partial V/\partial p)_S$ when T_{BP}.......(3.336 ±0.4)·$10^{-11}$$m^2$/N

Thermal capacity, C_p (T_{BP})................(28.484 ±0.05)J/(mole·deg)
Thermal capacity, C_v (T_{BP})................(25.95 ±0.5)J/(mole·deg)
Entropy, $S^0_{234.28}$ ....(59.353 ±0.3)J/(mole·deg)

Enthalpy, $|I^0_{234.28} - I^0_{0.1\text{atm}}|$............(5245.1 ±10)J/mole

Temperature of the transition of T_c from
a normal state to superconductive..(4.16 ±0.01) deg K
Change in thermal capacity ΔC_p when T_{BP}..(0.19 ±0.02)·10^{-3}J/(mole·deg)
Molar volume when 0 deg K................(13.786 ±0.04) cc/mole
Gruneisen's constant, $\Gamma = \alpha V/K_T C_v$........2.22 ±0.4
Parameters for a rhombohedral lattice
at 78 deg K.........................a=2.993 Å, α=70 deg 45 min
Temperature of the α-β transition........(79 ±2) deg K

It is expedient to compare the data on the properties of mercury to the results like efforts. The values of heat capacity and enthalpy the the MEI determined are compared with the computed results of Busey , Giauque (Ref. 11) and those in the reference manual (Ref. 10).

The values of enthalpy coincide within the limit of estimated error. In structuring Busey's and Giauque's dependency $C_p(T)$ in areas of low temperature, Pickards and Simon's data (Ref. 20) which are noticeably incorrect, were used, that is why the discrepancy in the values for C_p when the temp is 15 deg K is understandable.

The coefficient for thermal expansion of mercury in interval of 0 to 234 deg K in presented in Grosse's work (Ref. 44) and in the NBE monograph (Ref. 45); a comparison is presented in Table 6.

The NBE data conform adequately in the entire temperature interval. There is considerable disagreement with Grosse's data in the area of extrapolation (T=0 to 100 deg K).

In so far as various data were used as points of departure, our computed molar volumes differed considerably from Grosse's results.

Grosse did not analyze the experimental works critically. On the one hand he probably overestimated the accuracy of the X-ray analysis of solid mercury. On the other hand, in computing the changes of mercury's volume during the liquifaction, Grosse simply averaged the experimental data; however, the work of Bridgman is more reliable. That is why Grosse's data points on the volume of solid mercury at the melting point and at T=0 deg K are doubtful. Table 7 compares the molar volume of mercury that we got from our work and from Grosse's work.

In Table 8 we present the values of heat capacity *Cp*, the caloric properties of solid mercury determined at 1 deg K pacing and their initial differences. Table 9 shows the value of thermal properties of solid mercury *V*, α , K_T, K_S and heat capacity *Cv* mainly distributed by a 10 deg K pace.

Let us make some comment regarding the completion of Tables 8 and 9. We did not level out the values according to differences, but rounded them out by the usual rules of the nine-scale table determined for M-20. Although the table of caloric functions were joined only according to *Cp*, the initial differences in heat capacity *Cp* change regularly only at the joints except in the area of 189 - 193 deg K. There is a noticeable jump of the curved line $\alpha(T)$ (Table 5) in the transition to the extrapolation area according to Gruneisen's rule ($T<110$ deg K)

The recurvature points of heat capacity *Cp* and *Cv* are noticeably displaced. Strangely, the curve of thermal capacity *Cp* and *Cv*(T) (Tables 8 and 9) diminishes near the melting point. In this area the behaviour of the *Cp* and *Cv* line, the aharmonic oscillations of the mesh structure and the effect of vacancy formation is determined. At the melting point, the value of aharmonic insertion into the thermal capacity of mercury is 0.5-1%; they correspond exactly to the mark (sign) in computing different works (Refs. 46 and 47). The effect of gap formations should increase the curvature. It seems natural that, taken as a whole, the curvature near the melting point should increase, at least for the isobaric thermal capacity. We can achieve this by changing the value *Cp* from Table 8. within the limit of error of Busey's and Gianque's experiments ∿0.1%.

The analysis performed indicates that it is necessary to explore anew the properties of solid mercury with greater precision.

We need precise thermal capacity data for α-phase where $T=10-30$ deg K, to explore thermal capacity of β-phase to determine the coefficient of volumetric expansion of mercury when $T<111$ deg K, to investigate the velocity of sound in solid mercury, to establish critical experiments to determine the contractibility at $T\rightarrow 0$, and to determine exactly (with a degree of error less than ±0.2%) the change of volume of mercury when melting. For the sake of expediency, we must also investigate the dispersion of neutrons in solid mercury to determine the spectrum of mesh-structure oscillations.

The authors continue their work toward completing tables of mercury's properties and will gratefully accept any comments concerning this problem

Table 1. Data on basic experimental efforts regarding thermal capacity of solid mercury by the caloric method.

Author	Year	Laboratory	Temp Interval, deg K	No. of Points	Relative error, ΔC_p,%
Pollitser (16)	1911	Physico-Chem. Institute, U of Berlin, Ger.	61-233	17	1.0
Pollitser (17)	1913	ditto	31-168	5	1.0
Simon (18)	1922	ditto	19-232	15	0.5-1.5
Simon (19)	1923	ditto	10-13.4	7	-
Carpenter, Studli (22)	1930	U. of Southhamton, G.B.	197-234	21	
Pichard, Simon(20)	1948	Claerendon Lab.,Oxford	3.5-95		0.5-1.5
Busey, Giauque, (11)	1953	U. of Calif. Berkely	15-234	65	3 at 15 deg K 1 at 20 deg K 0.1 at T 35>deg K
Smith, Wolcott, (21)	1956	Clarendon Lab.,Oxford	1.3-21		-
Van der Hoeven(23)	1964	Purdue Univ, USA	0.35-4.27	54	3.0
Phillips, Lambert, Gardner, (24)	1964	U. of Calif. Berkely	0.1-1.0		3.0

