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ТЕПЛОФИЗИЧЕСКИЕ ХАРАКТЕРИСТИКИ ВЕЩЕСТВ

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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, $a/c=\sqrt{2}$ 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 consideration 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 non-additivity 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), Bærschall (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 ±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 $\leq$ 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

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

where

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

Einstein's formation for harmonic oscillators and

$$\varphi(\nu) -$$

is the function of mesh oscillation depending on frequency. The function $\varphi(\nu)$ 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 $\varphi(\nu)$ 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 compu r.

In the multiple-term selection process the areas overlapped, with the exception of joint with Tc, 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_σ, in various sources, oscillated from 4,153 (Ref.7) to 4,167 deg K (Ref.30). We took the average value of T_σ=(4.16 ± 0.01) deg K.

Here are the approximating multiple terms

$$C_p(T) = \sum_{i}^{m} a_i T^i. \qquad (5)$$

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_o=760$mm\ Hg$.

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

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 $\delta(S-S_o) = \delta(I-I_o) \approx 3\%$, in interval 15-35 deg K $\sim 1\%$, and in interval 35 - melting point $\sim 0.1\%$. 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 $\Delta (I^o-I^o_o)$, are presented in table 3.

In this way the limiting relative degree of error of determining entropy with melting point $\sim 0.5\%$, and consequently the degree of error of entropy $\sim 0.1\%$ 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 $S_{o,\alpha} = S_{o,z} = 0$. 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 $\overline{\theta}_\alpha = 97$ deg K and $\overline{\theta}_\beta = 118$ 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 $_x t=3.16\cdot10^{-11}$ 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 $T\to0\frac{dK_T}{d_T}\to0$;

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

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

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 $\Delta C_p=C_p^{\prime}-C_p^{TB}=0$ are within the limit of error.

In extrapolating the data of Bigg (Ref. 35), at the melting point of mercury, we get $V^{\prime}$=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 $\alpha^{\prime}_{234,3}=(18.1\pm0.02)\cdot10^{-5}\text{deg}^{-1}$.

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

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

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

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

By utilizing the listed data with the help of Eq. 8, we can find $K_{2\,3\,4\,.\,3}^{TB}=(3.66 \pm 0.4)\cdot 10^{-11}$ m^2/N.

We prefer this value of contractibility even though it makes many assumptions recommended by Swenson (Ref 33) who found $K_{2\,3\,4\,.\,3}^{TB}=(3.82 \pm 0.02)\cdot 10^{-11}$ m^2/N in extrapolating his data to the melting point - this is close to $K_{2\,3\,4\,.\,3}^{\vartheta}$ 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 $K_{2\,3\,4\,.\,3}^{TB}$ gives us an acceptable dependability within a limit of error of ±10%

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

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 $\delta\alpha\leq 3\%$.

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.

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

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)

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

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 α. Grummach's values (Ref. 42) are too low: $\overline{\alpha}(195 \div 234 \text{ deg K}) = 12.3 \cdot 10^{-5} \text{deg}^{-1}$. So are these by about 10%: $(78 \mp 194 \text{ deg K}) = 12 \cdot 10^{-5} \text{ deg}^{-1}$ (Ref. 43). The magnitude $\alpha = 12.8 \cdot 10^{-5}$, according to Gruneisen and Sckell (Ref. 9) coincides with the value $\alpha(80 \div 190 \text{ deg K}) = 13.1 \times 10^{-5} \text{deg}^{-1}$ 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: $V(82) = 13.865 \text{ cm}^3/\text{mole}$.

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

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

Utilizing the values we obtained for $\alpha(T)$ 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_o:

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

In as much as $\int_{T_{\text{n.a}}}^{0} \alpha dT \approx -0.025 \pm 0.0025$ (the error $\alpha(T)$ 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