Table 2. Coefficients a_i of polynomials describing the dependency $C_p(T) = \sum^{m} a_i T^i$

i	a_i При $0<T<4.16$	a_i При $4.16<T<60.598$	a_i При $60.598<T<234.28$
−1	0	0	−776,081718
0	0	−1,97926752	47,3654931
1	0	0,750133661	−0,403512788
2	0	$-0,118245093\cdot10^{-1}$	$0,439246578\cdot10^{-2}$
3	$0,275692589\cdot10^{-2}$	$0,486966166\cdot10^{-3}$	$-0,258008613\cdot10^{-4}$
4	$0,202439136\cdot10^{-1}$	$-0,158446718\cdot10^{-4}$	$0,780989701\cdot10^{-7}$
5	$-0,578427214\cdot10^{-1}$	$0,222021301\cdot10^{-6}$	$-0,929902517\cdot10^{-10}$
6	$0,749918233\cdot10^{-1}$	$-0,110524244\cdot10^{-8}$	0
7	$-0,482081354\cdot10^{-1}$	0	0
8	$0,173551546\cdot10^{-1}$	0	0
9	$-0,359854892\cdot10^{-2}$	0	0
10	$0,403751347\cdot10^{-3}$	0	0
11	$-0,190657737\cdot10^{-4}$	0	0

Table 3.Errors in determining the caloric function of solid mercury

T, °K	δC_p, %	S°	ΔS°	$I^\circ - I^\circ_0$	$\Delta(I^\circ - I^\circ_0)$	$(\Phi^\circ - I^\circ_0)$	$\Delta(\Phi^\circ - I^\circ_0)$
		дж/(моль·град) J/(mole·deg)		дж/моль J/mole			
15	3	5,07	0,15	48,6	1,5	27,4	0,8
35	1	15,11	0,25	298,5	4,0	230,5	4,8
234,28	0,1	59,35	0,29	5245,1	8,9	8660,1	59,1

Table 4.

$$\delta C_v = f(\delta C_p,\ \delta\alpha,\ \delta\varkappa_T,\ \delta T)$$

T, °K	δC_p, %	$\delta(C_p - C_v)$, %	$\frac{C_p - C_v}{C_p}$	$\frac{C_p - C_v}{C_p}\delta(C_p - C_v)$, %	δC_v, %
4—15	3	50	0,001	0,05	3
15—35	1	50	0,006	0,3	1,3
35—110	0,1	50	0,024	1,2	1,3
110—170	0,1	16	0,047	0,8	0,9
170—234	0,1	20	0,090	1,8	1,9

Table 5. A comparison of the caloric function of solid mercury

C_p, kJ/(kmole·deg) | $|I - I^c_0|$, kJ/(kmole)

T, °K	C_p, кдж/(кмоль·град), по данным			$\lvert I - I^\circ_0\rvert$, кдж/кмоль, по данным		
	MEI МЭИ	[11]	[10]	MEI МЭИ	[11]	[10]
15	7,61	7,34	7,63	48,6	45,1	—
100	24,26	24,25	24,3	1704	1702	1708
234,28	28,48	24,48	28,5	5245	5240	5230

Table 6. A comparison of the coefficients of thermal expansion

deg

T, °K	$\alpha \cdot 10^{-5}$, град$^{-1}$, по данным		
	MEI МЭИ	Grosse Гроссе [44]	NBS НБЭ [45]
0	0	0	0
10	2,13	0,82	2,1
20	4,65	4,00	4,5
50	9,04	8,70	8,7
100	11,22	11,05	11,1
150	12,33	12,28	12,33
200	14,49	14,00	14,34
234,28	16,73	17,10	17,16

Table 7. A comparison of the molar volume of mercury

V, cm^3/mole,

T, °K	V, см^3/моль, по данным	
	Grosse (44) Гроссе [44]	MEI МЭИ
0	13,8479	13,786
78	13,9314	13,859
100	13,9312	13,892
150	14,0096	13,974
200	14,0930	14,067
234,28	14,1725	14,142

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Table 8. The caloric properties of solid mercury (α-phase) at atmospheric pressure

T, °K	t, °C	c_p, kJ/(kmole·deg)		$i^0-i_0^0$, kJ/kmole		S^0, кдж/(кмоль·град) kJ/(kmole·deg)		$-(\Phi^0-i_0^0)$, kJ/kmole	
0	−273,15	0	6	0	2	0	2	0	0
1	−272,15	0.006	93	0.002	38	0.002	23	0,000	10
2	−271,15	0.099	298	0.040	230	0,025	89	0.010	62
3	−270,15	0,397	501	0,270	633	0.114	179	0.072	196
4	−269,15	0,898	—	0,903	—	0,293	—	0,268	—
4,16$^{(s)}$	−268,99	0,988	—	1,054	—	0,330	—	0,318	—
4,16$^{(n)}$	−268,99	0,968	—	1,054	—	0,330	—	0,318	—
5	−268,15	1,529	655	2,104	1858	0,558	337	0,686	721
6	−267,15	2,184	643	3,962	2506	0,895	385	1,407	1084
7	−266,15	2,827	632	6,468	3144	1,280	419	2,491	1487
8	−265,15	3,459	621	9,612	3771	1,699	443	3,978	1919
9	−264,15	4,080	612	13,383	4387	2,142	462	5,897	2371
10	−263,15	4,692	603	17,770	4994	2,604	475	8,268	2840
11	−262,15	5,295	593	22,764	5592	3,079	486	11,108	3322
12	−261,15	5,588	584	28,356	6182	3,565	495	14,430	3812
13	−260,15	6,472	576	34,538	6760	4,060	501	18,242	4310
14	−259,15	7,048	566	41,298	7332	4,561	506	22,552	4813
15	−258,15	7,614	557	48,630	7894	5,067	509	27,365	5321
16	−257,15	8,171	547	56,524	8445	5,576	511	32,686	5831
17	−256,15	8,718	538	64,969	8988	6,087	514	38,517	6344
18	−255,15	9,256	527	73,957	9521	6,601	515	44,861	6858
19	−254,15	9,783	517	83,478	1043	7,116	515	51,719	7373
20	−253,15	10,300	506	93,521	1055	7,631	515	59,092	7888
21	−252,15	10,806	494	104,07	1106	8,146	514	66,980	8402
22	−251,15	11,300	482	115,13	1154	8,660	513	75,382	8916
23	−250,15	11,782	470	126,67	1202	9,173	511	84,298	9429
24	−249,15	12,252		138,69		9,684		93,727	

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s-superconductive state; n-normal state

Продолжение

T, °K	t, °C	C_p^0, кдж/(кмоль·град)		$H^0-H_0^0$, кдж/кмоль		S^0, кдж/(кмоль·град)		$-(\Phi^0-H_0^0)$, кдж/кмоль	
			457		1248		509		993
25	−248,15	12,709		151,17		10,193		103,66	
			444		1293		507		1045
26	−247,15	13,153		164,10		10,700		114,11	
			431		1337		505		1095
27	−246,15	13,584		177,47		11,205		125,06	
			418		1379		502		1146
28	−245,15	14,002		191,26		11,707		136,52	
			403		1421		498		1196
29	−244,15	14,405		205,47		12,205		148,48	
			390		1460		495		1245
30	−243,15	14,795		220,07		12,700		160,93	
			375		1498		491		1295
31	−242,15	15,170		235,05		13,191		173,88	
			362		1536		488		1343
32	−241,15	15,532		250,41		13,679		187,31	
			347		1570		483		1392
33	−240,15	15,879		266,11		14,162		201,23	
			333		1605		479		1440
34	−239,15	16,212		282,16		14,641		215,63	
			320		1638		475		1488
35	−238,15	16,532		298,54		15,116		230,51	
			306		1668		470		1535
36	−237,15	16,838		315,22		15,586		245,86	
			292		1699		465		1582
37	−236,15	17,130		332,21		16,051		261,68	
			279		1727		461		1628
38	−235,15	17,409		349,48		16,512		277,96	
			267		1754		455		1674
39	−234,15	17,676		367,02		16,967		294,70	
			254		1780		451		1720
40	−233,15	17,930		384,82		17,418		311,90	
			243		1806		446		1764
41	−232,15	18,173		402,88		17,864		329,54	
			232		1829		441		1808
42	−231,15	18,405		421,17		18,305		347,62	
			221		1851		435		1853
43	−230,15	18,626		439,68		18,740		366,15	
			211		1873		431		1895
44	−229,15	18,837		458,41		19,171		385,10	
			202		1894		425		1938
45	−228,15	19,039		477,35		19,596		404,48	
			193		1914		421		1981
46	−227,15	19,232		496,49		20,017		424,29	
			186		1933		416		2023
47	−226,15	19,418		515,82		20,433		444,52	
			178		1950		410		2064
48	−225,15	19,596		535,32		20,843		465,16	
			173		1968		406		2104
49	−224,15	19,769		555,00		21,249		486,20	
			166		1986		401		2145
50	−223,15	19,935		574,86		21,650		507,65	
			162		2001		396		2185
51	−222,15	20,097		594,87		22,046		529,50	
			156		2018		392		2224
52	−221,15	20,253		615,05		22,438		551,74	
			153		2033		387		2263
53	−220,15	20,406		635,38		22,825		574,37	
			149		2048		383		2302
54	−219,15	20,555		655,86		23,208		597,39	

T, °K	t, °C
55	−218,1
56	−217,1
57	−216,1
58	−215,1
59	−214,1
60	−213,1
61	−212,1
62	−211,
63	−210,
64	−209,
65	−208,
66	−207
67	−206
68	−20
69	−20
70	−20
71	−20
72	−20
73	−2
74	−
75	−
76	−
77	−
78	−
79	−
80	−
81	−
82	−
83	−
84	−

Продолжение

T, °K	t, °C	C_p, кдж/(кмоль·град)		$I^\circ - I_0^0$, кдж/кмоль		S°, кдж/(кмоль·град)		$-(\Phi^\circ - I_0^0)$, кдж/кмоль	
			147		2063		379		2340
55	—218,15	20,702		676,49		23,587		620,79	
			144		2077		374		2378
56	—217,15	20,816		697,26		23,961		644,57	
			141		2092		370		2414
57	—216,15	20,987		718,18		24,331		668,71	
			138		2106		367		2452
58	—215,15	21,125		739,24		24,698		693,23	
			136		2119		362		2488
59	—214,15	21,261		760,43		25,060		718,11	
			133		2133		358		2524
60	—213,15	21,394		781,76		25,418		743,35	
			125		2145		355		2559
61	—212,15	21,519		803,21		25,773		768,94	
			116		2158		351		2595
62	—211,15	21,635		824,79		26,124		794,89	
			111		2169		347		2630
63	—210,15	21,746		846,48		26,471		821,19	
			107		2180		343		2664
64	—209,15	21,853		868,28		26,814		847,83	
			103		2191		340		2699
65	—208,15	21,956		890,19		27,154		874,82	
			100		2200		336		2732
66	—207,15	22,056		912,19		27,490		902,14	
			97		2211		332		2765
67	—206,15	22,153		934,30		27,822		929,79	
			93		2220		329		2799
68	—205,15	22,246		956,50		28,151		957,78	
			91		2229		326		2832
69	—204,15	22,337		978,79		28,477		986,10	
			88		224		322		286
70	—203,15	22,425		1001,2		28,799		1014,7	
			85		224		318		290
71	—202,15	22,510		1023,6		29,117		1043,7	
			83		226		316		293
72	—201,15	22,593		1046,2		29,433		1073,0	
			80		226		312		296
73	—200,15	22,673		1068,8		29,745		1102,6	
			79		227		309		299
74	—199,15	22,752		1091,5		30,054		1132,5	
			76		228		306		302
75	—198,15	22,828		1114,3		30,360		1162,7	
			74		229		303		305
76	—197,15	22,902		1137,2		30,663		1193,2	
			72		229		300		308
77	—196,15	22,974		1160,1		30,963		1224,0	
			70		230		296		311
78	—195,15	23,044		1183,1		31,259		1255,1	
			68		231		294		314
79	—194,15	23,112		1206,2		31,553		1286,5	
			67		232		291		317
80	—193,15	23,179		1229,4		31,844		1318,2	
			66		232		288		320
81	—192,15	24,245		1252,6		32,132		1350,2	
			64		233		286		323
82	—191,15	23,309		1275,9		32,418		1382,5	
			62		233		283		325
83	—190,15	23,371		1299,2		32,701		1415,0	
			61		234		280		329
84	—189,15	23,432		1322,6		32,981		1447,9	