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

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 δCp and $\delta(Cp - Cv)$ influence the degree of error δCv 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

$$K_S = \varkappa_T \frac{C_v}{C_p}. \qquad (17)$$

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^{-3}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, Cp (T_{BP}).....(28.484 ±0.05)J/(mole·deg)
Thermal capacity, Cv (T_{BP}).....(25.95 ±0.5)J/(mole·deg)
Entropy, $S^0_{234.28}$ .....(59.353 ±0.3)J/(mole·deg)
Enthalpy, $|I^0_{234.28} - I^0_{0.1atm}|$.....(5245.1 ±10)J/mole
Temperature of the transition of Tc from a normal state to superconductive..(4.16 ±0.01) deg K
Change in thermal capacity ΔCp 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, $\Gamma = \alpha V/K_T Cv$.....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 $Cp(T)$ 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 Cp 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 α(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 $\sim$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$\to$0, and to determine exactly (with a degree of error less than $\pm$0.2%) the change of volume of mercury when melting. For the sake of expediency, we must alsc 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, ΔCp, %
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 South-hamton, 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	При $0<T<4.16$	При $4.16<T<60.398$	При $60.398<T<234.28$
−1	0	0	−770,081718
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	$-0,578127214\cdot10^{-1}$	$0,222021301\cdot10^{-6}$	$-0,929902517\cdot10^{-10}$
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^0	ΔS^0	$I^0-I_0^0$	$\Delta(I^0-I_0^0)$	$(\Phi^0-I_0^0)$	$\Delta(\Phi^0-I_0^0)$
		Дж/(кмоль·град)		Дж/кмоль			
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	3660,1	59,1

Table 4.

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

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

T, °K	C_p, кДж/(кмоль·град), по данным			$I-I_0^0$, кДж/кмоль, по данным		
	МЭИ	[11]	[10]	МЭИ	[11]	[10]
15	7,61	7,34	7,63	48,6	45,1	—
100	24,26	24,25	24,3	1704	1702	1705
234,28	28,48	24,48	28,5	5245	5240	5230

Table 6. A comparison of the coefficients of thermal expansion

T, °K	$\alpha \cdot 10^{-5}$, $град^{-1}$, по данным		
	МЭИ	Гроссе [4]	НБЭ [5]
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

T, °K	V, $см^3$/моль, по данным	
	Гроссе [4]	МЭИ
0	13,8179	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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Таблица 8

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)		$-(\Phi^0-I_0^0)$, 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	

s-superconductive state; n-normal state

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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
25	−248,15	12,709	151,17	10,193	103,66
		457	1248	509	993
26	−247,15	13,153	164,10	10,700	114,11
		444	1293	507	1045
27	−246,15	13,584	177,47	11,205	125,06
		431	1337	505	1095
28	−245,15	14,002	191,26	11,707	136,52
		418	1379	502	1146
29	−244,15	14,405	205,47	12,205	148,48
		403	1421	498	1196
30	−243,15	14,795	220,07	12,700	160,93
		390	1460	495	1245
31	−242,15	15,170	235,05	13,191	173,88
		375	1498	491	1295
32	−241,15	15,532	250,41	13,679	187,31
		362	1536	488	1343
33	−240,15	15,879	266,1[illegible]	14,162	201,23
		347	1570	483	1392
34	−239,15	16,212	282,16	14,641	215,63
		333	1605	479	1410
35	−238,15	16,532	298,54	15,116	230,51
		320	1638	475	1488
36	−237,15	16,838	315,22	15,586	245,86
		306	1663	470	1535
37	−236,15	17,130	332,21	16,051	261,68
		292	1699	465	1582
38	−235,15	17,409	349,48	16,512	277,96
		279	1727	461	1628
39	−234,15	17,676	367,02	16,967	294,70
		267	1754	455	1674
40	−233,15	17,930	384,82	17,418	311,90
		254	1780	451	1720
41	−232,15	18,173	402,88	17,864	329,54
		243	1806	446	1764
42	−231,15	18,405	421,17	18,305	347,62
		232	1829	441	1808
43	−230,15	18,626	439,68	18,740	366,15
		221	1851	435	1853
44	−229,15	18,837	458,41	19,171	385,10
		211	1873	431	1895
45	−228,15	19,039	477,35	19,596	404,48
		202	1891	425	1938
46	−227,15	19,232	496,49	20,017	424,29
		193	1914	421	1981
47	−226,15	19,418	515,82	20,433	444,52
		186	1933	416	2023
48	−225,15	19,596	535,32	20,843	465,16
		178	1950	410	2064
49	−224,15	19,769	555,00	21,249	486,20
		173	1968	406	2104
50	−223,15	19,935	574,86	21,650	507,65
		166	1936	401	2145
51	−222,15	20,097	594,87	22,046	529,50
		162	2001	396	2185
52	−221,15	20,253	615,05	22,438	551,74
		156	2018	392	2224
53	−220,15	20,406	635,38	22,825	574,37
		153	2033	387	2263
54	−219,15	20,555	655,86	23,208	597,39
		149	2018	383	2302