Продолжение

T, °K	t, °C	C_p, кдж/(кмоль·град)	$I^0-I_0^0$, кдж/кмоль	S^0, кдж/(кмоль·град)	$-(\Phi^0-I_0^0)$, кдж/кмоль
		59	235	278	331
85	—188,15	23,491	1346,1	33,259	1481,0
		59	235	275	334
86	—187,15	23,550	1369,6	33,534	1514,4
		57	236	273	337
87	—186,15	23,607	1393,2	33,807	1548,1
		56	236	270	339
88	—185,15	23,663	1416,8	34,077	1582,0
		55	237	268	342
89	—184,15	23,718	1440,5	34,345	1616,2
		53	237	265	345
90	—183,15	23,771	1464,2	34,610	1650,7
		53	238	263	347
91	—182,15	23,824	1488,0	34,873	1685,4
		52	239	261	350
92	—181,15	23,876	1511,9	35,134	1720,4
		50	239	258	353
93	—180,15	23,926	1535,8	35,392	1755,7
		50	239	256	355
94	—179,15	23,976	1559,7	35,648	1791,2
		49	240	254	358
95	—178,15	24,025	1583,7	35,902	1827,0
		48	241	252	360
96	—177,15	24,073	1607,8	36,154	1863,0
		47	241	250	363
97	—176,15	24,120	1631,9	36,404	1899,3
		47	241	247	365
98	—175,15	24,167	1656,0	36,651	1935,8
		45	242	246	368
99	—174,15	24,212	1680,2	36,897	1972,6
		45	242	244	370
100	—173,15	24,257	1704,4	37,141	2009,6
		44	243	241	373
101	—172,15	24,301	1728,7	37,382	2046,9
		44	243	240	375
102	—171,15	24,345	1753,0	37,622	2084,4
		42	244	238	377
103	—170,15	24,387	1777,4	37,860	2122,1
		42	244	235	380
104	—169,15	24,429	1801,8	38,095	2160,1
		42	245	234	382
105	—168,15	24,471	1826,3	38,329	2198,3
		41	245	233	385
106	—167,15	24,512	1850,8	38,562	2236,8
		40	245	230	386
107	—166,15	24,552	1875,3	38,792	2275,4
		39	246	228	389
108	—165,15	24,591	1899,9	39,020	2314,3
		39	246	227	392
109	—164,15	24,630	1924,5	39,247	2353,5
		38	246	225	393
110	—163,15	24,668	1949,1	39,472	2392,8
		38	247	224	396
111	—162,15	24,706	1973,8	39,696	2432,4
		38	247	222	398
112	—161,15	24,744	1998,5	39,918	2472,2
		37	248	220	401
113	—160,15	24,781	2023,3	40,138	2512,3
		36	248	218	402
114	—159,15	24,817	2048,1	40,356	2552,5

T, °K	t, °C
115	—158,1
116	—157,1
117	—156,1
118	—155,1
119	—154,
120	—153,
121	—152,
122	—15
123	—15
124	—14
125	—1
126	—1
127	—1
128	—1
129	—
130	—
131	—
132	—
133	—
134	—
135	—
136	—
137	—
138	—
139	—
140	—
141	—
142	—
143	—
144	—

$-(\Phi^\circ-I_0^0)$, …ж/кмоль	
	331
.0	334
.4	337
.1	339
.0	342
.2	345
.7	347
.4	350
.4	353
.7	355
.2	358
.0	360
3.0	363
9.3	365
.8	368
2.6	370
9.6	373
6.9	375
4.4	377
2.1	380
0.1	382
8.3	385
6.8	386
5.4	389
4.3	392
3.5	393
2.8	396
2.4	398
2.2	401
2.3	402
2.5	