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	−205
69	−204
70	−203
71	−202
72	−201
73	−2
74	−1
75	−1
76	−1
77	−1
78	−1
79	−1
80	−1
81	−1
82	−
83	−
84	−

Продолжение

T, °K	t, °C	C_p, кдж/(кмоль·град)	$I^\circ - I^\circ_0$, кдж/кмоль	S°, кдж/(кмоль·град)	$-(\Phi^\circ - I^\circ_0)$, кдж/кмоль
55	−218,15	20,702	676,49	23,587	620,79
		147	2063	379	2340
56	−217,15	20,846	697,26	23,961	644,57
		144	2077	374	2378
57	−216,15	20,987	718,18	24,331	668,71
		141	2092	370	2414
58	−215,15	21,125	739,24	24,698	693,23
		138	2106	367	2452
59	−214,15	21,261	760,43	25,060	718,11
		136	2119	362	2488
60	−213,15	21,394	781,76	25,418	743,35
		133	2133	358	2524
61	−212,15	21,519	803,21	25,773	768,94
		125	2145	355	2559
62	−211,15	21,635	824,79	26,124	794,89
		116	2158	351	2595
63	−210,15	21,746	846,48	26,471	821,19
		111	2169	347	2630
64	−209,15	21,853	868,28	26,814	847,83
		107	2180	343	2664
65	−208,15	21,956	890,19	27,154	874,82
		103	2191	340	2699
66	−207,15	22,056	912,19	27,490	902,14
		100	2200	336	2732
67	−206,15	22,153	934,30	27,822	929,79
		97	2211	332	2765
68	−205,15	22,246	956,50	28,151	957,78
		93	2220	329	2799
69	−204,15	22,337	978,79	28,477	986,10
		91	2229	326	2832
70	−203,15	22,425	1001,2	28,799	1014,7
		88	224	322	286
71	−202,15	22,510	1023,6	29,117	1043,7
		85	224	318	290
72	−201,15	22,593	1046,2	29,433	1073,0
		83	226	316	293
73	−200,15	22,673	1068,8	29,745	1102,6
		80	226	312	296
74	−199,15	22,752	1091,5	30,054	1132,5
		79	227	309	299
75	−198,15	22,828	1114,3	30,360	1162,7
		76	228	306	302
76	−197,15	22,902	1137,2	30,663	1193,2
		74	229	303	305
77	−196,15	22,974	1160,1	30,963	1224,0
		72	229	300	308
78	−195,15	23,044	1183,1	31,259	1255,1
		70	230	296	311
79	−194,15	23,112	1206,2	31,553	1286,5
		68	231	294	314
80	−193,15	23,179	1229,4	31,844	1318,2
		67	232	291	317
81	−192,15	24,245	1252,6	32,132	1350,2
		66	232	288	320
82	−191,15	23,309	1275,9	32,418	1382,5
		64	233	286	323
83	−190,15	23,371	1299,2	32,701	1415,0
		62	233	283	325
84	−189,15	23,432	1322,6	32,981	1447,9
		61	234	280	329

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
85	−188,15	23,491	1316,1	33,259	1481,0
		59	235	278	331
86	−187,15	23,550	1369,6	33,534	1514,4
		59	235	275	334
87	−186,15	23,607	1393,2	33,807	1548,1
		57	236	273	337
88	−185,15	23,663	1416,8	34,077	1582,0
		56	236	270	339
89	−184,15	23,718	1440,5	34,345	1616,2
		55	237	268	342
90	−183,15	23,771	1464,2	34,610	1650,7
		53	237	265	345
91	−182,15	23,824	1488,0	34,873	1685,4
		53	238	263	347
92	−181,15	23,876	1511,9	35,134	1720,4
		52	239	261	350
93	−180,15	23,926	1535,8	35,392	1755,7
		50	239	258	353
94	−179,15	23,976	1559,7	35,648	1791,2
		50	239	256	355
95	−178,15	24,025	1583,7	35,902	1827,0
		49	240	254	358
96	−177,15	24,073	1607,8	36,154	1863,0
		48	241	252	360
97	−176,15	24,120	1631,9	36,404	1899,3
		47	241	250	363
98	−175,15	24,167	1656,0	36,651	1935,8
		47	241	247	365
99	−174,15	24,212	1680,2	36,897	1972,6
		45	242	246	368
100	−173,15	24,257	1701,4	37,141	2009,6
		45	242	244	370
101	−172,15	24,301	1728,7	37,382	2046,9
		44	243	241	373
102	−171,15	24,345	1753,0	37,622	2084,4
		44	243	240	375
103	−170,15	24,387	1777,4	37,860	2122,1
		42	244	238	377
104	−169,15	24,429	1801,8	38,095	2160,1
		42	244	235	380
105	−168,15	24,471	1826,3	38,329	2198,3
		42	245	234	382
106	−167,15	24,512	1850,8	38,562	2236,8
		41	245	233	385
107	−166,15	24,552	1875,3	38,792	2275,4
		40	246	230	386
108	−165,15	24,591	1899,9	39,020	2314,3
		39	246	228	389
109	−164,15	24,630	1924,5	39,247	2353,5
		39	246	227	392
110	−163,15	24,668	1949,1	39,472	2392,8
		38	247	225	393
111	−162,15	24,706	1973,8	39,696	2432,4
		38	247	224	396
112	−161,15	24,744	1998,5	39,918	2472,2
		37	248	222	398
113	−160,15	24,781	2023,3	40,138	2512,3
		36	248	220	401
114	−159,15	24,817	2048,1	40,356	2552,5
				218	402

T, °K	t, °C
115	−158,1
116	−157,1
117	−156,1
118	−155,1
119	−154,
120	−153,
121	−152,
122	−151
123	−150
124	−14
125	−1
126	−1
127	−1
128	−1
129	−1
130	−1
131	−
132	−
133	−
134	−
135	−
136	-
137	
138	
139	
140	
141	
142	
143	
144	

Продолжение

T, °K	t, °C	c_p^0, кдж/(кмоль·град)	$i^0-i_0^0$, кдж/кмоль	S^0, кдж/(кмоль·град)	$-(\Phi^0-i_0^0)$, кдж/кмоль
115	—158,15	24,853	2072,9	40,573	2593,0
116	—157,15	24,888	2097,8	40,788	2633,7
117	—156,15	24,923	2122,7	41,002	2674,5
118	—155,15	24,957	2147,6	41,214	2715,6
119	—154,15	24,991	2172,6	41,425	2757,0
120	—153,15	25,025	2197,6	41,634	2798,5
121	—152,15	25,058	2222,6	41,842	2840,2
122	—151,15	25,091	2247,7	42,049	2882,1
123	—150,15	25,123	2272,8	42,254	2924,3
124	—149,15	25,155	2298,0	42,457	2966,7
125	—148,15	25,187	2323,2	42,659	3009,3
126	—147,15	25,218	2348,4	42,860	3052,0
127	—146,15	25,249	2373,6	43,060	3095,0
128	—145,15	25,280	2398,9	43,258	3138,1
129	—144,15	25,310	2424,2	43,455	3181,5
130	—143,15	25,340	2449,5	43,650	3225,0
131	—142,15	25,370	2474,8	43,844	3268,8
132	—141,15	25,400	2500,2	44,038	3312,7
133	—140,15	25,429	2525,6	44,229	3356,9
134	—139,15	25,458	2551,0	44,420	3401,2
135	—138,15	25,487	2576,5	44,609	3445,7
136	—137,15	25,515	2602,0	44,797	3490,4
137	—136,15	25,543	2627,5	44,984	3535,3
138	—135,15	25,571	2653,1	45,170	3580,4
139	—134,15	25,599	2678,7	45,355	3625,6
140	—133,15	25,627	2704,3	45,539	3671,1
141	—132,15	25,654	2729,9	45,721	3716,7
142	—131,15	25,681	2755,6	45,903	3762,5
143	—130,15	25,708	2781,3	46,083	3808,5
144	—129,15	25,735	2807,0	46,262	3854,7