Продолжение

T, °K	t, °C	C_p°, кдж/(кмоль·град)		$I^\circ-I_0^0$, кдж/кмоль		S°, кдж/(кмоль·град)		$-(\Phi^\circ-I_0^0)$, кдж/кмоль	
115	—158,15	24,853	36	2072,9	248	40,573	217	2593,0	405
116	—157,15	24,888	35	2097,8	249	40,788	215	2633,7	407
117	—156,15	24,923	35	2122,7	249	41,002	214	2674,5	408
118	—155,15	24,957	34	2147,6	249	41,214	212	2715,6	411
119	—154,15	24,991	34	2172,6	250	41,425	211	2757,0	414
120	—153,15	25,025	34	2197,6	250	41,634	209	2798,5	415
121	—152,15	25,058	33	2222,6	250	41,842	208	2840,2	417
122	—151,15	25,091	33	2247,7	251	42,049	207	2882,1	419
123	—150,15	25,123	32	2272,8	251	42,254	205	2924,3	422
124	—149,15	25,155	32	2298,0	252	42,457	203	2966,7	424
125	—148,15	25,187	32	2323,2	252	42,659	202	3009,3	426
126	—147,15	25,218	31	2348,4	252	42,860	201	3052,0	427
127	—146,15	25,249	31	2373,6	252	43,060	200	3095,0	430
128	—145,15	25,280	31	2398,9	253	43,258	198	3138,1	431
129	—144,15	25,310	30	2424,2	253	43,455	197	3181,5	434
130	—143,15	25,340	30	2449,5	253	43,650	195	3225,0	435
131	—142,15	25,370	30	2474,8	253	43,844	194	3268,8	438
132	—141,15	25,400	30	2500,2	254	44,038	194	3312,7	439
133	—140,15	25,429	29	2525,6	254	44,229	191	3356,9	442
134	—139,15	25,458	29	2551,0	254	44,420	191	3401,2	443
135	—138,15	25,487	29	2576,5	255	44,609	189	3445,7	445
136	—137,15	25,515	28	2602,0	255	44,797	188	3490,4	447
137	—136,15	25,543	28	2627,5	255	44,984	187	3535,3	449
138	—135,15	25,571	28	2653,1	256	45,170	186	3580,4	451
139	—134,15	25,599	28	2678,7	256	45,355	185	3625,6	452
140	—133,15	25,627	28	2704,3	256	45,539	184	3671,1	455
141	—132,15	25,654	27	2729,9	256	45,721	182	3716,7	456
142	—131,15	25,681	27	2755,6	257	45,903	182	3762,5	458
143	—130,15	25,708	27	2781,3	257	46,083	180	3808,5	460
144	—129,15	25,735	27	2807,0	257	46,262	179	3854,7	462

Продолжение

T, °K	t, °C	C_p, кдж/(кмоль·град)		$I^0-I_0^0$, кдж/кмоль		S^0, кдж/(кмоль·град)		$-(\Phi^0-I_0^0)$, кдж/кмоль	
145	—128,15	25,762	27	2832,8	258	46,410	178	3901,0	463
146	—127,15	25,789	27	2858,6	258	46,617	177	3947,6	466
147	—126,15	25,815	26	2884,4	258	46,794	177	3994,3	467
148	—125,15	25,841	26	2910.2	258	46,969	175	4041,2	469
149	—124,15	25,867	26	2936,0	258	47,143	174	4088,2	470
150	—123,15	25,893	26	2951,9	259	47,316	173	4135,4	472
151	—122,15	25,929	26	2987,8	259	47,488	172	4182,8	474
152	—121,15	25,945	26	3013.7	259	47,659	171	4230,4	476
153	—120,15	25,971	26	3039,7	260	47,829	170	4278,2	478
154	—119,15	25,997	26	3065,7	260	47,999	170	4326,1	479
155	—118,15	26,023	26	3091,7	260	48,167	168	4374,2	481
156	—117,15	26,049	26	3117,7	260	48,334	167	4422,4	482
157	—116,15	26,075	26	3143,8	261	48,501	167	4470,8	484
158	—115,15	26,100	25	3169,9	261	48,666	165	4519,4	486
159	—114,15	26,126	26	3196,0	261	48,831	165	4568,2	488
160	—113,15	26,152	26	3222,1	261	48,995	164	4617,1	489
161	—112,15	26,178	26	3248,3	262	49,158	163	4666,2	491
162	—111,15	26,203	25	3274,5	262	49,320	162	4715,4	492
163	—110,15	26,229	26	3300,7	262	49,482	162	4764,8	494
164	—109,15	26,255	26	3326,9	262	49,642	160	4814,4	496
165	—108,15	26,281	26	3353,2	263	49,802	160	4864,1	497
166	—107,15	26,307	26	3379,5	263	49,961	159	4914,0	499
167	—106,15	26,333	26	3405,8	263	50,119	158	4964,0	500
168	—105,15	26,359	26	3432,2	264	50,276	157	5014,2	502
169	—104,15	26,385	26	3458,6	264	50,433	157	5064,6	504
170	—103,15	26,412	27	3465,0	264	50,589	156	5115,1	505
171	—102,15	26,438	26	3511,4	264	50,744	155	5165,7	506
172	—101,15	26,464	26	3537,8	264	50,898	154	5216,5	508
173	—100,15	26,491	27	3564,3	265	51,051	153	5267,5	510
174	— 99,15	26,518	27	3590,8	265	51,204	153	5318,6	511

T, °K	t, °C
175	—98,15
176	—97,15
177	—96,15
178	—95,15
179	—94,15
180	—93,15
181	—92,15
182	—91,15
183	—90,15
184	—89,15
185	—88,15
186	—87,15
187	—86,15
188	—85,15
189	—84,15
190	—83,15
191	—82,15
192	—81,15
193	—80,15
194	—79,1
195	—78,1
196	—77,
197	—76,1
198	—75,1
199	—74,
200	—73.
201	—72.
202	—71.
203	—70.
204	—

$-(\Phi^*-I_0^0)$, кдж/кмоль	
3901,0	463
3947,6	466
3994,3	467
4041,2	469
4088,2	470
4135,4	472
4182,8	474
4230,4	476
4278,2	478
4326,1	479
4374,2	481
4422,4	482
4470,8	484
4519,4	486
4568,2	488
4617,1	489
4666,2	491
4715,4	492
4764,8	494
4814,4	496
4864,1	497
4914,0	499
4964,0	500
5014,2	502
5064,6	504
5115,1	505
5165,7	506
5216,5	508
5267,5	510
5318,6	511

Продолжение

T, °K	t, °C	C_p, кдж/(кмоль·град)		$I^\circ-I_0^0$, кдж/кмоль		S°, кдж/(кмоль·град)		$-(\Phi^*-I_0^0)$, кдж/кмоль	
175	−98,15	26,544	26	3617,3	265	51,356	152	5369,9	513
176	−97,15	26,571	27	3643,9	266	51,507	151	5421,4	515
177	−96,15	26,699	28	3670,5	266	51,658	151	5473,0	516
178	−95,15	26,626	27	3697,1	266	51,808	150	5524,7	517
179	−94,15	26,653	27	3723,7	266	51,957	149	5576,6	519
180	−93,15	26,681	28	3750,4	267	52,106	149	5628,6	520
181	−92,15	26,709	28	3777,1	267	52,254	148	5680,8	522
182	−91,15	26,737	28	3803,8	267	52,401	147	5733,1	523
183	−90,15	26,765	28	3830,6	268	52,547	146	5785,6	525
184	−89,15	26,793	28	3857,4	268	52,693	146	5838,2	526
185	−88,15	26,821	28	3884,2	268	52,838	145	5891,0	528
186	−87,15	26,850	29	3911,0	268	52,983	145	5943,9	529
187	−86,15	26,879	29	3937,9	269	53,127	144	5996,9	530
188	−85,15	26,908	29	3964,8	269	53,271	144	6050,1	532
189	−84,15	26,937	29	3991,7	269	53,414	143	6103,4	533
190	−83,15	26,967	30	4018,7	270	53,556	142	6156,9	535
191	−82,15	26,997	30	4045,7	270	53,698	142	6210,5	536
192	−81,15	27,027	30	4072,7	270	53,839	141	6264,3	538
193	−80,15	27,057	30	4099,7	270	53,979	140	6318,2	539
194	−79,15	27,088	31	4126,8	271	54,119	140	6372,3	541
195	−78,15	27,119	31	4153,9	271	54,258	139	6426,5	542
196	−77,15	27,150	31	4181,0	271	54,397	139	6480,8	543
197	−76,15	27,181	31	4208,2	272	54,535	138	6535,3	545
198	−75,15	27,212	31	4235,4	272	54,673	138	6589,9	546
199	−74,15	27,244	32	4262,6	272	54,810	137	6644,6	547
200	−73,15	27,276	32	4289,8	272	54,947	137	6699,5	549
201	−72,15	27,308	32	4317,1	273	55,083	136	6754,5	550
202	−71,15	27,340	32	4344,4	273	55,219	136	6809,7	552
203	−70,15	27,373	33	4371,8	274	55,354	135	6865,0	553
204	−69,15	27,406	33	4399,2	274	55,488	134	6920,4	554

Продолжение

T, °K	t, °C	C_p, кдж/(кмоль·град)		$H^\circ - H_0^\circ$, кдж/кмоль		S°, кдж/(кмоль·град)		$-(\Phi^\circ - H_0^\circ)$, кдж/кмоль	
205	−68,15	27,439	33	4426,6	274	55,622	134	6975,9	555
206	−67,15	27,472	33	4454,1	275	55,756	134	7031,6	557
207	−66,15	27,506	34	4481,6	275	55,889	133	7087,4	558
208	−65,15	27,540	34	4509,1	275	56,022	133	7143,4	560
209	−64,15	27,574	34	4536,7	276	56,154	132	7199,5	561
210	−63,15	27,608	34	4564,3	276	56,286	132	7255,7	562
211	−62,15	27,642	34	4591,9	276	56,417	131	7312,1	564
212	−61,15	27,677	35	4619,5	276	56,548	131	7368,6	565
213	−60,15	27,712	35	4647,2	277	56,678	130	7425,2	566
214	−59,15	27,747	35	4674,9	277	56,808	130	7481,9	567
215	−58,15	27,782	35	4702,7	278	56,937	129	7538,8	569
216	−57,15	27,817	35	4730,5	278	57,066	129	7595,8	570
217	−56,15	27,853	36	4758,3	278	57,195	129	7652,9	571
218	−55,15	27,889	36	4786,2	279	57,323	128	7710,2	573
219	−54,15	27,925	36	4814,1	279	57,451	128	7767,6	574
220	−53,15	27,961	36	4842,0	279	57,578	127	7825,1	575
221	−52,15	27,997	36	4870,0	280	57,705	127	7882,7	576
222	−51,15	28,033	36	4898,0	280	57,831	126	7940,5	578
223	−50,15	28,070	37	4926,1	281	57,957	126	7998,4	579
224	−49,15	28,106	36	4954,2	281	58,083	126	8056,4	580
225	−48,15	28,143	37	4982,3	281	58,208	125	8114,5	581
226	−47,15	28,179	36	5010,5	282	58,333	125	8172,8	583
227	−46,15	28,216	37	5038,7	282	58,458	125	8231,2	584
228	−45,14	28,253	37	5066,9	282	58,582	124	8289,7	585
229	−44,15	28,290	37	5095,2	283	58,706	124	8348,3	586
230	−43,15	28,327	37	5123,5	283	58,829	123	8407,1	588
231	−42,15	28,364	37	5151,8	283	58,952	123	8466,0	589
232	−41,15	28,401	37	5180,2	284	59,074	122	8525,0	590
233	−40,15	28,437	36	5208,6	284	59,196	122	8584,1	591
234	−39,15	28,474	37	5237,1	285	59,318	122	8643,4	593
234,28	−38,87	28,484	10	5245,1	80	59,353	35	8660,1	167