Продолжение

T, °K	t, °C	C_p, кдж/(кмоль·град)	$I^\circ - I^\circ_0$, кдж/кмоль	S°, кдж/(кмоль·град)	$-(\Phi^\circ - I^\circ_0)$, кдж/кмоль
145	—128,15	25,762	2832,8	46,410	3901,0
146	—127,15	25,789	2858,6	46,617	3947,6
147	—126,15	25,815	2884,4	46,794	3994,3
148	—125,15	25,841	2910,2	46,969	4041,2
149	—124,15	25,867	2936,0	47,143	4088,2
150	—123,15	25,893	2951,9	47,316	4135,4
151	—122,15	25,929	2987,8	47,488	4182,8
152	—121,15	25,945	3013,7	47,659	4230,4
153	—120,15	25,971	3039,7	47,829	4278,2
154	—119,15	25,997	3065,7	47,999	4326,1
155	—118,15	26,023	3091,7	48,167	4374,2
156	—117,15	26,049	3117,7	48,334	4422,4
157	—116,15	26,075	3143,8	48,501	4470,8
158	—115,15	26,100	3169,9	48,666	4519,4
159	—114,15	26,126	3196,0	48,831	4568,2
160	—113,15	26,152	3222,1	48,995	4617,1
161	—112,15	26,178	3248,3	49,158	4666,2
162	—111,15	26,203	3274,5	49,320	4715,4
163	—110,15	26,229	3300,7	49,482	4764,8
164	—109,15	26,255	3326,9	49,642	4814,4
165	—108,15	26,281	3353,2	49,802	4864,1
166	—107,15	26,307	3379,5	49,961	4914,0
167	—106,15	26,333	3405,8	50,119	4964,0
168	—105,15	26,359	3432,2	50,276	5014,2
169	—104,15	26,385	3458,6	50,433	5064,6
170	—103,15	26,412	3485,0	50,589	5115,1
171	—102,15	26,438	3511,4	50,744	5165,7
172	—101,15	26,464	3537,8	50,898	5216,5
173	—100,15	26,491	3564,3	51,051	5267,5
174	— 99,15	26,518	3590,8	51,204	5318,6

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	—79,15
195	—78,15
196	—77,15
197	—76,15
198	—75,15
199	—74,15
200	—73,15
201	—72,15
202	—71,15
203	—70,15
204	—69,15