табл. 9) уменьшаетс
линий C_p и C_v опре
шетки и эффектом
оценки вклада ан

**Термодинамические сво
от 0°K до точки плавлен**

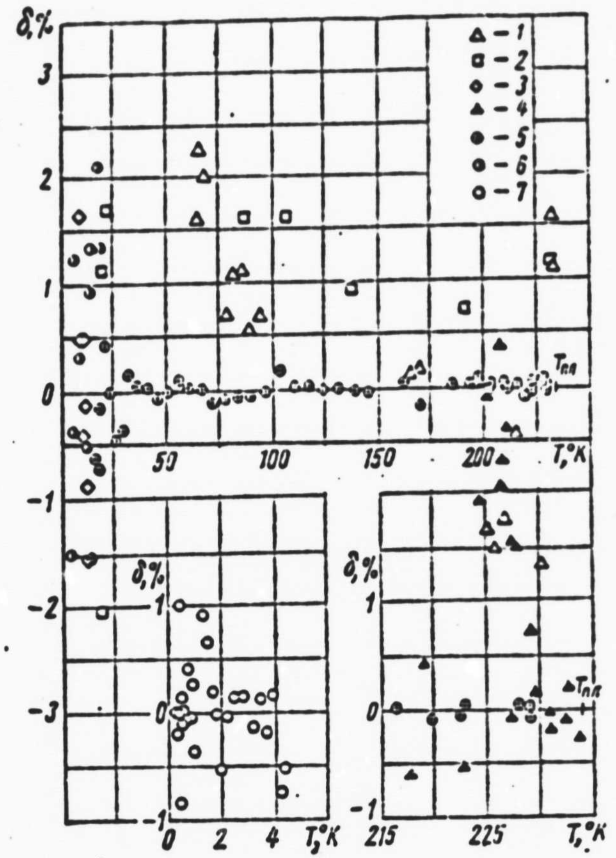
T, °K	[illegible]	[illegible]
0	13,786	2,
5	13,786	2,
10	13,787	2,
20	13,791	2,
30	13,799	2,
40	13,809	2,
50	13,821	2,
60	13,834	2,
70	13,848	2,
80	13,862	2,
90	13,877	2,
100	13,892	2,
110	13,908	2,
120	13,924	3,
130	13,940	3,
140	13,957	3,
150	13,974	3,
160	13,992	3,
170	14,010	3,
180	14,028	3,
190	14,047	3,
200	14,067	3,
210	14,088	3,
220	14,110	3,
230	14,132	[illegible]
234,28	14,142	[illegible]

±0,2%) изменен
довать рассеян
колебаний реше
Авторы про
с благодарност

1. Вукало
1000°C и давлен

Table 9. Thermodynamic properties of solid mercury (alpha-phase) from 0 deg K to melting point at atmospheric pressure

T, °K	$V \cdot 10^3$, м³/кмоль	$\varkappa_T \cdot 10^{11}$, м²/н	$\alpha \cdot 10^{-5}$, град$^{-1}$	C_p, кдж/(кмоль · град)	$\varkappa_S \cdot 10^{11}$, м²/н
0	13,786	2,807	0	0	2,807
5	13.786	2,807	0,692	1,529	2,807
10	13.787	2,809	2.123	4,690	2,807
20	13,791	2,813	4,660	10,279	2,808
30	13,799	2,821	6,693	14,729	2,808
40	13,809	2,832	8,115	17,802	2,812
50	13,821	2,846	9,035	19,737	2,818
60	13,834	2,863	9,718	21,120	2,826
70	13,848	2,883	10,219	22,074	2,838
80	13,862	2,907	10,606	22,750	2,853
90	13,877	2,933	10,931	23,263	2,871
100	13,892	2,963	11,220	23,667	2,891
110	13,908	2,995	11,486	23,995	2,915
120	13,924	3.031	11,656	24,276	2,940
130	13,940	3.070	11,829	24,514	2.970
140	13,957	3,112	12,054	24,714	3,001
150	13,974	3,157	12,330	24,883	3,034
160	13,992	3,205	12,659	25,032	3,068
170	14,010	3,257	13,040	25,167	3,103
180	14,028	3,311	13,473	25.296	3.139
190	14,047	3.369	13,957	25,423	3,175
200	14,067	3,429	14,494	25,552	3,212
210	14,088	3,493	15,082	25,681	3,249
220	14,110	3,560	15,723	25,806	3,286
230	14,132	3,630	16,415	25,917	3,322
234,28	14,142	3,661	16,728	25,956	3,336



$$\delta = \frac{C_p^{\text{оп}} - C_p^{\text{расч}}}{C_p^{\text{расч}}} \cdot 100\%$$

Fig. 1. Deviation of the experimental data obtained by various authors fbom an approximated dependence $C_p(T)$: 1-Pollitser's data (16 and 17), 2-Simon 1922 (18), 3-Simon, 1923 (19), 4-Carpenter and Studli (22), 5-Busey and Guaugua (11), 6-Smith and Wolcott (21), 7 Van der Hoven and P. Keezom (23)

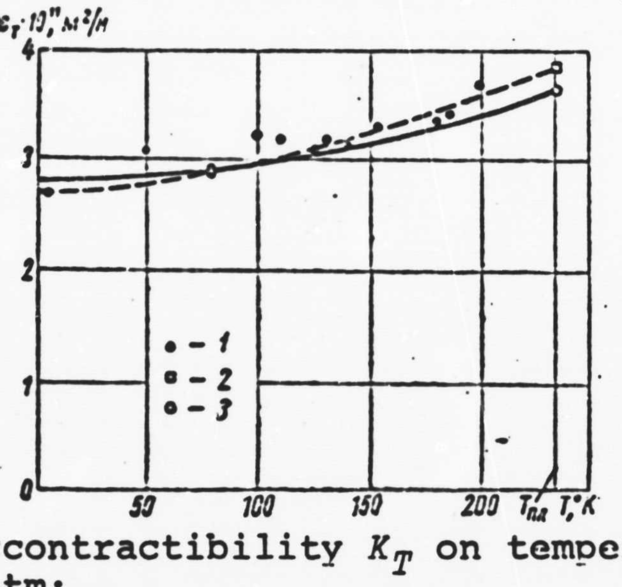


Fig. 2. Dependence of isothermiccontractibility K_T on temperature at normal pressure p=1 atm: 1-Swenson's test data (33), 2-the value K_T^J at T_{BP} obtained by extrapolation of Pena's test data (40), the value K_T^{TB} T_{BP} computed by equation 7, dahed - dependence described by Swenson's data.