Продолжение

$-(S^\circ - I_0^\circ)$, кдж/кмоль	T, °K	t, °C	C_p, кдж/(кмоль·град)	$I^\circ - I_0^\circ$, кдж/кмоль	S°, кдж/(кмоль·град)	$-(S^\circ - I_0^\circ)$, кдж/кмоль
3991,0 463	175	−98,15	26,544 26	3617,3 265	51,356 152	5369,9 513
3947,6 466	176	−97,15	26,571 27	3643,9 266	51,507 151	5421,4 515
3904,3 467	177	−96,15	26,599 28	3670,5 266	51,658 151	5473,0 516
4041,2 469	178	−95,15	26,626 27	3697,1 266	51,808 150	5524,7 517
4088,2 470	179	−94,15	26,653 27	3723,7 266	51,957 149	5576,6 519
4135,4 472	180	−93,15	26,681 28	3750,4 267	52,106 149	5628,6 520
4182,8 474	181	−92,15	26,709 28	3777,1 267	52,254 148	5680,8 522
4230,4 476	182	−91,15	26,737 28	3803,8 267	52,401 147	5733,1 523
4278,2 478	183	−90,15	26,765 28	3830,6 268	52,547 146	5785,6 525
4326,1 479	184	−89,15	26,793 28	3857,4 268	52,693 146	5838,2 526
4374,2 481	185	−88,15	26,821 28	3884,2 268	52,838 145	5891,0 528
4422,4 482	186	−87,15	26,850 29	3911,0 268	52,983 145	5943,9 529
4470,8 484	187	−86,15	26,879 29	3937,9 269	53,127 144	5996,9 530
4519,4 486	188	−85,15	26,908 29	3964,8 269	53,271 144	6050,1 532
4568,2 488	189	−84,15	26,937 29	3991,7 269	53,414 143	6103,4 533
4617,1 489	190	−83,15	26,967 30	4018,7 270	53,556 142	6156,9 535
4666,2 491	191	−82,15	26,997 30	4045,7 270	53,698 142	6210,5 536
4715,4 492	192	−81,15	27,027 30	4072,7 270	53,839 141	6264,3 538
4764,8 494	193	−80,15	27,057 30	4099,7 270	53,979 140	6318,2 539
4814,4 496	194	−79,15	27,088 31	4126,8 271	54,119 140	6372,3 541
4864,1 497	195	−78,15	27,119 31	4153,9 271	54,258 139	6426,5 542
4914,0 499	196	−77,15	27,150 31	4181,0 271	54,397 139	6480,8 543
4964,0 500	197	−76,15	27,181 31	4208,2 272	54,535 138	6535,3 545
5014,2 502	198	−75,15	27,212 31	4235,4 272	54,673 138	6589,9 546
5064,6 504	199	−74,15	27,244 32	4262,6 272	54,810 137	6644,6 547
5115,1 505	200	−73,15	27,276 32	4289,8 272	54,947 137	6699,5 549
5165,7 506	201	−72,15	27,308 32	4317,1 273	55,083 136	6754,5 550
5216,5 508	202	−71,15	27,340 32	4344,4 273	55,219 136	6809,7 552
5267,5 510	203	−70,15	27,373 33	4371,8 274	55,354 135	6865,0 553
5318,6 511	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)	$T^\circ - I_0^\circ$, кдж/кмоль	S°, кдж/(кмоль·град)	$-(\Phi^\circ - I_0^\circ)$, 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 35	4591,9 276	56,417 131	7312,1 564
212	−61,15	27,677 35	4619,5 277	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	4674,9 278	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 36	4730,5 278	57,066 129	7595,8 570
217	−56,15	27,853 36	4758,3 279	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

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

Термодинамические свой
от 0°K до точки плавл

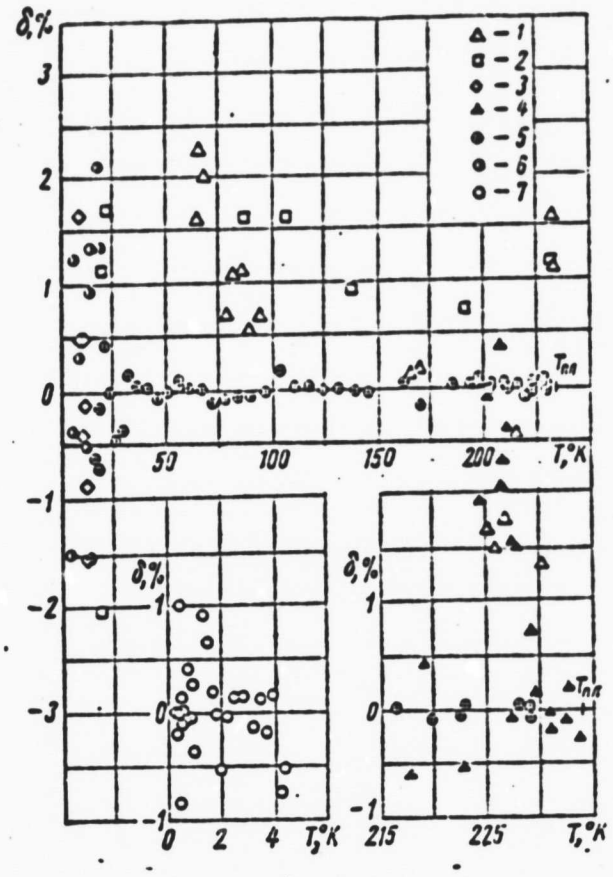
T, °K	$T^\circ - I_0^\circ$, кдж/кмоль	S°, кдж/(кмоль·град)
0	13,786	2,8
5	13,786	2,8
10	13,787	2,8
20	13,791	2,8
30	13,799	2,8
40	13,809	2,8
50	13,821	2,8
60	13,834	2,8
70	13,848	2,8
80	13,862	2,8
90	13,877	2,8
100	13,892	2,8
110	13,908	2,8
120	13,924	3,0
130	13,940	3,0
140	13,957	3,1
150	13,974	3,1
160	13,992	3,1
170	14,010	3,1
180	14,028	3,2
190	14,047	3,2
200	14,067	3,2
210	14,086	3,2
220	14,110	3,2
230	14,132	3,2
234,28	14,142	3,2

±0,2%) измене
довать рассеяни
колебаний реше
Авторы при
с благодарност

1. Вукало
1000°C и давлени

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	2,806
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



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

Fig. 1. Deviation of the experimental data obtained by various authors from 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)

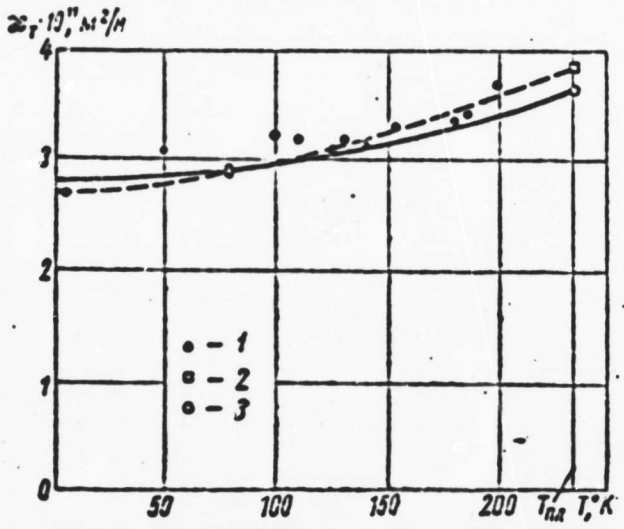


Fig. 2. Dependence of isothermiccontractibility K_T on temperature at normal pressure p=1 atm:
1-Swenson's test data (33), 2-the value K_T^J at T_{BP} obtained by extrapolation of Pena's test data (40), the value K_T^{TB} T_{BP} computed by equation 7, dahed - dependence described by Swenson's data.

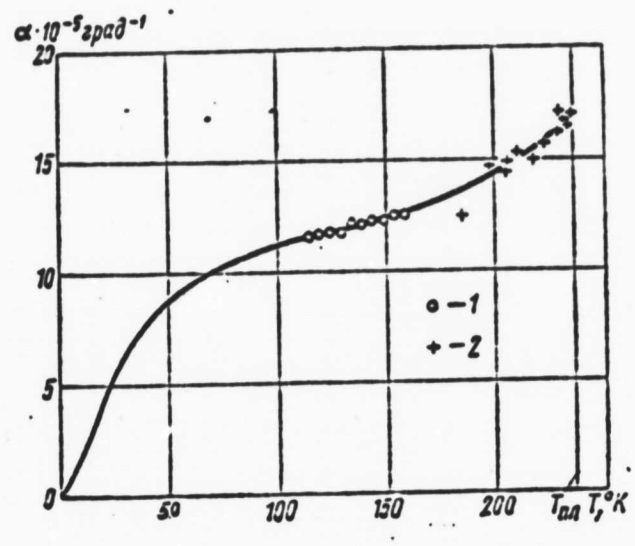
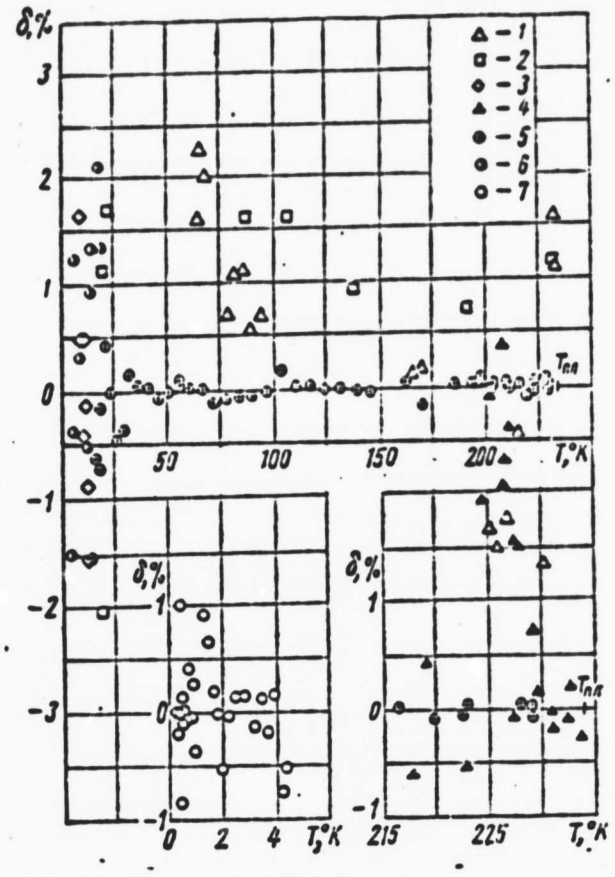