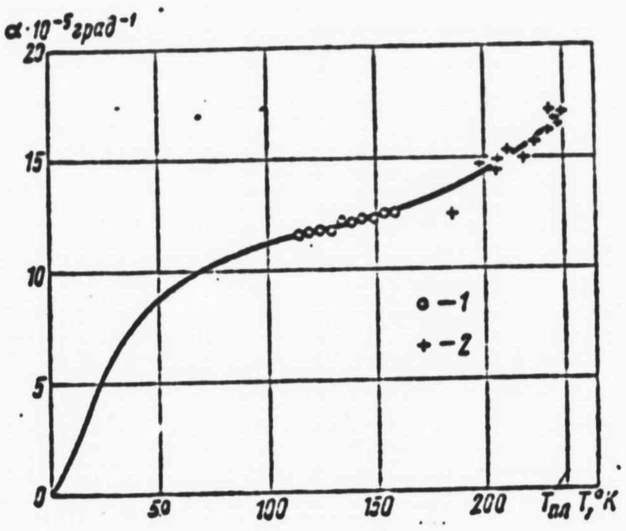
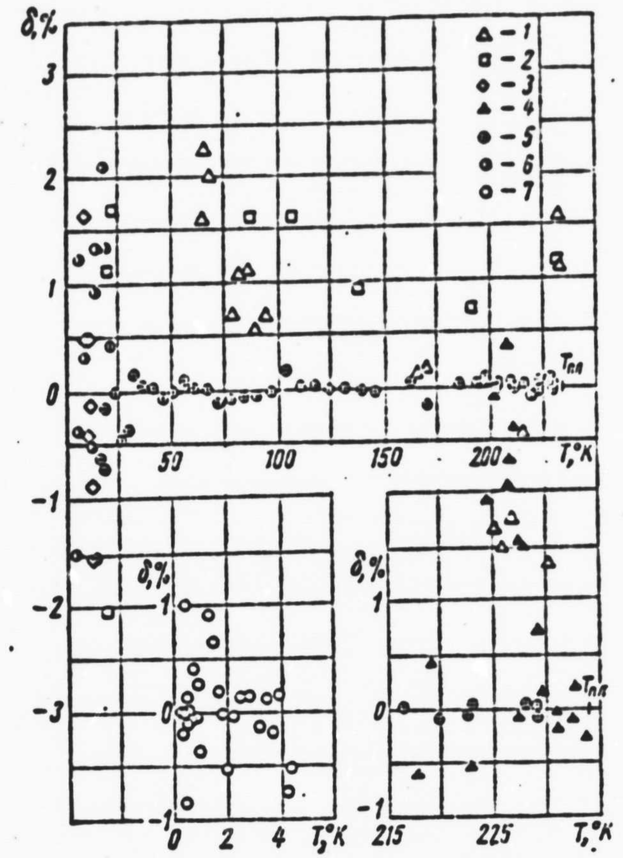


Fig. 3. The dependence of the coefficient for thermal expansion α on temperature at normal pressure p=1 atm. 1-Carpenter and Oukli's test data, 2- Hill's (38)



$$\delta = \frac{C_p^{\text{оп}} - C_p^{\text{расч}}}{C_p^{\text{расч}}} \cdot 100\%$$

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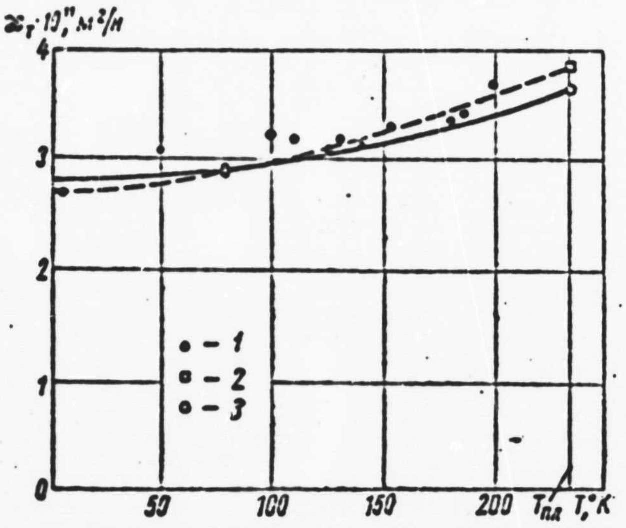

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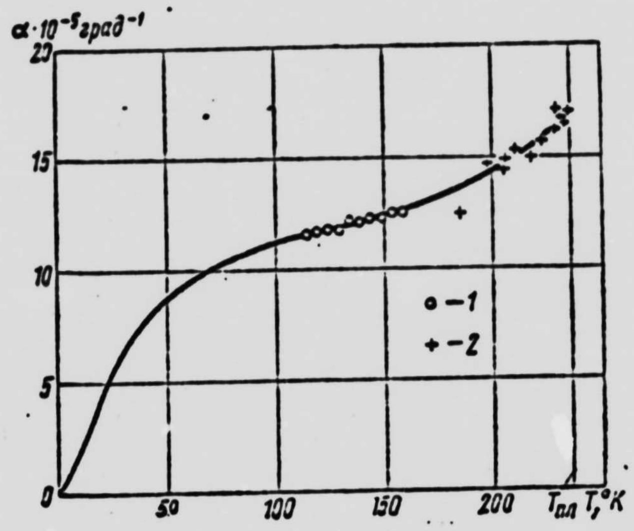

Fig. 3. The dependence of the coefficient for thermal expansion α on temperature at normal pressure p=1 atm. 1-Carpenter and Oukli's test data, 2- Hill's (38)

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