Fig. 3. The dependence of the coefficient for thermal expansion α on temperature at normal pressure p=1 atm. 1-Carpenter and Oukli's test data, 2- Hill's (38)



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

Fig. 1. Deviation of the experimental data obtained by various authors from 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)

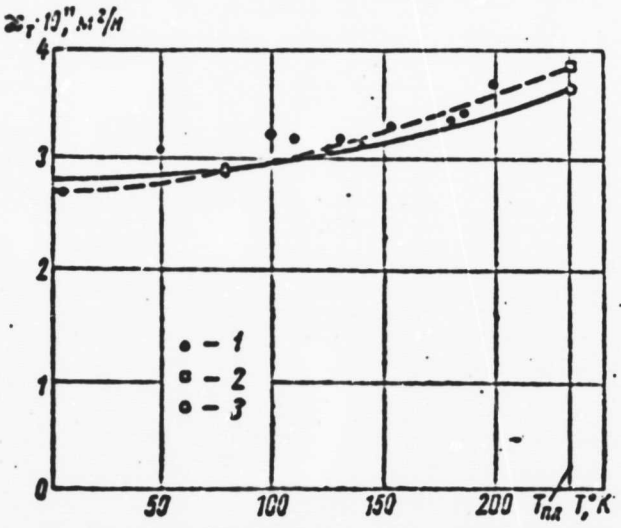


Fig. 2. Dependence of isothermiccontractibility K_T on temperature at normal pressure p=1 atm:
1-Swenson's test data (33), 2-the value K_T^J at T_{BP} obtained by extrapolation of Pena's test data (40), the value K_T^{TB} T_{BP} computed by equation 7, dahed - dependence described by Swenson's data.

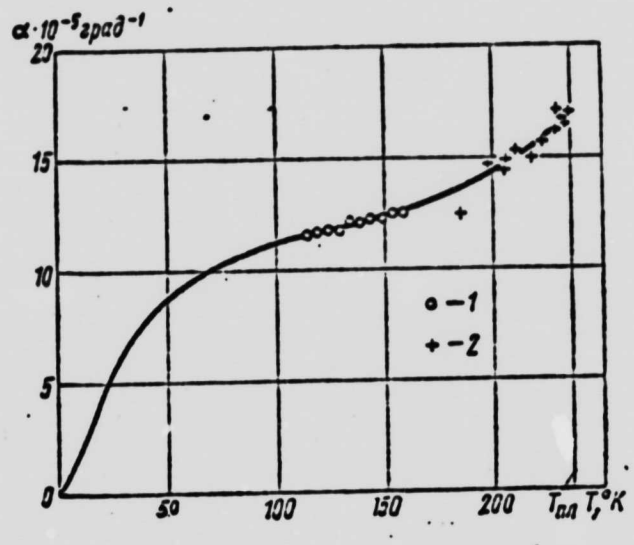


Fig. 3. The dependence of the coefficient for thermal expansion α on temperature at normal pressure p=1 atm. 1-Carpenter and Oukli's test data, 2- Hill's (38)

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